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Metal−Organic Frameworks from Silicon- and Germanium-Centered Tetrahedral Ligands

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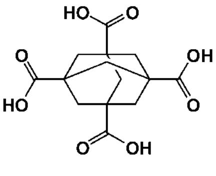
Metal−organic frameworks (MOFs) have been constructed from the reaction of $Si(C_6H_4CO_2H)_4$ and of $Ge(C_6H_4CO_2H)_4$ with Zn(II). The two structures are quite different from each other, and both are different from that of the known MOF of $C(C_6H_4CO_2H)_4$ with Zn(II). The zinc portion of the carbon system is a dinuclear zinc-oxo cluster with square-planar geometry, that of the silicon system consists of zinc-oxo chains containing two zinc atoms with different geometries, and that of the germanium system consists of linear zinc-oxo clusters containing three zinc atoms with two different geometries. For the silicon system, the secondary building unit around zinc is a distorted tetrahedron, whereas for the germanium system, the secondary building unit around zinc is a bipyramid with eight coordination. The differences in morphology may be due to the more open geometry provided as the M−C bond increases from carbon to germanium. Both MOFs have considerable vacancy in the crystal lattice, calculated to be ca. 42% for the silicon system and ca. 46% for the germanium system. Gas sorption experiments on the germanium system indicated significant uptake of both nitrogen and carbon dioxide.

Porous materials with large, regular, accessible cages or channels are increasingly in demand for applications in separations, catalysis, chemosensing, molecular storage, and nanoreactors. Pore size, pore shape, and the chemical properties of the pore lining can determine specificity of admission or exclusion of materials to the pores and reactivity within the pores. Traditionally, zeolites and molecular sieves have fulfilled these roles. Usually found naturally and composed of the most widely available elements in the earth's crust, these materials offer many advantageous properties, including stability, rigidity, specificity, and low cost. They can be altered only minimally, however, to optimize their properties. Introduction of organic components to the surfaces or pore linings offers a semisynthetic alternative. Far more useful are fully synthetic materials, whose properties can be tuned by the choice of starting materials.

Such materials have been realized in the form of polymers made up generally of two multidentate components: metallic units connected by organic bridges.[1–5] Properties could be altered by selection and variation of both the metal and the organic bridge. Because each component can bind to more than one unit of the other, infinite polymers result. If both components are bidentate, one-dimensional, or linear, polymers result. If at least one component is tridentate but planar, two-dimensional, or planar, polymers result. If at least one component is tetradentate or nonplanar, three-dimensional polymers result. These polymers often are regular, crystalline, and highly stable and offer high porosity due to vacancies that result naturally during their crystallization. The most widespread organic ligands are polycarboxylic acids and polypyridines.[1–5] Numerous transition metals have been used, such as Cu(II), Zn(II), Cd(II), Ni(II), Co(II), and Mn(II). The complete rigidity of all components of the structure permits little flexibility within the crystal. The terms coordination polymers, organic–inorganic hybrids, organic zeolites, and metal−organic frameworks (MOFs) have been given to these materials.

The current study has focused on organic components constructed around a tetrahedral center. With connections directed tetrahedrally from such a center, complex three-dimensional networks, or reticulations, are expected. Three such organic components (**1−3**) have produced MOFs by reaction with Zn(II). Despite the similarity of geometry and identity of the metal ion, the resulting topologies in the crystal proved to be quite different.[6] Differences also are seen when the frameworks are constructed from the same organic ligands with Cd(II)



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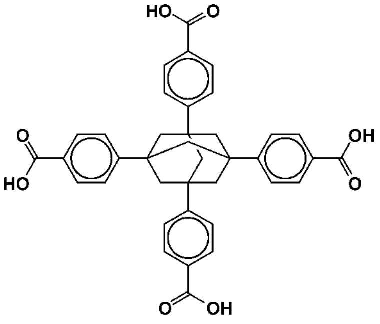

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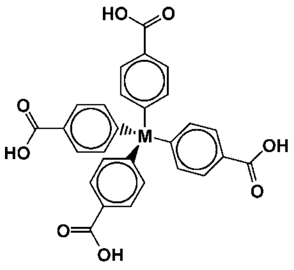

3, M = C
4, M = Si
5, M = Ge

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Table 1. Some Crystallographic Parameters

