A three dimensional porous metal–organic framework [Fe$_4$L$_6$·(DMF)$_3$·(H$_2$O)$_{10}$] constructed from neutral discrete Fe$_4$L$_6$ pyramids [H$_2$L = 1,3-benzodihydroxamix acid]†

Yan Bai, Dong Guo, Chun-ying Duan,* Dong-bin Dang, Ke-liang Pang and Qing-jin Meng*

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: duancy@nju.edu.cn

A 3-D porous zeolite-like metal–organic framework surviving guest removal is assembled from a well-defined tetrahedral Fe$_4$L$_6$ cavity by the cooperativity of hydrogen bonds and π–π stacking.

The coordination paradigm pioneered by Lehn and Sauvage, and as developed in the groups of Stang, Fujita, Raymond and others for closed systems, has allowed for the synthesis of an enormous number and variety of discrete, isolable, supramolecular structures based on assemblies featuring well-defined nanoscale cavities.[1,2] However, a small number of these have subsequently been used as building blocks for microporous materials which comprise an important component of the emerging chemistry of microporous molecular materials,[3] since the nominal requirements for functional microporous molecular materials formation are compounds featuring: accessible cavities of useful size, no catenation, no counter ions, and sufficient stability to withstand removal of solvent molecules.

On the other hand, as the simplest platonic polyhedron, tetrahedral clusters have attracted more attention because of their intrinsic beauty and interesting host–guest chemistry, as well as the fact that they illustrate some basic construction principles necessary to assemble highly symmetric polyhedra.[4] In this paper we report a novel and rather beautiful crystalline porous structure assembled from the neutral platonic polyhedron. The ligand (Scheme 1) used here is one of the simplest hydroxamates; it is said that such ligands[5] are suitable for constructing tetrahedral M$_4$L$_6$ cavities with +3 charged metal ions of octahedral coordination geometry such as Fe^{3+}. The polyhedron formed has advantages for the polymerization into modular porous open framework solids: a) the hydrogen atoms attached to the nitrogen atoms and the six phenyl rings of the ligands in the polyhedron have the potential to contact with others through hydrogen bonds or π–π interactions, from which the polyhedron serves as a tetrahedral building block or an octahedral building block;[6] b) the replacement in a vertex of a framework net by an Fe$_4$L$_6$ cluster, a process termed decoration, results in open structures with high rigidity and without a tendency to interpenetrate, while optimal pore volumes may be achieved;[7] c) the introduction of a neutral polyhedron as SBU into a porous framework suggests a number of potentially exciting applications involving selective molecular transport, sensing, or chemical transformations.[8]

Ligand H$_2$L was prepared through the reaction of isophthaloyl dichloride with hydroxylamine. The polyhedron **1** was achieved by simply diffusing a solution of Fe(NO$_3$)$_3$·9H$_2$O into a solution of H$_2$L in the presence of base.‡ Crystallographic study of complex **1**
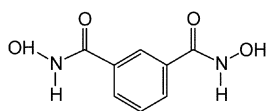
has unequivocally confirmed the tetrahedral geometry of the Fe$_4$L$_6$ cluster.§ ¶The asymmetry unit consists of two crystallographically independent units, corresponding to ΔΔΔΔ and ΛΛΛΛ enantiomers, respectively; each lies on a special position with C_3 symmetry, a subgroup of T_d. The four metal ions in one polyhedron are separated by an average of 8.85 Å. Fig. 1 shows the ΔΔΔΔ isomer of the polyhedron; each iron ion is pseudo-octahedrally coordinated by three bidentate hydroxamate binding units from three separated ligands in a *fac* configuration. Each ligand loses two protons and coordinates to two metal centers as a bridge between two metal ions to span one edge of the tetrahedron. The polyhedron has a relatively open, rigid cavity, which is partially filled with three crystallographically identical DMF molecules.

