Coordination Polymers

A Metal–Organic Framework with the Zeolite MTN Topology Containing Large Cages of Volume 2.5 nm^3**

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Metal–organic framework (MOF) coordination polymers have attracted tremendous attention because of their intriguing molecular topologies and their potentially useful ion-exchange, adsorption, catalytic, fluorescence, and magnetic properties.[1–7] By taking advantage of the well-defined coordination geometries of metal centers as nodes, the structures of various minerals, such as quartz diamond,[8,9] perovskite,[10] rutile,[11] PtS,[12,13] and feldspar,[14] with specific functionalities, have been artificially reproduced by replacing monoatomic anions (O^{2-}, S^{2-}) with polyatomic organic bridging ligands as linkers. To meet the increasing demand for large-pore frameworks that are suitable for catalyzing reactions of large molecules, successful synthetic strategies for the preparation of large-pore metal–organic polymers with a genuine zeolite topology are still a huge challenge.

The expansion and decoration of the topological networks of inorganic materials, which is an effective and powerful synthetic strategy, has been shown to produce a new generation of highly porous metal–organic polymers.[15,16] During the course of our work, Férey et al. described a novel metal–organic hybrid compound, $[Cr_3F(H_2O)_3O\{C_6H_3(CO_2)_3\}_2]\cdot n H_2O$ (MIL-100, $n \approx 28$),[17] with the zeolite MTN topology from Cr^{3+} ions and benzene-1,3,5-tricarboxylate, whose structure was determined by powder X-ray diffraction simulation. Our strategy for preparing such a metal–organic framework with large pores is based on expanding the zeolite topologies[18,19] by constructing metal–organic tetrahedral building blocks with four connections. In this work, we consider the hexamethylenetetramine (hmt) ligand to be the best candidate because it contains four coordinating N atoms, similar to the mode of the SiO_4 building block in zeolites. The cadmium ion was chosen as the bridge on account of the equatorial-plane locations of its trigonal-bipyramidal coordination geometry; these locations are easily coordinated by water molecules. Thus, a metal–organic tetrahedral building block TM_4 (T = tetrahedrally coordinated molecule; M = transition-metal ion), in which the M-T-M angles range from 108 to 120°, was constructed from an hmt molecule and four cadmium ions. We present herein a new metal–organic framework with zeolite topology constructed from this tetrahedral building block. The novel open-framework metal–organic polymer $[\{Cd(H_2O)_3\}_{34}(N_4C_6H_{12})_{17}]Cl_{68}\cdot 46\,H_2O\cdot 68\,DMF$ (**1**; DMF = *N*,*N*-dimethylformamide) possesses the zeolite MTN topology (MTN = zeolite socony mobil – thirty-nine) with two types of 5^{12} and 6^45^{12} cages. The 6^45^{12} cage has a volume of about 2522 Å^3 (a van der Waals sphere with a diameter of 16.8 Å would just fit inside the void). To the best of our knowledge, architectures with large cages have rarely been reported so far for metal–organic polymers (such as MOF-101[20] and MIL-100[17]).

Polymer **1** was synthesized under mild conditions. In a typical procedure, a mixture of $CdCl_2\cdot 2.5\,H_2O$ and hmt (10:1) was prepared in DMF/ethanol/H_2O (5:3:3) containing HCl, and then a solution of triethylamine in DMF was allowed to diffuse into the above mixture at room temperature to adjust the pH value of the solution. After standing for a month, colorless octahedron-shaped crystals of **1** were collected with a 67% yield based on cadmium. This complex is stable in air, soluble in water, methanol, and ethanol, slightly soluble in DMF, but insoluble in acetonitrile and nitromethane.

X-ray crystallographic analysis revealed that polymer **1**[21] consists of a 3D open framework with the zeolite MTN topology. Each cadmium ion is coordinated by two nitrogen atoms from two different hmt ligands and three coordinated water molecules (Figure 1). The hmt ligands adopt a tetrahe-