	MOF-36	**Si4A-Zn**	**Ge4A-Zn**
space group	*$P4_2/mmc$*	*Pnna*	*Pnnn*
cluster geometry	square-planar dinuclear zinc-oxo cluster	zinc-oxo chain	linear trinuclear zinc-oxo cluster
C−M−C bond angle, deg	103.54(6)	105.09(16)	105.89(11)
	103.54(79)	105.52(11)	108.19(10)
	112.52(6)	108.79(12)	109.23(11)
	112.52(6)	108.79(12)	110.14(10)
	112.52(6)	114.45(12)	111.94(11)
	112.52(6)	114.45(12)	111.24(9)
M-C bond length, Å	1.546(7)	1.870(3)	1.941(2)
	1.546(7)	1.870(3)	1.944(3)
	1.546(7)	1.872(4)	1.947(2)
	1.546(15)	1.872(4)	1.948(3)

ions.[6,7] In the present study we retained the geometry offered by **3** but changed the central atom M to silicon (**4**) and germanium (**5**). In addition to retaining a constant theme for the organic geometry, the Si and Ge systems illustrate the ease with which quaternary centers can be built around these atoms. The Si system was prepared in an earlier study,[7] and the Ge system is new. The series **3**−**5** exemplifies the effect of the single change whereby the M−C bond is lengthened (C to Si to Ge). These systems were allowed to react with zinc nitrate to form crystalline MOFs.

Results

Tetrakis(4-carboxyphenyl)silicon (**4**) was prepared as before.[8] Tetrakis(4-carboxyphenyl)germanium (**5**) was prepared by reaction of 1,4-dibromobenzene with tetrachlorogermanium to form tetrakis(4-bromophenyl)germanium, which was converted to the tetralithium derivative for reaction with carbon dioxide. These tetracarboxylic acids (**4** and **5**) were allowed to react with zinc nitrate hexahydrate to produce crystals as described in the Experimental Section. We designate the MOF formed from **4** and Zn(II) as **Si4A-Zn** and that from **5** and Zn(II) as **Ge4A-Zn** ("4A" denotes the presence of four carboxylic acid groups on each M). Single crystals were subjected to X-ray diffraction. Some crystallographic results are presented in Table 1, along with analogous results for the carbon derivative from the reaction of **3** with Zn(II) to form MOF-36.[6] Details of the crystal structures are provided in the Supporting Information.

The program Platon[9] was used to calculate the solvent accessible pore volume of the MOFs, after solvent molecules not directly connected to the metals were removed. Accelrys MS modeling[10] was used to calculate the occupied volume and the free volume of a unit cell. These results are given in Table 2.

Table 2. Calculations of Pore Volume

	free vol,[a] Å^3	occupied vol,[a] Å^3	total vol,[a] Å^3	free vol/ total vol, %	pore vol,[b] %	ratio of columns 5 to 4
Si4A-Zn	1583.04	2280.72	3863.76	41.0	41.8	1.02
Ge4A-Zn	3656.58	4449.49	8106.07	45.1	46.4	1.03
MOF-36	4121.05	2862.78	6983.83	59.0	61.6	1.04

[a] Calculations by Accelrys MS modeling (version 3.2). [b] Calculations by Platon for Windows Taskbar (version 1.081).

Nitrogen and carbon dioxide sorption experiments were carried out on **Ge4A-Zn**. Nitrogen sorption indicated type I behavior, typical for microporous materials, with some hysteresis between the adsorption and desorption isotherms. The BET surface area calculated from the nitrogen sorption isotherms is 417.7 m^2 g^{-1}, and the micropore volume is 0.277 cm^3 g^{-1}, typical for MOF materials. The BET surface area calculated from the carbon dioxide isotherms is 284.2 m^2 g^{-1}, and the micropore volume is 0.122 cm^3 g^{-1}. See Supporting Information for sorption data.

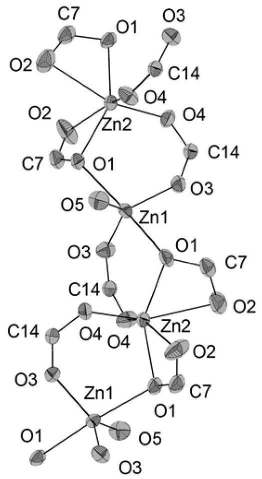

Figure 1. Zinc-oxo chain of **Si4A-Zn** with 50% probability level thermal ellipsoids.

