2710 *Inorg. Chem.* **2000,** *39,* 2710−2711

Three-Dimensional Framework Constructed Using Nanometer-Sized Metallamacrocycle as a Secondary Building Unit

Mooshin Moon, Inhoe Kim, and Myoung Soo Lah*

Department of Chemistry, College of Science, Hanyang University, 1271 Sa-1-dong, Ansan, Kyunggi-do 425-791, Korea

Received September 8, 1999

Research on microporous structures has concentrated largely on inorganic materials such as aluminosilicates and aluminophosphates.[1] The assembly of microporous materials from organic molecule and metal ion building blocks is an emerging area that is yielding new generations of open supramolecular architecture.[2] An important strategy for the construction of metal−organic open framework structures concerns the self-assembly of the appropriate metal salts and a tailored ligand in an appropriate solvent. However, nature tends to avoid a vacuum, and identical copies interpenetrate to fill the space.[3] The design and synthesis of new framework materials containing large pores is a continuous challenge. A new strategy for the construction of a microporous material is to use inorganic clusters as secondary building units in the assembly of the extended networks.[4] In this study, we tried to construct a new open framework structure using a large organic−inorganic hybrid secondary building unit that would prevent the interpenetration of identical copies.

We have recently synthesized a nanometer-sized hexanuclear manganese metallamacrocycle using a chelating pentadentate ligand.[5] Each metal center in the hexanuclear manganese metallamacrocycle has been coordinated by five donor atoms from two chelating pentadentate ligands and an additional donor atom from a solvent molecule. Three solvent molecules coordinated at the metal centers are in one face of the cluster, and the other three solvent molecules coordinated at the other metal centers are in the other face of the cluster. In this study, we have tried to synthesize a new open framework material using a nanometer-sized rigid building block. We exchanged the coordinated solvent molecules of the metallamacrocycle using an exobidentate ligand to construct a three-dimensional framework.

When an *N*-acetylsalicylhydrazidate (ashz^{3-}) was used as a pentadentate ligand for an octahedral manganese(III) ion and a 1,2-bis(4-pyridyl)ethane (bpea) was used as an exobidentate ligand, a self-assembled three-dimensional molecular open framework was easily constructed.[6] The hexanuclear manganese metallamacrocycle served as a discrete molecular building block, and the exobidentate ligand bpea connected the building block. A diagram of the open framework $[Mn_6(ashz)_6(DMF)_2(bpea)_2]_n$ (**1**) is shown in Figure 1.[7] The building block, hexanuclear manganese metallamacrocycle $[Mn_6(ashz)_6]$, was similar to the previously reported hexanuclear manganese metallamacrocycle $[Mn_6(fshz)_6(MeOH)_6]$.[5] All building blocks were connected by exobidentate ligands, where the intermetal distance spaced by an exobidentate ligand was about 13.8 Å. The framework has four nanometer-sized channels along the crystallographic *c* axis per unit cell (Figures 1 and 2). Many solvent molecules were packed into the channels in the crystal structure. The framework was estimated to occupy only about 51% of the crystal volume by the PLATON program.[8] The average van der Waals diameter of the solvent channels was estimated to be approximately 16 Å. The size of the narrowest neck of the channel was 5.5 Å × 8.2 Å, and the largest diameter of the channel was 20 Å. Interestingly, only four of the six coordinated solvent molecules in each metallamacrocycle were substituted by the exobidentate bridging ligand bpea, and two unsubstituted coordinated solvent molecules were exposed in the channels (Figure 3).

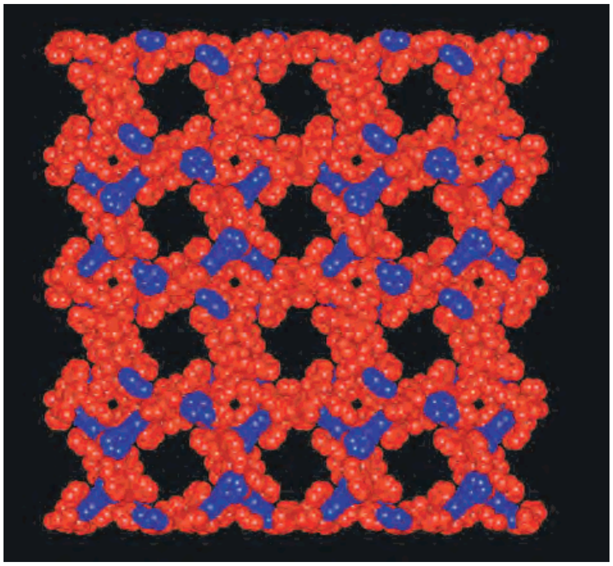

Figure 1. Space filling diagram of the framework, $[Mn_6(ashz)_6(DMF)_2(bpea)_2]_n$ (**1**). All DMF molecules were omitted. Color code: red, metallamacrocycle; blue, bpea.

