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Coexistence of Planar and Chair-Shaped Cyclic Water Hexamers in a Unique Cyclohexanehexacarboxylate-Bridged Metal–Organic Framework

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Received August 7, 2005; Revised Manuscript Received December 9, 2005

ABSTRACT: The hydrothermal reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with *cis,cis,cis,cis,cis,cis*-1,2,3,4,5,6-cyclohexane-hexacarboxylic acid (**L**) generates a unique three-dimensional metal–organic framework (MOF) of $[\text{Co}_3(\text{L-6H})(\text{H}_2\text{O})_6]_n$ (**1**). X-ray crystallography reveals that each **L-6H** ligand changes its conformation to a *trans,trans,trans,trans,trans* form to connect nine Co(II) atoms, and each Co(II) atom is connected to three **L-6H** ligands, leading to a MOF structure with high symmetry of $R\bar{3}$. The coexistence of planar and chair-shaped cyclic water hexamers is found in this MOF. Magnetic studies show the occurrence of the field-dependent magnetic transition.

Great interest has been focused on the rapidly expanding field of hydrogen-bonded water clusters or networks based on the fundamental importance of water in many biological, chemical, and physical processes as well as methane hydrates. So far, structural data of hydrogen-bonded water clusters (such as tetramers, pentamers, hexamers, octamers, and decamers) or polymeric species of chain, tape, or layer structures trapped in metal–organic frameworks (MOFs) as well as in organic molecular crystals are very important for correctly describing the association of water molecules in different surroundings.^{1–3} Of those aggregates, hexamer water species are particularly interesting due to their various conformations including chair,⁴ boat,^{4e,5} and planar⁶ forms that have been characterized in MOF or organic crystalline hosts. The planar ring is the basic structural motif found in the ice II structure⁷ under high pressure and also a prominent structural unit⁸ in liquid water as determined by computer simulations. Recently, Nauta and Miller detected a quasiplanar hexamer within a helium droplet and found that the lattice of a special crystalline host may offer an environment for stabilizing a higher energy hexamer.^{9a} Bernal and Bear reported a twist-boat water hexamer, which was one of the possible conformers of “the smallest piece of ice” trapped within channels of a crystal of a dirhodium molecule.^{9b} However, it is still a challenge how to house or trap water aggregates of special shape in crystal hosts, and much work is required to investigate proper synthetic strategies leading to the desired species. We note that 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (**L**), similar to the well-explored 1,4-cyclohexanedicarboxylic acid and 1,3,5-cyclohexanetricarboxylic acid,¹⁰ is characteristic of multifunctional coordination sites and pH-dependent coordination fashions as well as flexible conformations (Chart 1). Although one could anticipate that it will be applied as a versatile ligand in construction of functional MOFs, no report on coordination chemistry of this ligand has been found so far. We report here an interesting MOF structure built from Co(II) and **L-6H**, in which each **L-6H** ligand changes its conformation to the *trans,trans,trans,trans,trans* form and connects nine Co(II) atoms, leading to a MOF structure with high symmetry of $R\bar{3}$. Remarkable is both planar and chair-shaped cyclic water hexamers, which are simultaneously trapped in this MOF and are unprecedented.

Reaction¹¹ of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, *cis,cis,cis,cis,cis,cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid hydrate (**L**· H_2O), NaOH, 2,2′-bipyridyl, and water (10 mL) in the molar ratio of 1.5:0.5:1.5:1.0:555 at 175 °C for 60 h yields bright purple crystals of $[\text{Co}_3(\text{L-6H})(\text{H}_2\text{O})_6]_n$ (**1**) (75%) in single phase. Phase purity of the bulk materials was