Discussion

The MOF of **Si4A-Zn** crystallizes in the orthorhombic space group *Pnna*. The simplest repeating structure is a Zn1−O1−Zn2−O1 chain connected to carboxylate groups from the organic component (Figure 1). One zinc atom (Zn1) has the geometry of a distorted trigonal bipyramid and is coordinated to a molecule of water (O5), to a single oxygen atom of one carboxylate group (O1), and to a single oxygen atom of a second carboxylate group (O3). Both O1 and O3 are repeated a second time from an additional carboxylate to bring the coordination number to five. The second zinc atom (Zn2) is six coordinated. One carboxyate group (C7) brings coordination from both oxygen atoms (O1 and O2), and this unit is repeated a second time. Note that O1 is shared between Zn1 and Zn2 and constitutes the bridging oxygen for the zinc oxo chain. Additionally, Zn2 is connected to a single oxygen atom O4 of a second carboxylate (C14), and this unit also occurs twice. Thus Zn2 is coordinated to two O1's, two O2's, and two O4's for hexacoordination. From the point of view of the carboxylate groups, one (C14) provides a bridge between the two zinc atoms (Zn1−O3−C14−O4−Zn2). The other (C7) serves as a bidentate ligand to Zn2 and a monodentate ligand to Zn1, with the result that one oxygen (O1) is bridged between the two zinc atoms. The water molecule (O5) is coordinated solely to Zn1. Any pair of zinc atoms is coordinated to a total of four carboxylate groups, so the overall formula of the repeating structure is $Zn_2(RCO_2)_4$ (H_2O). Because each organic molecule possesses four charged carboxylate groups, the metal/organic ratio is 2:1 to produce the overall neutral structure. Figure 1 illustrates two units of the repeating structure. The structure also contains one water

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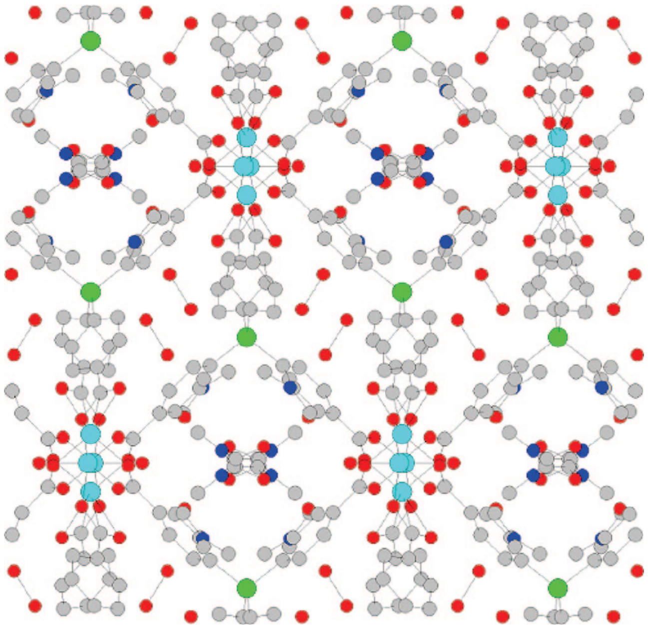

Figure 2. Reticulated framework of **Si4A-Zn** as viewed along the *b* axis, in which zinc is cyan, oxygen is red, carbon is gray, silicon is green, and nitrogen from dimethylformamide (solvent uncoordinated to the network) is blue.

molecule of solvation and 1.5 DMF molecules of solvation uncoordinated to the network.

Figure 2 shows the reticulated framework of **Si4A-Zn** from a perspective sighting along the *b* axis of the crystal. To understand the framework topology, it is helpful to consolidate the building blocks from which the network is constructed. A pair of zinc atoms in the zinc oxo chain is bonded to four carboxylate groups and may be considered roughly to represent a distorted tetrahedron. As depicted in Figure 3 (left), Zn2 is surrounded by the four carboxylate groups. The carboxylate groups are connected through benzene rings to four silicon atoms in green, each of which sits at the center of the nearly regular tetrahedron of the organic molecule. Figure 3 at the right shows how a single Zn2-centered distorted tetrahedron is surrounded by four Si-centered, nearly regular tetrahedra. The Si-centered tetrahedra in turn are surrounded by four of the distorted Zn-centered tetrahedra. The reticulated structure represents the extension of these motifs infinitely into three dimensions. There are, however, two interconnected such networks, when both zinc atoms in Figure 1 are taken into consideration. Zn1 also is surrounded by four carboxylate groups, only two of which are shown in Figure 3. Figure 4 shows a portion of the two interconnected networks, one (Zn1-centered) in blue and the other (Zn2-centered) carried over from Figure 3 (right) in yellow and green. These two networks are connected through the zinc-oxo chain and not (directly) via the Si-centered tetrahedral. There is no interpenetration of independent, identical networks, but rather a single network comprised of two identical but connected networks.