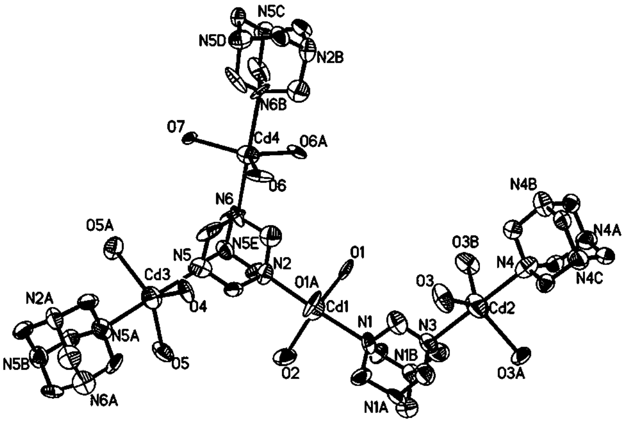

Figure 1. The coordination geometry of the cadmium ions in the asymmetric unit of polymer **1**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cd1—N1 2.455(8), Cd1—N2 2.385(7), Cd1—O1 2.445(4), Cd1—O2 2.466(7), Cd2—N3 2.468(13), Cd2—N4 2.421(16), Cd2—O3 2.459(6), Cd3—N5 2.440(6), Cd3—O4 2.485(5), Cd3—O5 2.419(5), Cd4—N6 2.513(8), Cd4—O6 2.453(4), Cd4—O7 2.448(7); N2-Cd1-N1 177.1(3), N2-Cd1-O1 90.12(13), O1-Cd1-N1 88.51(12), N2-Cd1-O2 90.2(3), N1-Cd1-O2 92.6(3), O1-Cd1-O2 118.36(13), N4-Cd2-N3 180.0(6), N4-Cd2-O3 89.64(17), N3-Cd2-O3 90.36(17), O5-Cd3-N5 92.50(17), N5-Cd3-O4 87.53(13), O5-Cd3-O4 114.69(15), O7-Cd4-N6 90.51(16), O6-Cd4-N6 89.74(8), O7-Cd4-O6 121.13(17).

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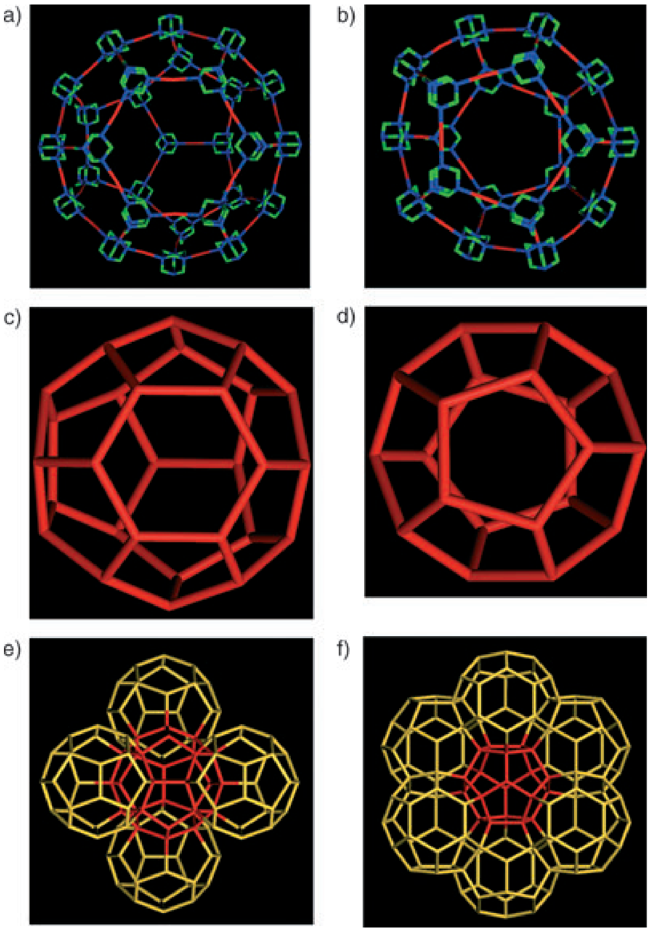

Figure 2. a) A large cage constructed from four six-membered rings (six {Cd_4(hmt)} tetrahedra) and twelve five-membered rings (five {Cd_4(hmt)} tetrahedra) and b) a small cage constructed from twelve five-membered rings (five {Cd_4(hmt)} tetrahedra) in the structure of polymer **1**. Cd red, N blue, C green; for clarity, the oxygen and hydrogen atoms are not shown. The topologies of the 6^45^{12} and 5^{12} cages are shown in (c) and (d), respectively. e) The 6^45^{12} cage in (c; red) sharing its four six-membered rings with four others (yellow). f) The 5^{12} cage in (d; red) sharing its six six-membered rings with six 6^45^{12} cages (c; yellow).

dral coordination geometry, with four different cadmium ions occupying the four coordination sites. The Cd–O lengths (2.419(5)–2.485(5) Å) are within the normal range,[22] and the Cd–N lengths (2.385(7)–2.513(8) Å) are close to those reported for other cadmium–nitrogen donor compounds.[23]