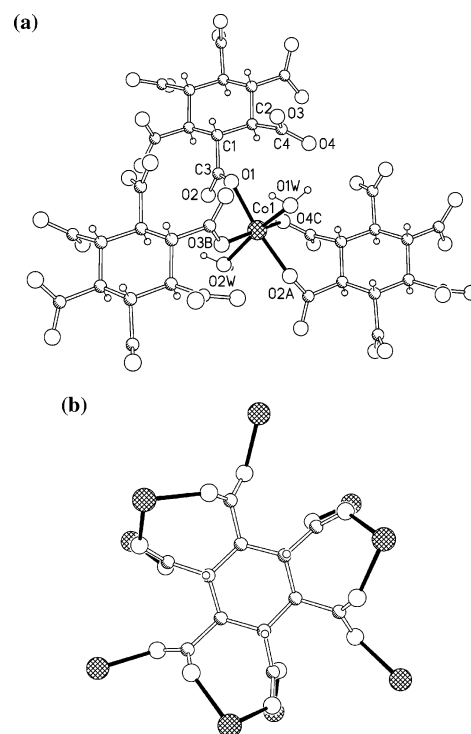


Figure 1. Perspective view showing coordination environment (a) and the bridging mode (b) of the **L-6H** in the structure of **1**.

confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study (Figure S1, Supporting Information).

X-ray structural analysis¹² reveals that **1** crystallizes in rhombohedral $R\bar{3}$ space group with the asymmetric unit consisting of one-third formula unit, and therefore there is only one crystallographically unique Co(II) atom, which lies in a general position, one unique **L-6H** ligand which lies across a 3-fold axis, and two aqua ligands. Each cyclohexane ring adopts a chair conformation, similar to that found for **L**· $3\text{H}_2\text{O}$.^{13a} However, all carboxylate groups lie on e-bond positions, suggesting that the conformation of the **L-6H** ligand (Chart 1) was changed from *cis,cis,cis,cis,cis* of **L** starting reagent into *trans,trans,trans,trans,trans* under the hydrothermal condition. Each Co(II) atom is coordinated in an octahedral geometry by four carboxylate O atoms from three **L-6H** ligands and two trans aqua ligands ($\text{Co1}-\text{O}(\text{carboxylate}) = 2.080(4)-2.108(4)$ Å, $\text{Co1}-\text{O}(\text{aqua}) = 2.122(4)$ and $2.139(4)$ Å; $\text{O}(1w)-\text{Co1}-\text{O}(2w) = 163.24(18)^\circ$) (Figure 1a). Each **L-6H** ligand connects nine Co(II) atoms through its six carboxylate groups, and

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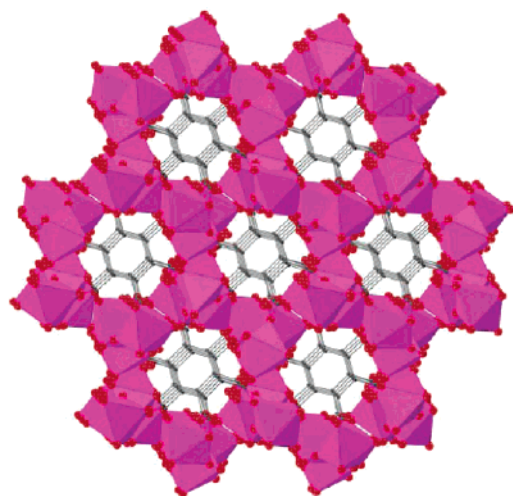
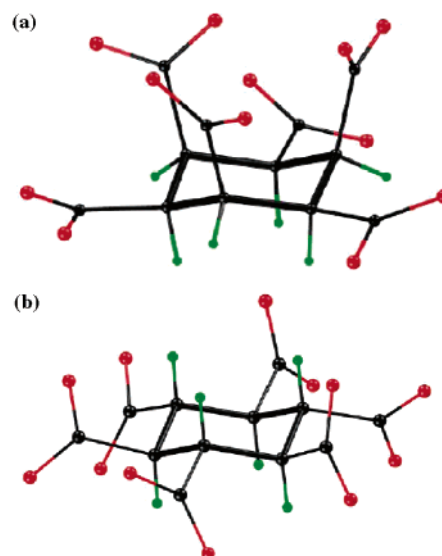


Figure 2. View of the 3-D coordination network along the *c*-axis in the structure of **1**.

each adopts a syn-anti μ_2 -bridging mode (Figure 1b). A 3-D MOF structure is therefore generated by the Co-carboxylate coordination (Figure 2). Moreover, neglecting the cyclohexane rings from a viewpoint of magnetic superexchange pathway, each Co(II) atom is connected by four syn-anti μ_2 -carboxylato bridges into a 3-D tetrahedrally connected Co–Co net (Figure S2, Supporting Information).