The MOF of **Ge4A-Zn** crystallizes in the orthorhombic space group *Pnnn*. The repeating structure contains a centrosymmetric linear array of three zinc ions (Figure 5). Although similar trizinc arrays have been observed previously in crystal structures,[11–13] these materials were not MOFs. They did not exist as three-dimensional frameworks because the axial or apical groups (the C14 carboxyl in **Ge4A-Zn**) were self-limiting structures like pyridine without additional ligands to extend the structure. The middle zinc atom (Zn1) in **Ge4A-Zn** sits on the crystallographic inversion point and is attached through oxo bridges to two identical Zn2 atoms. Zn1 is octahedrally coordinated to two O2 atoms (of the C7 carboxylate group), which bridge to the respective Zn2 atoms, and two pairs of O5 and O7 atoms from four carboxylate groups (two pairs each of C21 and C28), which bridge between the two zinc atoms (Zn−O−C−O−Zn). Zn2 is coordinated to O3 and O4 of the disordered carboxylic acid (C14). Zn2 also is coordinated to O2 (of carboxylate C7), which provides the bridge to Zn1. A second carboxylate (C21) and a third carboxylate (C28) bridge between the two zinc atoms, with O6 and O8 coordinated to Zn2 and O5 and O7 to Zn1. The Zn2−O1 (2.670(2) Å) bond may not be sufficiently long to be counted in the coordination number. The two values of the disordered Zn2−O3 bond are 1.956(6) and 2.509(7) Å, and of the disordered Zn2−O4 bond are 1.973(6) and 2.369(5). If the figures are averaged respectively to 2.233 and 2.171 Å, both interactions qualify as bonds. Thus the coordination number of Zn2 may be considered to be four to six, depending on how one counts the long bonds. The grouping O4−C14−O3 is from a carboxylic acid (CO_2H), whereas the other OCO units are charged carboxylates (CO_2^-). The presence of the proton on O3 or O4 probably contributes to the disorder in the C14 unit. The trizinc unit is coordinated to a total of six carboxylates (two each of C7, C21, and C28) and two carboxylic acids, giving an overall formula of $Zn_3(RCO_2)_6(CO_2H)_2$. The structure is electroneutral, with zinc and carboxylate charges balanced at six.

Figure 6 shows the reticulated framework of **Ge4A-Zn** from a perspective sighting along the *b* axis of the crystal. The crystal structure clearly contains two distinct channels. The approximate diameter of the larger channel is about 9 Å, and that of the smaller channel about 6 Å. Again it is helpful to consolidate the building blocks from which the network is constructed. The trizinc grouping can be represented by a Zn1-centered bipyramid with eight benzoate groupings irradiating outward (Figure 7, left), six equatorially and two apically. Each benzoate terminates at a nearly regular Ge-centered tetrahedron in green. Figure 7 (right) illustrates diagrammatically how the yellow bipyramid is surrounded by eight purple tetrahedra. Because each germanium tetrahedron is attached to four different Zn-centered bipyramids, the structure propagates throughout the crystal. Figure 8 shows how each of the eight Ge-centered tetrahedra that emanate from a single bipyramid bond to three other bipyramids.

The reticulated structures depicted in Figures 2 and 6 have considerable vacant space. We used two calculational approaches to assess the degree of vacancy for the series of zinc MOFs constructed from $M(C_6H_4)CO_2H$ (**3**−**5**): MOF-36, **Si4A-Zn**, and **Ge4A-Zn** (Table 2). Platon calculates the volume of the accessible void with a rolling ball probe (representing a water molecule, 1.2 Å in diameter). The result is the pore volume percentages given in the sixth column of Table 2. Accelrys compares the calculated space occupied by atoms of assigned van der Waals radii (third column) with the observed total cell volume (fourth column) to give the free volume (second column) by subtraction. The percentage of the accessible void then is calculated from the ratio (fifth column) of the free and total volumes. The two different methods lead to very similar results (sixth column). Differences might be expected if some of the

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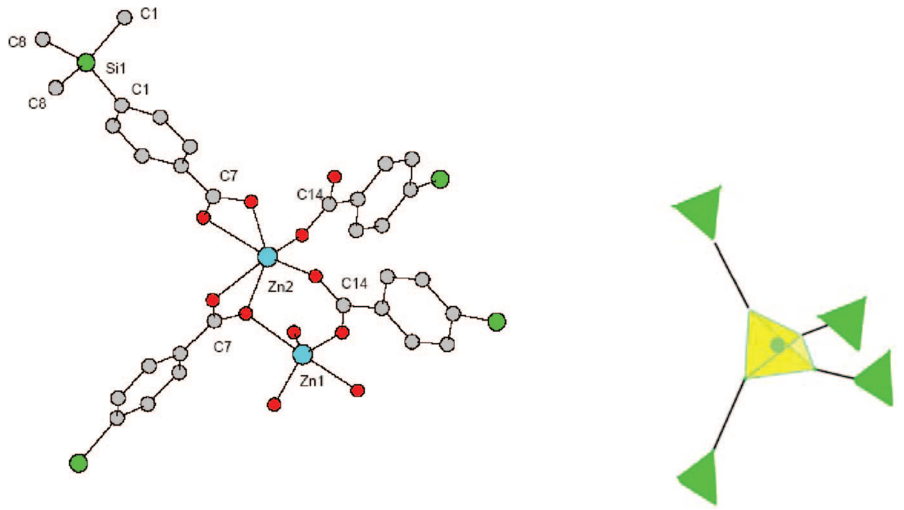

Figure 3. (left) The distorted tetrahedron with Zn2 at the center, surrounded by four carboxylate ligands, in which zinc is cyan, oxygen is red, carbon is gray, and silicon is green. The four carboxylate ligands are attached to the nearly regular tetrahedron around silicon. (right) A single Zn2-centered distorted tetrahedron in yellow surrounded by four Si-centered nearly regular tetrahedra in green.