---

(1) (a) Meier, W. M.; Olson, D. H.; Baerlocher, C. *Atlas of Zeolite Structure Types*, 4th ed.; Elsevier: London, 1996. (b) Dyer, A. *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1994; Vol. 8, pp 4363−4391.

(2) (a) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431−1434. (b) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861−2868. (c) Venkataraman, D.; Lee, S.; Moore, J. S.; Zhang, P.; Hirsch, K. A.; Gardner, G. B.; Covey, A. C.; Prentice, C. L. *Chem. Mater.* **1996**, *8*, 2030−2040.

(3) (a) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792−795. (b) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725−1727.

(4) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (b) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145−1147.

(5) Kwak, B.; Rhee, H.; Park, S.; Lah, M. S. *Inorg. Chem.* **1998**, *37*, 3599−3602.

(6) Synthesis of $[Mn_6(ashz)_6(DMF)_2(bpea)_2]_n$, **1**: A 0.0988 g (0.509 mmol) sample of *N*-acetylsalicylhydrazide (H_3ashz) was dissolved in 5 mL of DMF and 15 mL of hexane mixed solution. Then 0.0561 g (0.304 mmol) of 1,2-bis(pyridyl)ethane was added to the solution and stirred for 1 min. When all ligands were dissolved completely, 0.1287 g (0.525 mmol) of manganese (II) acetate tetrahydrate was added to the solution without stirring. The solution was allowed to stand for a week, whereupon dark-brown rectangular crystals were obtained (0.1668 g, 94.5% yield). Crystals were vacuum-dried. Anal. Calcd for $[Mn_6(ashz)_6(DMF)_2(bpea)_2]\cdot(H_2O)_5$ ($C_{84}H_{90}N_{18}O_{25}Mn_6$) (fw = 2081.37): C, 48.47; H, 4.36; N, 12.11; Mn, 15.84. Found: C, 48.62; H, 4.34; N, 12.15. Mn, 15.8.

(7) Crystal data for **1** at 190 K: 0.30 mm × 0.65 mm × 1.20 mm, dark brown crystal, tetragonal, $I4_1/a$, $a = b = 40.352(13)$ Å, $c = 17.813(8)$ Å; $V = 29005(18)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.381$ g cm^{-1}, μ(Mo Kα) = 0.591 mm^{-1}, $2\theta_{max} = 40°$. Final R1 = 0.0822 for 4968 reflections of $I > 2\sigma(I)$, R1 = 0.0939, wR2 = 0.2421 for all 5856 reflections.

(8) Platon program. Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194−201.

10.1021/ic991079f CCC: $19.00

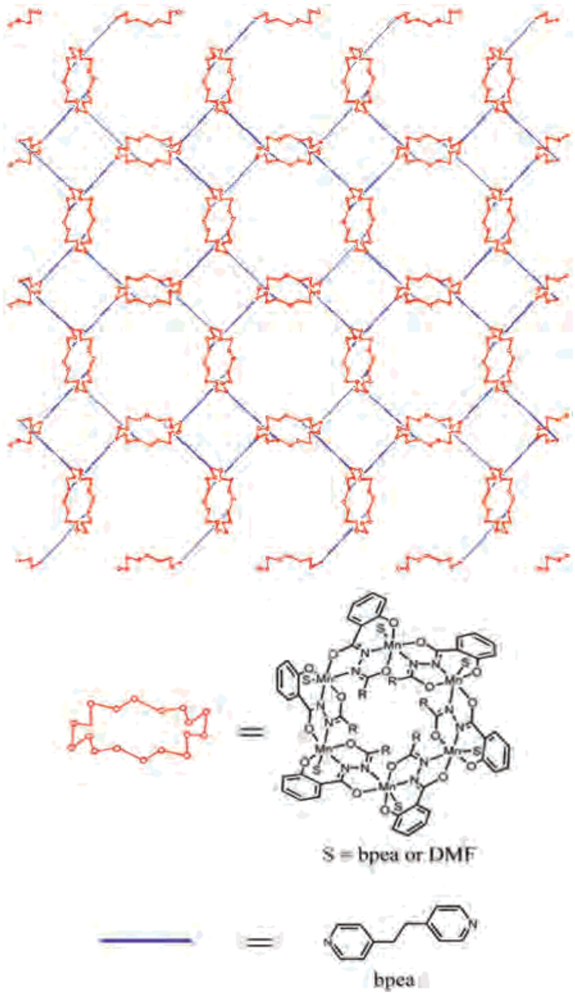

Figure 2. Schematic diagram of framework **1**. The metallamacrocycles presented as red macrocycles were networked by 4_1 or 4_3 screw symmetry related blue exobidentate bridging bpea ligands. The channels are along the crystallographic S_4 symmetry sites.