Remarkably, two types of cyclic water hexamers of $R_6^6(12)$ in chair and planar conformation (Figure 3a,b), respectively, are unambiguously trapped within the 3-D MOF structure of **1**. The chair hexamer is formed by hydrogen-bonding between the symmetry-related O1w atoms ($O1w \cdots O1w = 2.834(2)$ Å; $O1w-H1wb \cdots O1w = 175(3)^\circ$). Each chair hexamer further donates six hydrogen bonds with symmetry-related O4 atoms ($O1w \cdots O4a = 2.746(3)$ Å; $O1w-H1wa \cdots O4a = 159(3)^\circ$). Planar hexamer is from hydrogen-bonded symmetry-related O2w ($O2w \cdots O2w = 3.101(2)$ Å; $O2w-H2wb \cdots O2w = 174(4)^\circ$). It should be noted that the $O \cdots O$ distance in the chair ring is significantly longer than that ($O \cdots O$ 2.85 Å) in liquid water.^{13b} It seems to represent attempts of the water to fit into a cavity that is too large for

Chart 1. Schematic Presentation of the L-6H Ligand in *cis,cis,cis,cis,cis*- (a) and *trans,trans,trans,trans,trans*-conformations (b)



it. Each planar hexamer also donates six hydrogen bonds with symmetry-related O1 atoms ($O2w \cdots O1g = 2.876(3)$ Å; $O2w-H2wa \cdots O1g = 174(3)^\circ$). Noteworthy is that each planar hexamer is connected to six chair hexamers via the Co–water coordination (Figure 3c), and also each chair hexamer is connected to six planar hexamers via the Co–water coordination. Therefore, an unique high-symmetry 3-D Co–water net is generated (Figure 3d,e). It should be also noted that coexistence of planar and chair-shaped cyclic water hexamers in the same MOF structure is unprecedented. A rare comparable example was recently found in 1,4-[B(HO)₂]₂C₆H₄·4H₂O that contains hexameric units in chair and boat conformations, indicating a contribution to the structural elucidation of bulk water.^{4e}

The magnetic susceptibility of **1** was measured in the range of 2–300 K at 10 kOe. The $\chi(T)$ data between 50 and 300 K was fit to a modified Curie–Weiss Law, $\chi(T) = \chi_0 + C/(T - \theta)$ with a Weiss constant, $\theta = -27.73$ K, and a Curie constant, $C = 2.99$ cm³ mol⁻¹ K (Figure S3, Supporting Information), indicating a