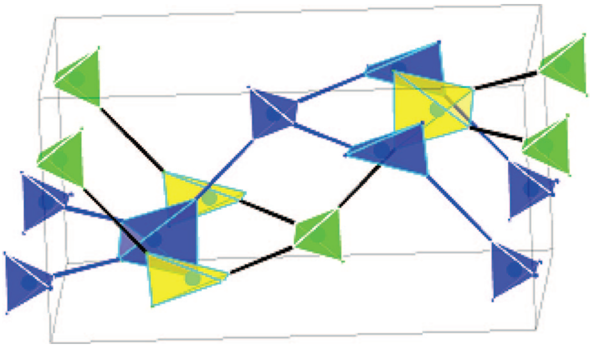

Figure 4. Network of yellow, Zn2-centered, distorted tetrahedra and green Si-centered regular tetrahedra, interconnected by a second, Zn-1-centered network in blue.

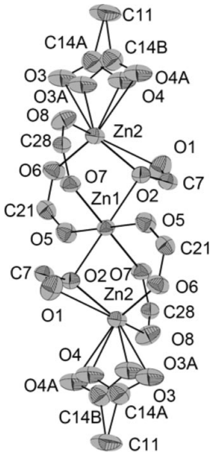

Figure 5. Zinc-oxo chain of **Ge4A-Zn** with 50% probability level thermal ellipsoids.

void is inaccessible to the rolling ball and hence is ignored by Platon. In fact, the results are within 1–3% of each other. The C-centered MOF offers the largest void percentage and the Si-centered MOF the least, but all three are in the range 40–60%, which is large for most crystals.[1–4] Since the void order of C > Ge > Si does not follow vertical placement in the periodic table, it must be the result primarily of the specific crystal type assumed by the MOF; that is, it is more of a supramolecular than a molecular property.

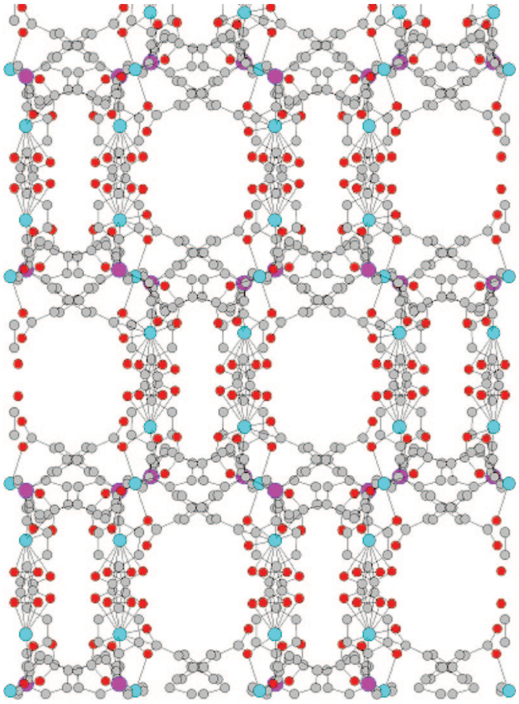

Figure 6. Reticulated framework of **Ge4A-Zn** as viewed along the *b* axis, in which zinc is cyan, oxygen is red, carbon is gray, and germanium is purple.

The existence of significant voids in the crystals raises the possibility that they can serve as reservoirs for gaseous species. Consequently, nitrogen and carbon dioxide adsorption and desorption experiments were carried out on **Ge4A-Zn**, the material with the larger voids (see Supporting Information). The BET surface area calculated from N_2 sorption isotherms was 417.7 $m^2\ g^{-1}$, and that calculated from CO_2 sorption isotherms was 284.2 $m^2\ g^{-1}$. The micropore volume calculated from N_2 sorption isotherms was 0.277 $cm^3\ g^{-1}$ and that calculated from CO_2 sorption isoterms was 0.122 $cm^3\ g^{-1}$. These results are typical for microporous materials[1–5] and demonstrate that **Ge4A-Zn** is a nonspecific adsorber, since it receives both N_2 and CO_2 effectively.

