A three dimensional porous metal–organic framework $[Fe_4L_6 \cdot (DMF)_3 \cdot (H_2O)_{10}]$ constructed from neutral discrete Fe_4L_6 pyramids $[H_2L = 1,3$ -benzodihydroxamix acid][†]

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A 3-D porous zeolite-like metal–organic framework surviving guest removal is assembled from a well-defined tetrahedral Fe₄L₆ 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 ligands⁵ are suitable for constructing tetrahedral M_4L_6 cavities with +3 charged metal ions of octahedral coordination geometry such as Fe³⁺. 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_4L_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_2L was prepared through the reaction of isophthaloyl dichloride with hydroxylamine. The polyhedron **1** was achieved by simply diffusing a solution of Fe(NO₃)₃·9H₂O into a solution of H_2L in the presence of base.[‡] Crystallographic study of complex **1**



† Electronic supplementary information (ESI) available: TGA and XRD patterns of 1 and 2. See http://www.rsc.org/suppdata/cc/b3/b306264c/ has unequivocally confirmed the tetrahedral geometry of the Fe₄L₆ cluster.§ ¶The asymmetry unit consists of two crystallographically independent units, corresponding to $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$ 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 $\Delta\Delta\Delta\Delta$ 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 $\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda\Lambda$ Fe₄L₆ polyhedron provides three donor hydrogen bonds and three acceptor hydrogen bonds $[N(11) \cdots O(26C) 2.84 \text{ Å}, N(11) - H(11A) \cdots O(26C) 162^\circ$, 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 Fe₄L₆ 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 $\Delta\Delta\Delta\Delta$ isomer of the Fe₄L₆ 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.

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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-singlecrystal 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.

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Notes and references

‡ Synthesis of complex 1: A solution of the H₂L ligand (0.018 g, 0.09 mmol) and KOH (0.002 g, 0.036 mmol) in methanol (6 mL) was layered onto a solution of Fe(NO₃)₃·9H₂O (0.04 g, 0.1 mmol) in DMF (4 mL). The solutions were left for two weeks at room temperature in darkness to give X-ray quality red block crystals in good yields. Yield: 86%. Elemental analysis (%) for (C₄₈H₃₆N₁₂O₂₄Fe₄)(C₃H₇NO)₃(H₂O)₁₀ 1: calcd: C 38.3, H 4.3, N 11.7; found: C 38.5, H 4.5, N 11.4%.

§ Crystal data of $(C_{48}H_{36}N_{12}O_{24}Fe_4)(C_3H_7NO)_3(H_2O)_{10}, M_r = 1787.74, crystallized in the cubic space group <math>P2_13$ with a = 27.642(2) Å, V = 21120(2) Å³, Z = 8. $\rho_{calc} = 1.124$ Mg m⁻³, T = 293(2), $\mu = 0.612$ mm⁻¹, GOOF = 0.986, Intensity data were collected on a Bruker CCD system. The structure was solved by direct methods. 85354 measured reflections of which 12373 reflections are independent and all include in the refinement. $R_1 = 0.077$, $wR_2 = 0.208$ (all data, refined against $|F^2|$). The water molecules were refined isotropically and with non-unit occupancies. Since there are left and right hand molecules in pairs, we tried to resolve the structure using a centro-symmetric space group such as $Pa\overline{3}$ or $Pn\overline{3}$, however, no suitable space group can be found. The mean $|E^*E - 1|$ of only 0.60 also supports the choice of the reported acentric space group. CCDC 201192. See http://www.rsc.org/supdata/cc/b3/b306264c/ for crystallo-graphic data in .ci for other electronic format. ¶

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