The framework of polymer **1** contains two kinds of cages composed of tetrahedral {Cd_4(hmt)} building blocks. The large 6^45^{12} cage (Figure 2a,c) consists of four six-membered rings (made of six tetrahedrally coordinated hmt molecules) of about 12.3 × 13.1 Å^2 (as measured between the centers of opposite atoms) and twelve five-membered rings of about 10.4 × 10.4 Å^2 in diameter. The small 5^{12} cage (Figure 2b,d) consists of twelve five-membered rings. Each 6^45^{12} cage in polymer **1** shares its six-membered rings with four neighboring 6^45^{12} cages (Figure 2e) and five-membered rings with twelve neighboring 5^{12} cages, while each 5^{12} cage in **1** shares its five-membered rings with six neighboring 6^45^{12} cages (Figure 2 f) and six neighboring 5^{12} cages. In this way, all of these cages give rise to the 3D framework of polymer **1** with the MTN topology.[24] Figure 3 shows two kinds of windows for the five- and six-membered rings along the [110] direction. The same structure exists along five other directions (such as [101], [011], [110], 101], and [011]).

Unlike most zeolites, polymer **1** has a positively charged framework. The charge-balancing chlorine anions in the cages could not be directly located in the crystal structure analysis. However, inductively coupled plasma analysis[25] and mass-spectrometric analysis[26] indicated that the molar ratio of cadmium to chlorine is 1:2. In addition, elemental analysis[27] and thermal gravimetric analysis (TGA)[28] showed that each formula unit of polymer **1** includes about 46 guest H_2O and 68 DMF molecules. Anion exchange was carried out for the cationic framework[29–31] by substituting SCN^- for Cl^- in the cages. Typically, a 200-mg sample of the coordination polymer was treated at room temperature with 5 mL of DMF containing 3 M KSCN. After stirring for 20 min the product was filtered, washed with pure DMF, and then dried in air. The IR spectra of the exchanged product show new SCN^- bands (2075 cm^{-1}); the other signals of the IR spectrum and the powder XRD pattern remain virtually unchanged, which

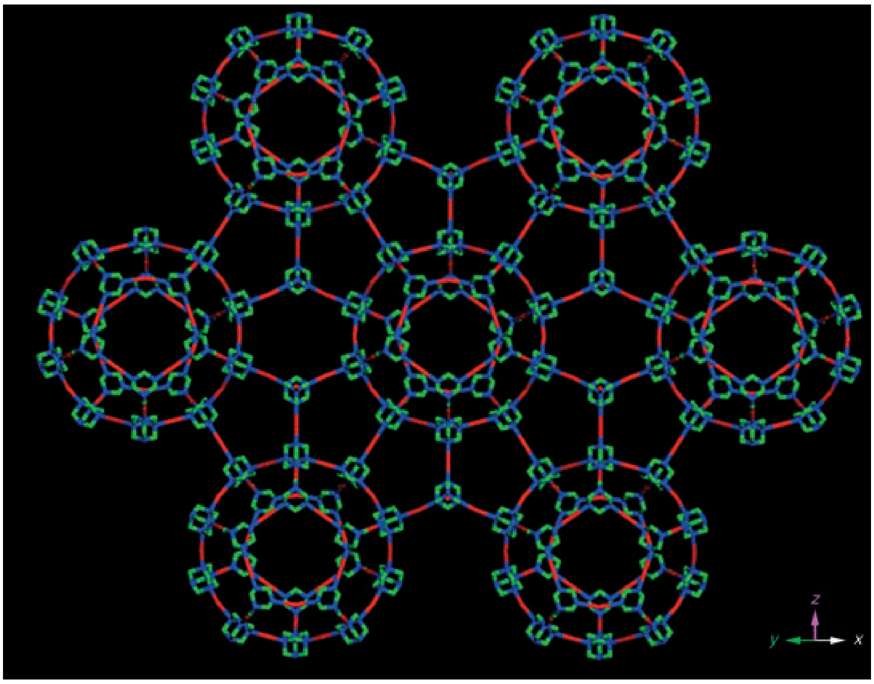

Figure 3. Infinite 3D coordination framework of polymer **1** viewed along the [110] direction. The windows of the six-membered rings (six {Cd_4(hmt)} tetrahedra) are about 12.3 × 13.1 Å^2 (measured between atom centers), and the windows of the five-membered rings (five {Cd_4(hmt)} tetrahedra) are about 10.4 × 10.4 Å^2 in this structure. Cd red, N blue, C green; for clarity, the oxygen and hydrogen atoms are not shown.

suggests that the skeleton is retained after anion exchange (see Supporting Information).