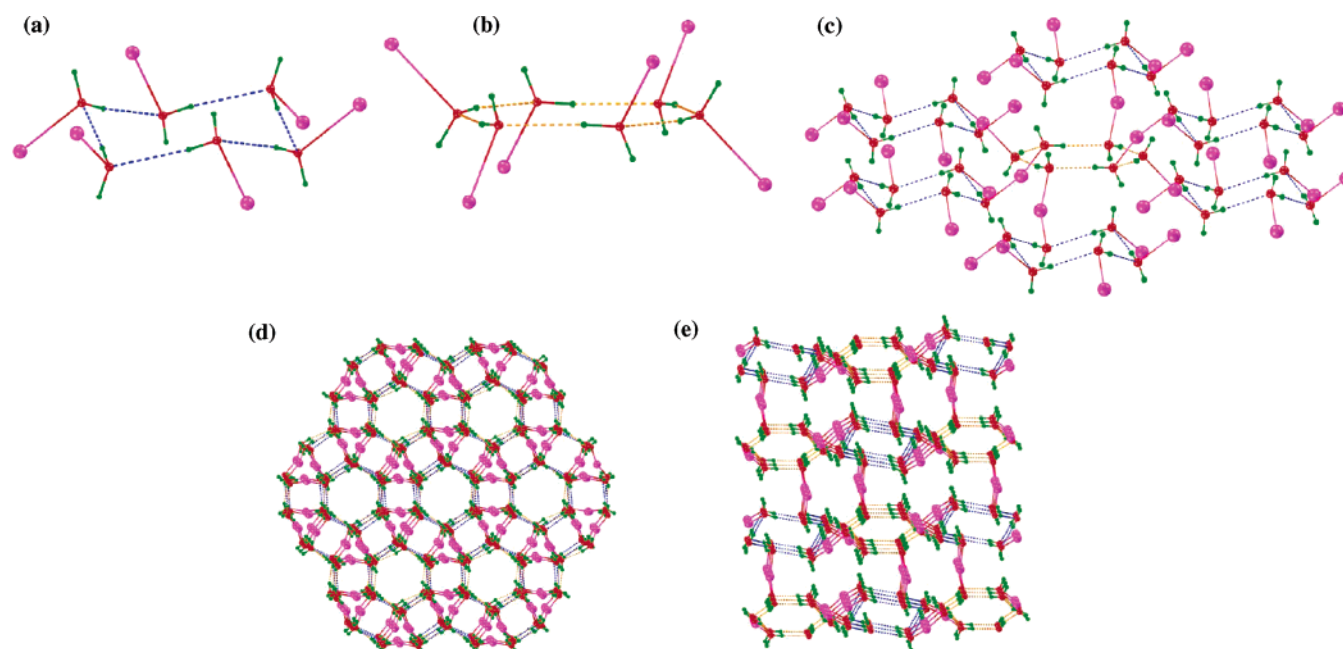


Figure 3. Perspective views showing the chair (a) and coplanar (b) cyclic water hexamer units, the connectivity between the coplanar and coplanar units (c), and the 3-D Co–water net via the metal coordination along the *c*-axis (d) and *a*-axis (e) in **1**.

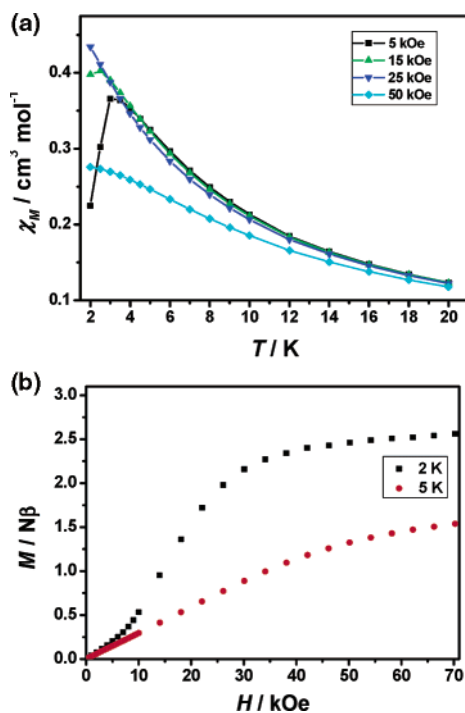


Figure 4. χ_M (per Co) vs T plot at different external fields (a) and field-dependent magnetization (b) of **1** at different temperature.

significant antiferromagnetic coupling between the Co(II) $S = 3/2$ spins through the syn-anti carboxylato bridges. According to the 3-D net connectivity, only one effective magnetic exchange pathway is present within the net via syn-anti μ_2 -carboxylato bridges. The room temperature effective magnetic moment value per Co(II) ion, defined as $\mu_{\text{eff}} = 2.83C^{1/2}$, is $4.89 \mu_B$ for **1**, which is significant higher than the expected spin-only value ($3.87 \mu_B$) due to the orbital contribution of the Co(II) ion.

The magnetic behaviors of **1** are further characterized by temperature- and field-dependent measurements at low temperature. The magnetization maximum disappears at or above 15 kOe (Figure 4a), indicating that the antiferromagnetic interactions are overcome by the external field. These features are the characteristics of metamagnetic behaviors,¹⁴ which are further confirmed by the field dependence of magnetization (Figure 4b). The field-cooled (FC) magnetization at 20 Oe shows the appearance of a sharp peak at ca. 3.0 K (Figure S4, Supporting Information), suggesting the occurrence of a long-range antiferromagnetic ordering.

The thermal gravimetric analysis (TGA) of **1** under an atmospheric environment shows an onset of water loss at higher temperatures above 155 °C and the 3-D MOF begins to decompose above 345 °C (Figure S5, Supporting Information). The first weight loss of 17.1% from 160 to 310 °C is in accordance with the loss of two coordinated water molecules per Co (calculated: 17.2%), while the second weight loss corresponds to the removal of all the organic components to yield Co_3O_4 (found: 37.3%; calculated: 38.4%). Two endothermic peaks (310, 350 °C) in the DTA curve also record the weight loss processes of various groups.