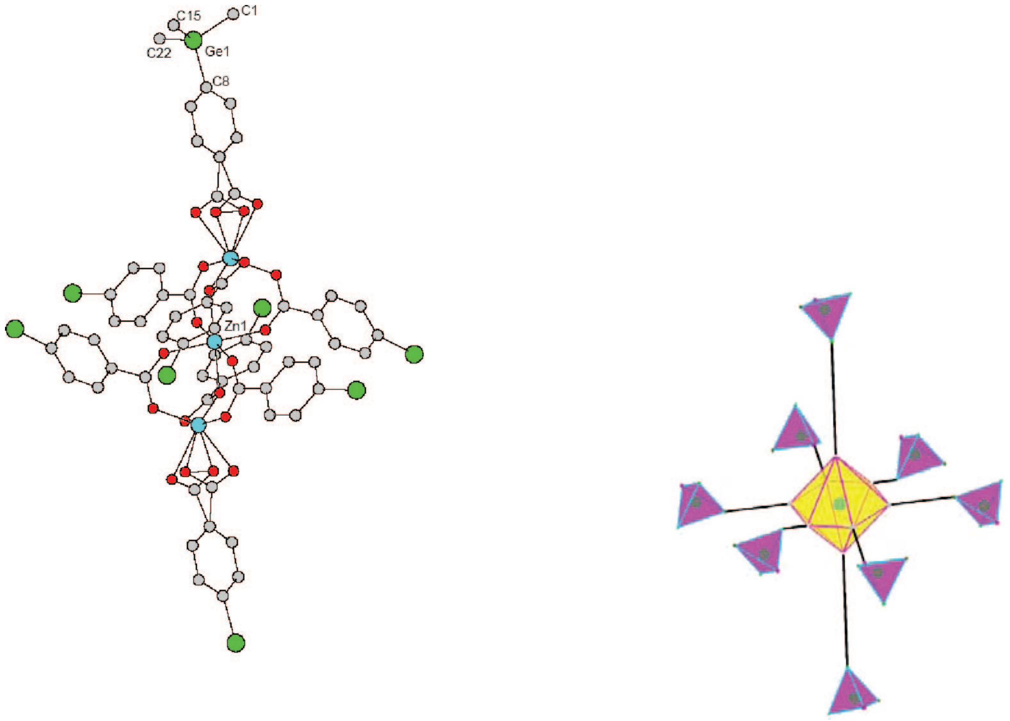

Figure 7. (left) Bipyramid represented by three zinc atoms at the center, surrounded by eight carboxylate ligands, in which Zn is cyan, oxygen is red, carbon is gray, and germanium is green. The eight carboxylate ligands are attached to the regular tetrahedron around germanium. (right) A single Zn-centered bipyramid in yellow surrounded by eight Ge-centered regular tetrahedra in purple.

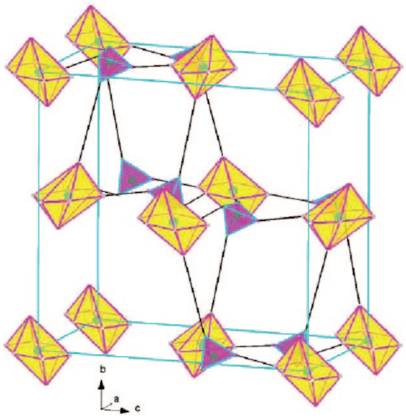

Figure 8. Connectivity of the yellow Zn-centered bipyramids with the purple Ge-centered tetrahedra.

Conclusions

Despite the similarity in structure of the organic ligands **3**−**5** [$M(C_6H_4CO_2H)_4$, M = C, Si, Ge], their MOFs with Zn(II) have very different crystal morphologies. The carbon congener, MOF-36, crystallizes in the tetragonal space group $P4_2/mmc$ (#131).[6] The zinc portion of the structure consists of dinuclear zinc-oxo clusters in which the geometry around the zinc atoms is square planar. The silicon congener, **Si4A-Zn**, crystallizes in the orthorhombic space group *Pnna* (#52). The zinc portion consists of zinc-oxo chains with two different, alternating zinc atoms. The geometry around one zinc atom is a distorted trigonal bipyramid (five-coordinate), and that around the other is a distorted octahedron (six-coordinate). The germanium congener, **Ge4A-Zn**, crystallizes in the orthorhombic space group *Pnnn* (#48). The zinc portion consists of linear trinuclear zinc-oxo clusters with an inversion center at the central zinc atom. The central zinc has octahedral (six-coordinate) geometry, and the terminal zinc has four to six coordination, depending on how bonds are counted that are slightly long.