In conclusion, the novel 3D metal–organic framework polymer **1** with the zeolite MTN topology has been synthesized from the metal–organic tetrahedral building block TM_4. The framework of **1** greatly expands the original structure of MTN and possesses large cages with a volume of about 2522 $Å^3$. Other structures with zeolite or zeolite-like topologies and large cages should be obtainable by following a similar synthetic strategy. We believe that such metal–organic framework coordination polymers will come to be seen as a genuine third generation of zeolites that contain the same structures as traditional zeolites but offer several fundamental advantages, including ion-exchange, adsorption, and catalytic properties.

Experimental Section

1: $CdCl_2 \cdot 2.5\,H_2O$ (0.228 g, 0.1 mmol), HCl (0.1 mL, 2 M solution), hmt (0.014 g, 0.01 mmol), DMF (5 mL), ethanol (3 mL), and H_2O (3 mL) were placed in a 25-mL vial and stirred. After stirring in air for 1 h, the vial was placed in a 100-mL beaker containing a solution of triethylamine (0.1 mL) in DMF (8 mL), and then sealed and left for 30 days at room temperature. The resulting colorless octahedron-shaped crystals of **1** were collected (67 % yield based on cadmium). The complex is stable in air, soluble in water, methanol, and ethanol, slightly soluble in DMF, but insoluble in acetonitrile and nitromethane. FTIR (KBr): $\tilde{\nu} = 3448$ (s), 2939 (w), 2360 (w), 1651 (s), 1466 (w), 1388 (w), 1242 (m), 1111 (w), 1011 (s), 818 (m), 694 (m), 579 (w) cm^{-1}.

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[21] A colorless crystal of **1** ($0.30 \times 0.30 \times 0.28$ mm^3) was selected for X-ray structural analysis on a Bruker SMART CCD diffractometer at 298 K. The compound crystallized in the space group $Fd\bar{3}m$, cubic, $a = 48.9411(12)$ Å, $V = 117225(5)$ $Å^3$, $Z = 8$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.185$ $Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 1.558$ mm^{-1}, $F(000) = 40800$. A total of 108996 reflections were collected in the range $3.72 < \theta < 28.27$, of which 6526 were unique. The structure was solved and refined by full-matrix least-squares on F^2 (SHELXL-97; G. M. Sheldrick, SHELXL-97, program for X-ray crystal structure refinement, University of Göttingen, Göttingen, Germany). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined in a riding mode. Final $R1$ value 0.1891 (0.0799 after SQUEEZE) for 3121 independent reflections ($I > 2\sigma(I)$). The solvent-accessible volume was assessed using the PLATON software (A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34) and the contribution of the chlorine anions and the disordered solvent to the diffraction pattern was subtracted from the observed data by the "SQUEEZE" method as implemented in PLATON (P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194). The SQUEEZE-bypass method referred to therein is widely used in crystallographic analysis of compounds containing substantial amounts of disordered solvent that cannot be located precisely from diffraction data. CCDC-253194 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[25] Inductively coupled plasma (ICP) analysis (Perkin-Elmer Optima 3300 DV ICP instrument) indicated that each gram of the complex contains 1.569×10^{-4} mol of cadmium.

[26] Polymer **1** (0.05148 g) and H_2O (15.0 mL) were placed in a 25-mL vial and stirred. A solution of $AgNO_3$ (0.5 g) in H_2O (3.0 mL) was then slowly added. After stirring in air for 1 h, the precipitate of AgCl was filtered off, washed with H_2O (3×4 mL), and calcined in a crucible at a constant rate (10 °C min^{-1}) to 800 °C for 30 min. The final quantity of AgCl was 0.04493 g, which gives 3.135×10^{-4} mol of chlorine per gram of complex.

[27] Elemental analysis (%; Perkin-Elmer 2400 elemental analyzer) calcd for $C_{306}H_{976}O_{216}N_{136}Cd_{34}Cl_{68}$: C 22.61, H 6.05, N 11.72; found: C 22.53, H 6.11, N 11.65.

[28] TGA shows a weight loss of 5.24% during the first step (35–75°C), which corresponds to the loss of 46 guest water molecules (calcd: 5.10%). The weight loss of 11.18% during the second step (75–130°C) is attributed to the removal of 25 guest DMF molecules (calcd: 11.24%). The weight loss of 30.41% during the third step (140–245°C) is in accordance with the removal of 43 guest DMF molecules and 102 coordinated water molecules (calcd: 30.64%). (The IR spectrum of **1** displays bands at $\tilde{\nu} =$ 1651 and 2939 cm^{-1} because of $\nu_{C=O}$ and the asymmetric stretching vibration of the methyl group of the guest DMF molecules, respectively.) Decomposition of **1** began above 300°C.

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