Synthesis and Structure of a 3-D Metal-Organic Framework, [Cd$_2$(1,4-cyclohexanedicarboxylate)$_2$·DMF], Comprising Unusual Two Different Ligand Conformations

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Metal-organic frameworks (MOFs) which are inorganic and organic hybrid polymeric crystalline solid materials have drawn much attention of many researchers because of wide variety of application of the materials including gas sorption, separation, catalysis, magnetism, sensing, drug delivery and transport. Drastic increase of the number of MOF structures deposited in Cambridge Structure Database (CSD) which is directly related to the number of publications in MOF research field reflects the recent extensive interest in the research of MOFs. Although research interest on MOFs has mainly focused on application of the materials, their rational design principles to construct intriguing architectures and topologies is still important issue in the research of MOFs. Judicious choice of ligands and metal ions and control of their connectivity allow controlling resulting network structure of MOFs and hence physical properties of the resulting materials.

It is worth noting that a number of MOFs reported up to date have employed rigid spacer ligands, for instance benzinedicarboxylates have successfully generated a great number of extended network structures. However, MOFs constructed by flexible ligands such as fumarate have been less investigated, which is probably due to their low symmetry and flexibility of backbones of ligands making it more difficult to predict and control the structure of resulting MOFs. Cyclohexanediacarboxylic acid and its derivatives provide unique opportunity for designed construction of MOFs using flexible ligands because of the good bridging ability and limited flexible motions of the ligands, which allow easier control of the final structures. For example, 1,4-cyclohexanediacarboxylic acid (1,4-chdcH$_2$) is a flexible ditopic ligand which possesses three possible conformations of two carboxylate groups, $a,a$-trans-chdc, $e,e$-trans-chdc, and $e,a$-cis-chdcH (Scheme 1).

There have been numerous reported MOFs constructed from 1,4-chdcH$_2$ and various metal cations. Jung and Kim reported interesting 2-D coordination polymers constructed by alternative $e,e$-trans-chdc and $a,a$-cis-chdcH (partially deprotonated) (1:1) and 3-D coordination polymers constructed by $e,e$-trans-chdc and $a,a$-cis-chdc (1:2). However, to the best of our knowledge, the coordination polymers comprising of $e,e$-trans-chdc and $a,a$-trans-chdc has not yet been reported. Herein, we report synthesis and structure of an unprecedented 3-D MOF, [Cd$_2$(chdc)$_2$·DMF] (1), which is constructed by two conformational isomers of 1,4-chdc, $e,e$-trans-chdc and $a,a$-trans-chdc in different molar ratio (3:1).

Results and Discussion

Solvothermal reaction of Cd(NO$_3$)$_2$·4H$_2$O and 1,4-chdcH$_2$ in 1:1.2 molar ratio in DMF at 90 °C for 3 days afforded colorless crystals of the three-dimensional MOF (1). The structure of 1 was determined by X-ray crystallography using micro-focused X-ray diffractometer. The crystal data and structure refinement for complex 1 are summarized in Table 1.

The crystal structure of 1 is constructed from the tri-nuclear SBUs which consist three crystallographically non-equivalent six-coordinated Cd centers, Cd1, Cd3, and Cd2. The coordination spheres of CdO$_6$ in the Cd1 and Cd2 metal centers are best described as slightly distorted octahedrons, but that of CdO$_6$ in Cd3 is described as a highly distorted

Scheme 1. Three possible conformations of chdcH$_2$. 
octahedron. Among three metal centers, there is no coordinated solvent molecule on Cd2 and Cd3, whereas there are two coordinated DMF molecules on Cd1 resulting in the formation of the slightly distorted octahedral geometry. The bond lengths (Å) and bond angles (°) for 1 are summarized in Table S3.

Carboxylate of a µ-2a(Cd3-Cd2)-chdc ligand bridges two metal centers, Cd3 and Cd2, by adopting a bi-dentate coordination mode where the Cd3 center coordinates O1 of the carboxylate and the Cd2 center coordinates O2 of the carboxylate. The carboxylate of the other µ-2b(Cd3-Cd2)-chdc ligand also connects two metal centers, Cd3 and Cd2, with similar coordination mode of the carboxylate of the µ-2a(Cd3-Cd2)-chdc. Carboxylate of a µ-2c(Cd1-Cd3)-chdc ligand also bridge two metal centers, Cd1 and Cd3, with similar coordination mode of others. However, carboxylate of a µ-3(Cd1-Cd3-Cd2)-chdc shows totally different coordination mode with others, connecting three metal centers through two oxygen atoms of the carboxylate, where O7 of the carboxylate coordinates to both Cd1 and Cd3 and O8 of the carboxylate coordinates to Cd2. The X-ray crystal structure of 1 with the atomic numbering scheme is shown in Figure 1. Therefore, we found four different coordination modes in 1 from four different 1,4-chdc ligands.