Whereas the secondary building unit for **Si4A-Zn** has four coordination around the zinc portion and four coordination around silicon (Figure 3), the secondary building unit for **Ge4A-Zn** has eight coordination around the zinc portion and four coordination around germanium (Figure 7). Networks with connectivity larger than six are rare.[14] The space group *Pnnn* is relatively unusual. There are only two reports of three-dimensional networks with this space group. These are constructed of cyano groups with either silver[15] or copper[16] ions. There are no MOFs constructed from carboxylate groups and metal ions with this space group.

The three MOFs were produced under identical conditions with a common metal ion and organic ligands that differ only in the central atom M. The organic ligands have the same tetrahedral geometry (C−M−C angles in Table 1) and differ primarily in the M−C bond lengths (Table 1). The identity of the central atom affects the acidity of the carboxyl groups, but any role of carboxylic acidity is not obvious. The differences in morphology may be due to the more open geometry provided as the M−C bond increases from carbon to germanium. In these systems the longest bonds provide the highest effective coordination in the secondary building blocks (eight coordination for germanium). That such small differences in structure and reactivity can generate such large differences in the crystal structures illustrates the subtlety of the process of crystal growth.

Experimental Section

Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN.

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Tetrakis(4-carboxyphenyl)silicon (**4**) was prepared according to the literature.[8]

Synthesis of Si4A-Zn. To a 20 mL vial were added 33.4 mg (0.06 mmol) of **4** and 56 mg (0.2 mmol) of zinc nitrate hexahydrate. DMF (4.5 mL), ethanol (4.5 mL), and water (3.6 mL) were added to dissolve the organic ligand and the salt. The mixture was shocked by ultrasonic sound for 10 min. The solution was filtered through fritted glass (fine) into three 4 mL vials, which were sealed with Teflon-lined caps. These vials were placed in an oil bath. The bath was heated slowly (over a day) to 75 °C, held at that temperature for 3 days, and then cooled to room temperature. Colorless crystals were collected and dried under vacuum (10 Torr) at room temperature for three days, with an overall yield of 38%. Anal. Calcd for $(SiC_{28}H_{16}O_8)_2Zn_4(H_2O)(C_3H_7NO)_3$: C, 51.50; H, 3.66; N, 2.77. Found: C, 51.58; H, 3.88; N, 2.55. Drying procedures for elemental analysis and X-ray crystallography were different, so that there are differences in solvation.

Tetrakis(4-bromophenyl)germanium. To a 250 mL Schlenk flask equipped with a magnetic stirring bar was added 4,4′-dibromobenzene (11.8 g, 50 mmol). The flask, sealed with a septum, was placed under vacuum and filled with dry N_2 three times. Anhydrous ethyl ether (120 mL) was transferred into the flask with a double-ended needle. The flask then was placed into an ice/acetone bath and treated dropwise with butyllithium in hexane (20 mL, 50 mmol). The mixture was stirred for 30 min, and $GeCl_4$ (12 mmol in 20 mL ether) was added dropwise slowly. The ice/acetone bath was removed, and the mixture was stirred for 8 h at room temperature. Then 1 N aqueous HCl was added, and the resulting mixture was extracted with ether. The combined extracts were washed with water and brine, dried over $MgSO_4$, and filtered. The solvent was removed by rotary evaporation. Recystallization from 1,2-dichloroethane and benzene gave 5.6 g (67%) of colorless needle crystals. ^1H NMR ($CDCl_3$): δ 7.56 (d, 8 H, $^3J = 7.5$ Hz), 7.34 (d, 8 H, $^3J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$): δ 136.8, 133.5, 132.0, 125.0. EI-MS: M^+, calcd 695.7, found 695.9. Anal. Calcd: C, 41.38; H 2.31. Found: C, 41.68; H 2.33.

Tetrakis(4-carboxyphenyl)germanium (5). To a 250 mL Schlenk flask equipped with a magnetic stirring bar was added tetrakis(4-bromophenyl)germanium (0.70 g, 1 mmol). The flask, sealed with a septum, was placed under vacuum and filled with dry N_2 three times. Anhydrous THF (100 mL) was transferred into the flask with a double-ended needle. The flask then was immersed in a bath of acetone and dry ice. The system was cooled for 10 min, and *tert*-butyllithium in hexane (5.4 mL, 8.1 mmol) was added dropwise with a syringe. The mixture was stirred for 30 min, and then CO_2 was bubbled through it. After 30 min, the acetone/dry ice bath was removed, and the reaction system was warmed to room temperature. Solvent was removed by rotary evaporation, and water (50 mL) was added. Dilution with HCl solution (1 N) produced a white precipitate, which was removed by filtration and dissolved in a dilute solution of NaOH. The solution was filtered and reacidified with dilute HCl. The new white solid **5** was collected and dried: 0.32 g (58%). ^1H NMR (acetone-d_6): δ 8.136 (d, 8 H, $^3J = 8$ Hz), 7.728 (d, 8 H, $^3J = 8$ Hz). ^{13}C NMR (acetone-d_6): δ 167.0, 140.7, 135.6, 132.2, 129.7. ESI-MS: $[M - H]^+$, calcd, 557.03 (100%), 555.03 (70%), 553.03 (53%); obsd, 557.01 (100%), 555.14 (76%), 553.25 (50%); $[2(M - H)]^+$, calcd, 1112.06; found, 1112.57. Anal. Calcd: C, 60.37, H 3.62. Found: C, 60.15, H 3.75.