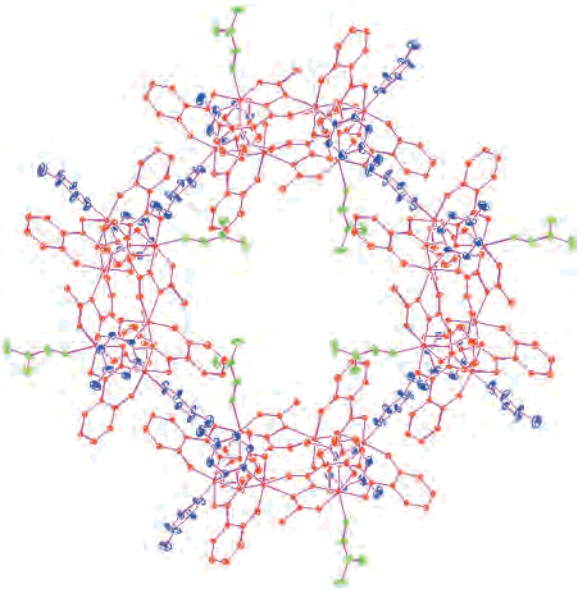

Figure 3. OETEP view (10% thermal ellipsoids) of one of the channels in the open framework. The DMF molecules coordinated to the metal centers were exposed to the channels. Color code: red, metallamacrocycle; blue, bpea; green, DMF.

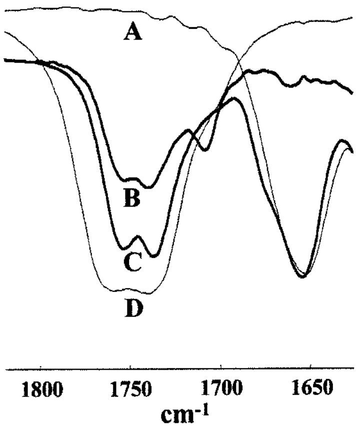

Figure 4. IR spectra of the framework $[Mn_6(ashz)_6(DMF)_2(bpea)_2]_n$ (**1**): (A) before soaking in dimethylmalonate; (B) after soaking in dimethylmalonate; (C) synthesized in DMF/dimethylmalonate mixed solvent system. (D) IR spectrum of dimethylmalonate.

It was possible to exchange the solvent molecules in the channels to other organic molecules reversibly (Figure 4). After soaking framework **1** in the various organic solvents (acetone, chloroform, methylene chloride, and ethyl acetate), only the stretching band corresponding to the DMF molecules in the channels disappeared in the IR spectrum of the framework.[9] The DMF molecules move out of the channels. When we soaked framework **1** in dimethylmalonate, not only did the stretching band corresponding to the DMF molecule (1653 cm^{-1}) disappear but also new bands corresponding to dimethylmalonate (1708, 1740, 1753 cm^{-1}) appeared (Figure 4B). The band at 1708 cm^{-1} represents the reduced bond strength of a carbonyl group. The carbonyl group of the dimethylmalonate is probably coordinated to the "active" metal center in the channels.[10] DMF molecules in the channels moved out of the channels, and dimethylmalonate molecules moved into the channels. When we soaked framework **1** in chloroform again, the bands corresponding to dimethylmalonate disappeared. In addition, we were able to synthesize the same framework in the DMF/dimethylmalonate mixed solvent system. The stretching band corresponding to the DMF and dimethylmalonate appeared in the IR spectrum of the framework, but there was no band corresponding to the coordinated dimethylmalonate (Figure 4C). However, when we soaked framework **1** in diethylphthalate, only the band corresponding to the DMF molecules disappeared. DMF molecules in the channels moved out of the channels, but sterically more demanding diethylphthalate molecules could not infiltrate the channels.

In conclusion, we have constructed a three-dimensional open framework using a nanoscale building block as a secondary building unit. The presence of "active" metal centers in a three-dimensional framework is extremely rare.[11] The "active" metal centers exposed in the channels might provide a unique environment for promoting the selective binding or activation of a guest molecule.

Supporting Information Available: Details of the crystal structure analysis, TGA, and DSC of **1** and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991079F

---

(9) The framework does not dissolve at all in the solvents used during the soaking experiment.

(10) The "active" metal center in the channels represents the metal center coordinated by a solvent molecule.

(11) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651−1657.