The most interesting structural feature of the complex in the solid state is that it forms a three-dimensional porous framework (Fig. 2). Each ΔΔΔΔ or ΛΛΛΛ Fe$_4$L$_6$ polyhedron provides three donor hydrogen bonds and three acceptor hydrogen bonds [N(11)···O(26C) 2.84 Å, N(11)–H(11A)···O(26C) 162°, or N(22)···O(14) 2.89 Å, N(22)–H(22A)···O(14) 168°, respectively, symmetry code C: $1 - x$, $0.5 + y$, $1.5 - z$] with six different Fe$_4$L$_6$ isomers in three directions to form a NaCl-like packing pattern with larger pores among the polyhedrons. The diameter of the spherical internal voids is *ca*. 13–15 Å and the windows of the MOF structure *ca*. 7–8 Å. The volume of a van der Waals sphere that would just fit inside the void is *ca*. 900 Å^3.[9] Three DMF molecules and ten water molecules per tetrahedral unit are found to fill the 3-D body. The six phenyl rings of each polyhedron are also stacked with the phenyl rings of the neighbors to stabilize the three-dimensional porous framework.[10] The dihedral angles of the stacked pairs I and IIID, II and IVE are 16.1 and 10.6° with the shortest inter-planar atom···atom separation *ca*. 3.45 Å, respectively [symmetry code D: $1 + x$, $-1 + z$, x; E: $0.5 - y$, $1 - z$, $0.5 - x$]. Interconnected systems of non-covalent interactions possess the property of being co-
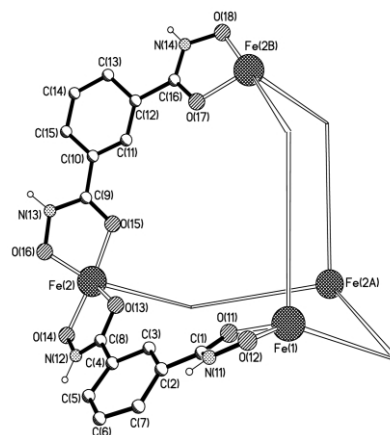
Fig. 1 Perspective view of the ΔΔΔΔ isomer of the Fe$_4$L$_6$ clusters, showing the tetrahedral shape of the molecule. Selected bond lengths (Å): Fe(1)–O(11) 2.067(6), Fe(1)–O(12) 1.968(6), Fe(2)–O(13) 2.020(8), Fe(2)–O(14) 1.977(8), Fe(2)–O(15) 2.045(7), Fe(2)–O(16) 1.988(8), Fe(2)–O(17B) 2.050(8), Fe(2)–O(18B) 1.987(7). Symmetry code A: $0.5 - y$, $1 - z$, $0.5 + x$; B: $-0.5 + z$, $0.5 - x$, $1 - y$.

H$_2$L

Scheme 1

† Electronic supplementary information (ESI) available: TGA and XRD patterns of **1** and **2**. See http://www.rsc.org/suppdata/cc/b3/b306264c/
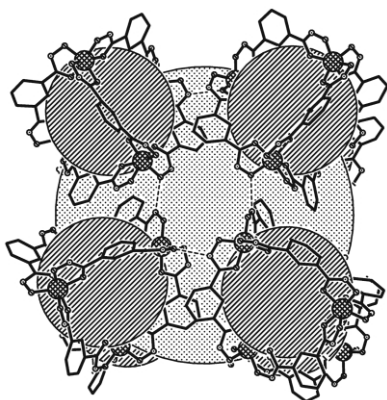
Fig. 2 Molecular packing of the clusters showing the large apertures and voids achieved by the cooperativity of hydrogen bonds and π–π stacking interactions, the solvent molecules are omitted for clarity.

operative, namely, the contacts enhance the strengths of each other and the interaction energy per contact is greater than the energy of an isolated interaction.[11] There are also hydrogen bonds which are found to connect the guest DMF molecules, water molecules and oxygen atoms of the clusters in the porous framework.

To evaluate the mobility of the guests within the framework, we examined the as-synthesized crystals by thermal gravimetric techniques. In flowing nitrogen, a crystalline sample of **1** was heated at a constant rate of 2 °C min⁻¹(see ESI†). A rapid weight loss of 23% was observed below 180 °C corresponding to the liberation of all DMF molecules and water molecules, a weight loss step between 200 °C and 350 °C was observed and is attributed to decomposition of the framework. A powder X-ray diffraction pattern of the sample **2**, which is obtained by heating complex **1** carefully to 180 °C to remove the solvents, shows that the positions of the most intense lines remain unchanged relative to the simulated pattern based upon the single-crystal data of the complex **1**. The good agreement between the peaks in both diagrams demonstrates that the porous framework is retained in the absence of guest molecules in the pores. It is said that extensive cooperativity between discrete molecules throughout the crystals is important for such materials to maintain the porous framework upon the guest removal. Since the structure which consists of a network of large cavities interconnected by channels appears to survive guest removal, it distinctly exhibits the 3-D porous zeolite-like network. Organic molecular crystals that undergo single-crystal-to-single-crystal phase transition upon guest uptake and release have been reported,[12] and while the cooperativity between the molecules throughout the crystal maintains the macroscopic integrity upon guest removal, there is a change in the overall packing arrangement of the host compounds. It is suggested that even weak dispersive forces can exert a profound influence on solid-state dynamics.