Synthesis of Ge4A-Zn. To a 20 mL vial were added 33.4 mg (0.06 mmol) of **5** and 56 mg (0.2 mmol) of zinc nitrate hexahydrate. DMF (4.5 mL), ethanol (4.5 mL), and water (3.6 mL) were added to dissolve the organic ligand and the salt. The mixture was shocked by ultrasonic sound for 10 min. The solution was filtered through fritted glass (fine) into three 4 mL vials, which were sealed with Teflon-lined caps. These vials were placed in an oil bath. The bath was heated slowly (over a day) to 75 °C, held at that temperature for 3 days, and then cooled to room temperature. Colorless crystals were collected and dried under vacuum (10 Torr) at room temperature for 3 days, with an overall yield of 38%. Anal. Calcd for $(GeC_{28}H_{17}O_8)_2Zn_3(C_3H_7NO)_2(H_2O)_{4.6}$: C, 48.56; H, 3.76; N, 1.83. Found: C, 48.54; H, 3.67; N, 1.72. Drying procedures for elemental analysis and X-ray crystallography were different, so that there are differences in solvation.

Sorption Measurements. The surface areas and micropore volumes were determined by N_2 adsorption at 77 K and by CO_2 adsorption at 297 K, respectively, using an Autosorb-1 volumetric sorption analyzer controlled by Autosorb-1 for Windows 1.19 software (Quantachrome). Prior to the experiments, the samples were degassed at 80 °C under vacuum for 12 h. Details are given in the Supporting Information.

Single Crystal Structure of Si4A-Zn. Crystals were mounted using oil (Infineum V8512) on a glass fiber. Measurements were made on a CCD area detector with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions but not refined, except as noted in the following. The reported molecular formula of $C_{32.5}H_{16}N_{1.5}O_{11.5}SiZn_2$ was obtained as follows. There are two structurally distinct Zn atoms (Figure 1), to which are attached one molecule of water and four carboxylate groups of the organic molecule, contributing a formula of $C_{28}H_{16}O_9SiZn_2$. Although the four carboxyl groups are attached to four Si atoms, those atoms are shared with four other Zn_2 centers, so that only a single Si atom is dedicated on average to each Zn_2 center. The hydrogen atoms on the structural water molecule were not included, as their calculated positions were unknown. In addition, the crystal structure contains one water of solvation and 1.5 DMF molecules of solvation (one fully occupied, one-half occupied), contributing $O(C_3NO)_{1.5}$ to the molecular formula, for the total given above with molecular weight 770 based on two Zn atoms. Further details are given in the Supporting Information.

Single Crystal Structure of Ge4A-Zn. Data were obtained in the same fashion as for **Si4a-Zn**. Hydrogen atoms were included at calculated positions but not refined, except as noted in the following. The reported molecular formula of $C_{74}H_{74}O_{22}N_6Ge_2Zn_3$ was obtained as follows (the actual reported formula was calculated on the basis of 1.5 Zn atoms, but we have doubled that number in order to correspond more clearly to the depiction in Figure 5). The three Zn atoms are attached to eight carboxylate or carboxyl groups, contributing a formula of $C_{56}H_{32}O_{16}Ge_2Zn_3$. The eight carboxylic groups are attached to eight Ge atoms, each of which is shared with four other Zn_3 centers, so that 8/4 or two Ge atoms are dedicated to each Zn_3 center. The two carboxyl H atoms are not included in this total, as their calculated positions are unknown. This formula corresponds to the calculated formula of molecular weight 1302. Refinements were carried out on this unit by squeezing out six DMF molecules of solvation. The DMF atoms, $(C_3H_7NO)_6$, then were reinstated after refinement to give the reported formula given above, with the reported molecular weight of 1741 based on three Zn atoms. Further details are given in the Supporting Information.

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Supporting Information Available: Sorption plots for **Ge4A-Zn**. Crystal data for **Si4A-Zn** and **Ge4A-Zn**. This material is available free of charge via the Internet at http://pubs.acs.org.

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