In addition, we also found interesting two different conformational isomers of 1, e,e-trans-chdc and a,a-trans-chdc, in the crystal structure. Among the four independent chdc ligands, three of them, µ-2a(Cd3-Cd2)-chdc, µ-2b(Cd3-Cd2)-chdc, and µ-3(Cd1-Cd3-Cd3)-chdc, adopt the e,e-trans conformation. However, although a,a-trans conformation is less stable than e,e-trans conformation due to 1,3-diaxial hindrance, one of the four chdc ligands, µ-2b(Cd3-Cd2)-chdc, adopts a,a-trans, which is rare conformation of chdc in MOF structures. In Figure 2, e,e-trans conformation and a,a-trans conformation of the chdc ligands are highlighted in blue and red, respectively.

The three different metal centers are repeatedly connected by four different chdc ligands resulting in a one-dimensional infinite zigzag shaped chain (Figure 3(a)). The one-dimensional zigzag shaped coordination complex of 1 was further extends its dimension into 3-D MOF through interconnections of four different 1,4-chdc ligands in 1 (Figure 3(b)).
removal of coordinated DMF molecules afforded pores in the framework structure (Figure 4). For assessing permanent porosity of the framework, thermogravimetric analysis (TGA) experiment was demonstrated (Figure S1). The profile showed removal of coordinated solvent molecules between 50 and 150 °C and plateau between 150 and 250 °C, which demonstrates stability of the framework upon removal of coordinated solvent molecules. In addition, variable temperature PXRD data was obtained in a temperature range from 25 to 400 °C (Figure 5). PXRD profiles of 25 °C and 50 °C are quite similar, whereas that of more than 100 °C starts to change and results in different structure. Although the changed conformation has not yet been studied, the peaks of the diffraction profiles clearly indicating the crystalline nature of the material. Minor difference between the PXRD patterns of the sample at 25 °C and that of simulated may suggests the presence of additional framework comprising other conformations of the ligand because of the flexible nature of the ligand. Gas sorption study of the framework showed non-porous nature of the material, which may be due to the structural change of the material during thermal activation process.

In summary, we successfully synthesized 3D MOF, [Cd₂(chdc)₂·DMF], constructed from a flexible carboxylated ligand 1,4-chdcH₂ and characterized the structure and properties of the material. Although 1,4-chdcH₂ mostly have e,e-trans-chdc and e,a-cis-chdc conformations in extended crystalline structures among four possible isomer conformations, the 1 was constructed 1,4-chdc with e,e-trans-chdc and a,a-trans-chdc in a 3:1 ratio, which was unprecedented in MOF structures. The framework clearly shows a structure of a,a-trans-chdc conformation isomer ligand, which is less favorable conformation, allows better understanding for the control of conformational isomers in solid state structures.

**Experimental Section**

**Materials and Methods.** All the chemicals were purchased from Aldrich and used as received without further purification. TGA data were obtained on a Perkin-Elmer Pyris 1 TGA instrument with a heating rate of 10 °C min⁻¹ under N₂ atmosphere. The X-ray powder diffraction profiles were recorded on a Bruker D8 Advance system equipped with a Cu sealed tube (λ = 1.54178 Å) at a scan rate of 3 deg min⁻¹.

**Synthesis of [Cd₂(chdc)₂·DMF] (1).** The colorless needle-shaped crystals of 1 suitable for X-ray crystallography were obtained by the solvothermal reaction. A mixture of Cd(NO₃)₂·4H₂O (0.36 g, 1.2 mmol) and trans-1,4-chdc (0.24 g, 1.4 mmol) was dissolved in DMF (1.3 mL). The reaction mixture was placed in a sealed-glass tube and heated at 90 °C for 3 days which results in formation of needle-shaped colorless crystals. The resulting crystals were collected by filtration and washed with DMF. The crystals were dried under dynamic vacuum at room temperature for 5 h (yield =
K. Crystal data for the compound has formula C\_Z = 8, V = 4485.1(2) Å\(^3\) for was determined by single crystal X-ray diffraction analysis.

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References