In summary, we have synthesized an interesting 3-D cobalt (II) coordination network of 1,2,3,4,5,6-cyclohexanhexacarboxylate. Magnetic studies reveal that **1** exhibits spontaneous magnetic ordering and magnetic transition. Detailed magnetic investigations on **1** and other complexes¹⁵ are underway.

Acknowledgment. This work was supported by the National Science Funds for Distinguished Young Scholars of China (No. 20525102), the NSFC (20471069), the FANEDD of China (200122), and Sun Yat-Sen University.

Supporting Information Available: X-ray crystallographic files in CIF format, a plot showing Co–Co net connectivity, simulated and experimental PXRD data, solid-state EPR spectrum measured at 9 K, plots of $\chi_M T$ and χ_M^{-1} (inset) for **1** at 10 kOe, temperature dependence of the field-cooled and zero-field-cooled magnetization, and TG data for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Synthesis of $[\text{Co}_3(\text{L-6H})(\text{H}_2\text{O})_6]_n$ (**1**). A mixture of NaOH (0.060 g, 1.50 mmol) in H_2O (5.0 mL), $\text{L} \cdot \text{H}_2\text{O}$ (0.183 g, 0.50 mmol), and 2,2'-dipyridyl (0.156 g, 1.0 mmol) was added to an aqueous solution (5.0 mL) of $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ (0.297 g, 1.5 mmol) and stirred. The resulting solution was heated in a stainless steel reactor with Teflon liner at 175 °C for 60 h. After a period of approximately 14 h cooling to room temperature, purple prismatic crystals of **1** were obtained, isolated by filtration and washed with water. Yield: 75%. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{Co}_3\text{O}_{18}$: C, 22.98; H, 2.90. Found: C, 22.95; H, 2.88. IR data (400–4000 cm^{-1}): 3486(s), 3316(s), 1607(vs), 1563(vs), 1405-(vs), 1331(s), 1313(s), 1198(w), 1103(w), 1075(w), 934(w), 865-(w), 807(m), 784(m), 759(m), 726(m), 579m(m), 553(w), 517(w).
- (12) X-ray single-crystal diffraction data collections were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal data for **1** (123 K): rhombohedral, space group R-3 (no. 148), $a = 14.314(1) \text{ \AA}$, $c = 14.673(2) \text{ \AA}$, $U = 2603.5(4) \text{ \AA}^3$, $Z = 6$, $\rho_{\text{calcd}} = 2.400 \text{ g cm}^{-3}$, μ (Mo K α) = 29.42 cm^{-1} . $R_1 = 0.0309$, $wR_2 = 0.0782$ (for all data).
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- (15) While preparing this communication, we obtained manganese(II) and iron(II) compounds isostructural with **1**. Crystal data for Mn compound: $\text{C}_{12}\text{H}_{18}\text{Mn}_3\text{O}_{18}$, $M = 615.08$, rhombohedral, space group R3 (No. 148), $a = 14.5568(11) \text{ \AA}$, $c = 14.9681(17) \text{ \AA}$, $U = 2746.8(4) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 6$, $\rho_{\text{calcd}} = 2.231 \text{ g cm}^{-3}$, μ (Mo K α) = 21.39 cm^{-1} . $R_1 = 0.0343$, $wR_2 = 0.0836$ (for all data). Crystal data for Fe compound: $\text{C}_{12}\text{H}_{18}\text{Fe}_3\text{O}_{18}$, $M = 617.81$, rhombohedral, space group R3 (no. 148), $a = 14.4344(11) \text{ \AA}$, $c = 14.785(2) \text{ \AA}$, $U = 2667.7(5) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 6$, $\rho_{\text{calcd}} = 2.307 \text{ g cm}^{-3}$, μ (Mo K α) = 21.39 cm^{-1} . $R_1 = 0.0343$, $wR_2 = 0.0897$ (for all data). These will be reported in a subsequent full paper.

CG050388F