Controlling the assembly of molecules in the solid state is currently recognized as one of the most important issues in the synthesis of functional materials. The present represents the first example of a 3-D porous framework assembled from discrete, neutral metal-containing polyhedrons. The ability to control both the formation and details of the structure of these materials offers an interesting approach to tune finely the electrical or optical properties in the crystal.

This work was supported by the National Natural Science Foundation of China. (No. 20131020). We thank Mr Liu Yong-jiang for collecting the crystal data.

Notes and references

1 (*a*) J. M. Lehn, *Supramolecular Chemistry*, VCH, New York, 1995 and references therein; (*b*) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796–798; (*c*) N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794–796.
2 (*a*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417–425; (*b*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502–518; (*c*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975–982.
3 (*a*) P. H. Dinolfo and J. T. Hupp, *Chem. Mater.*, 2001, **13**, 3113–3125; (*b*) K. Campbell, C. J. Kuehl, M. J. Ferguson, P. J. Stang and R. R. Tykwinski, *J. Am. Chem. Soc.*, 2002, **124**, 7266–7267.
4 (*a*) A. J. Terpin, M. Ziegler, D. W. Johnson and K. N. Raymond, *Angew. Chem., Int. Ed.*, 2001, **40**, 157–160; (*b*) R. W. Saalfrank, R. Burak, S. Reihs, N. Löw, F. Hampel, H. D. Stachel, J. Lentmaier, K. Peters, E. M. Peters and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 993–995; (*c*) J. S. Fleming, K. L. V. Mann, C. A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Angew. Chem., Int. Ed.*, 1998, **37**, 1279–1281.
5 T. Beissel, R. E. Powers, T. N. Parac and K. N. Raymond, *J. Am. Chem. Soc.*, 1999, **121**, 4200–4206.
6 (*a*) L. R. Macgillivray and J. L. Atwood, *Nature*, 1997, **389**, 469–472; (*b*) V. A. Russell, C. C. Evans, W. J. Li and M. D. Ward, *Science*, 1997, **276**, 575–579.
7 (*a*) H. L. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 2001, **402**, 276–279; (*b*) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474–484; (*c*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469–472.
8 (*a*) K. M. Benkstein, J. T. Hupp and C. L. Stern, *Angew. Chem., Int. Ed.*, 2000, **39**, 2891–2893; (*b*) O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed.*, 2000, **39**, 136–140; (*c*) P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71–80; (*d*) J. P. Collman, X. Zhang, B. V. J. Lee, E. S. Uffelman and J. I. Brauman, *Science*, 1993, **26**, 1404–1411.
9 The *van* der Waals radius of C(1.70 Å) was employed in the determination of distance parameters. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
10 The phenyl rings I, II, III and IV are defined by the atoms C(2), C(3), C(4), C(5), C(6) and C(7); C(10), C(11), C(12), C(13), C(14) and C(15); C(18), C(19), C(20), C(21), C(22) and C(23); C(26), C(27), C(28), C(29), C(30) and C(31), respectively.
11 (*a*) Z. H. Liu, C. Y. Duan, J. H. Li, Y. J. Liu, Y. H. Mei and X. Z. You, *New. J. Chem.*, 2000, **24**, 1057–1062; (*b*) Z. H. Liu, C. Y. Duan, J. Hu and X. Z. You, *Inorg. Chem.*, 1999, **38**, 1719–1724; (*c*) H. Mo, D. Guo, C. Y. Duan, Y. T. Li and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2002, 3422–3424.
12 (*a*) J. L. Atwood, L. J. Barbour, A. Jerga and B. L. Schottel, *Science*, 2002, **298**, 1000–1002 and references therein.