Two new 3D metal–organic frameworks of nanoscale cages constructed by Cd(II) and conformationally-flexible cyclohexanehexacarboxylate†

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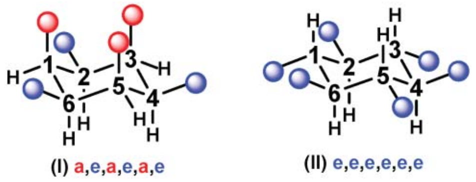
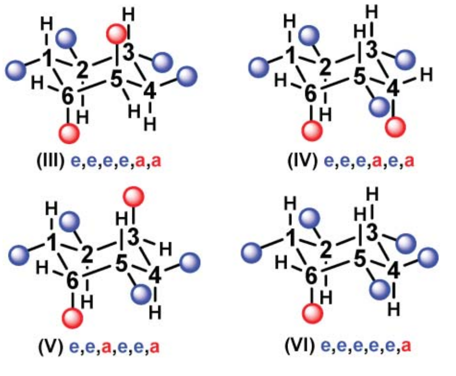
Hydrothermal reactions of $Cd(NO_3)_2 \cdot 4H_2O$ with a,e,a,e,a,e-1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6L^I) generate two new 3D MOFs with nanoscale cages, in which the L^I ligand in the first MOF transforms its conformation to the e,e,e,e,e,e form while the L^I ligand in the second MOF transforms its conformation to mixed e,e,e,e,e,e and e,e,e,e,a,a forms in a 1 : 3 ratio, showing the effect of the auxiliary sodium ion on stabilizing the intermediate conformations and on the construction of the heterometallic MOF strucutre.

The rapid development in metal–organic frameworks (MOFs) with fascinating structural topologies and functions has received considerable attention.[1,2] Rigid polycarboxylates, for example, benzenedicarboxylates, benzenetricarboxylates, pyromellitate, mellitate and pyridinepolycarboxylates, successfully produce various extended structures with metal ions.[3,4] In contrast, only a few coordination polymers based on those[5,6] of flexible conformations have been documented so far, probably due to the flexibility of the backbones which make it more difficult to predict and control the final coordination networks. Interestingly, many investigations have been successfully focused on the flexible 1,4-cyclohexanedicarboxylic acid (1,4-H_2chdc).[6] We note that 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (H_6**L**), similar to the well-explored 1,4-H_2chdc and analogous to mellitate, is characteristic of multifunctional coordination sites and pH-dependent coordination fashions and has versatile flexible conformations. Although one could anticipate that it will be applied as a versatile ligand in the construction of functional MOFs, no report on the coordination chemistry of this ligand has been documented before our work. In our recent work on H_6**L**, we observed its two preponderant conformations of **I** (3e + 3a) and **II** (6e) (Scheme 1).[7] Thermodynamically, conformation **I** is, to our knowledge, less stable than others,[8] but at the same time, has relatively smaller steric hindrance of the carboxylate groups. Both contrary factors will drive H_6**L** to make a compromise between energy and steric hindrance useful for metal coordination, which will provide us with a chance to trap intermediate conformations by tuning the reaction conditions. As part of our continuing investigation on this interesting metal–H_6**L** system, we paid our attention to trapping the new possible conformations between **I** and **II**, for example, 4e + 2a and 5e + 1a (Scheme 2) by hydrothermal methods, which have been successfully applied to tune or control conformation changes of the cyclohexanedicarboxylate and cyclohexanehexacarboxylate.[6,7b] Herein we report two novel 3D MOFs with nanoscale cages constructed by the conformationally-flexible H_6L ligand, namely, $[Cd_{12}(\mu_6\text{-}\mathbf{L^{II}})(\mu_{10}\text{-}\mathbf{L^{II}})_3(\mu_2\text{-}H_2O)_6(H_2O)_6] \cdot 16.5H_2O$ (**1**) and $Na_{12}[Cd_6(\mu_6\text{-}\mathbf{L^{II}})(\mu_6\text{-}\mathbf{L^{III}})_3] \cdot 27H_2O$ (**2**), in which a new conformation of 4e + 2a has been observed.



Scheme 1 The two observed conformations of the L^{6-} ligand: 3e + 3a (**I**) and 6e (**II**). Blue and red balls represent the carboxylates.

The hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$, $H_6\mathbf{L^I} \cdot H_2O$ and water in the molar ratio of 1.0 : 0.25 : 555 at 130 °C for 60 h yields colorless block crystals of **1** (yield 78%) in single phase, in which the $H_6\mathbf{L^I}$ ligand transforms its conformation from **I** to **II**. Colorless hexagonal crystals of **2** (yield 82%) in single phase were purely obtained from the hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$, $H_6\mathbf{L^I} \cdot H_2O$, NaOH and water in the molar ratio of 1.0 : 0.25 : 2.0 : 555 at 130 °C for 72 h, during which the $H_6\mathbf{L^I}$ ligand transforms its conformation from **I** to **II** and **III**.‡ Interestingly, when the above hydrothermal reaction of **2** was conducted at 150, 160 and 180 °C, the same product was also be obtained. Moreover, other bases such as LiOH, KOH and Et_3N employed in the above reaction system cannot generate crystals of **2**, suggesting that the Na(I) with the proper radius could act as a suitable template for the construction of the 3D MOF of **2** and stabilize the new intermediate conformation **III**. Phase purity of the bulk materials of **1** and **2** was confirmed by comparison of their powder diffraction patterns with those calculated from the single crystal study (Fig. S1†). Both **1** and **2** are insoluble in water and common organic solvents, such



Scheme 2 The possible conformations 4e + 2a (**III**–**V**) and 5e + 1a (**VI**) of the L^{6-} ligand between the observed conformations **I** and **II**.

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as methanol, acetone, acetonitrile, dichloromethane, tetrahydrofuran, *N*,*N*′-dimethylformamide and dimethyl sulfoxide. Both compounds are not photoluminescent at ambient temperature.

X-ray crystal structure analysis§ reveals there are two unique Cd(II) atoms (both lie on general positions), two $\mathbf{L^{II}}$ ligands (one lies on an inversion center and another lies across a $\bar{3}$ -axis) and two aqua ligands as well as lattice water molecules in the asymmetric unit of **1**. Cd(1) is in a greatly distorted octahedral coordination environment of three oxygens from the two different $\mathbf{L^{II}}$ ligands and three water ligands (Cd1–O_{water} = 2.279(5)–2.444(5) Å), in which two symmetry-related ones coordinate in a μ_2-mode while the other one coordinates in a terminal mode; Cd(2) is coordinated to five oxygens from four different $\mathbf{L^{II}}$ ligands. Interestingly, the $\mathbf{L^{II}}$ ligands adopt two types of bridging modes: μ_6-$\mathbf{L^{II}}$ and μ_{10}-$\mathbf{L^{II}}$ in a 1 : 3 ratio (Fig. 1a). Each μ_{10}-$\mathbf{L^{II}}$ connects four Cd(1) and six Cd(2) atoms, while each μ_6-$\mathbf{L^{II}}$ connects six Cd(2) atoms. Six μ_{10}-$\mathbf{L^{II}}$ and two μ_6-$\mathbf{L^{II}}$ ligands bridge thirty Cd(II) atoms to generate a nanoscale $Cd_{30}L^{II}{}_8$ cage of hexagonal prismatic shape with the dimensions 22.96 × 12.81 × 12.81 Å^3 (Fig. 1c). Two symmetry-related $Cd(2)_6(\mu_6\text{-}\mathbf{L^{II}})$ motifs compose both basal planes of each hexagonal prism, and six symmetry-related $Cd(1)_4Cd(2)_6(\mu_{10}\text{-}\mathbf{L^{II}})$ motifs compose the six side walls of each hexagonal prism *via* sharing some of the Cd atoms. There are open windows on the side walls of each cage. Each cage connects six neighbouring ones to generate a novel 3D MOF (Fig. 2a). An analysis using PLATON[9] suggests that the total void volume of **1** without water guests, V_{void}, occupies 23.9% of the crystal volume. The water guests are located at these cages and make contact with the MOF host *via* plentiful hydrogen-bonding interactions (O···O = 2.636(7)–3.132(9) Å).

The asymmetric unit of **2** consists of a unique Cd(II) atom which lies on a general position, a $\mathbf{L^{II}}$ ligand which lies across a $\bar{3}$-axis, a $\mathbf{L^{III}}$ ligand which lies across a 2-fold axis and lattice water molecules. Cd(1) is coordinated to six oxygen atoms (one of which is from the $\mathbf{L^{II}}$ ligand and five from three $\mathbf{L^{III}}$ ligands), forming a distorted trigonal prismatic environment (Fig. 1b). Remarkably, besides the $\mathbf{L^{II}}$ conformation, a new conformation $\mathbf{L^{III}}$ formed from the $H_6\mathbf{L^{I}}$ is trapped in **2**, which is presumably due to the introduction of Na(I) atoms within the cages that directly coordinate to the neighbouring carboxylates, resulting in different coordination environments of the Cd(II) atoms from those found for **1**. Both $\mathbf{L^{II}}$ and $\mathbf{L^{III}}$ ligands adopt μ_6-bridging modes and exist in a 1 : 3 ratio. Similarly to **1**, **2** is also a 3D MOF structure (Fig. 2b) constructed of nanoscale cages of hexagonal prismatic shapes. Each cage with the dimensions of 13.04 × 13.04 × 10.49 Å^3 (Fig. 1d) is composed of eighteen Cd(II) atoms, two μ_6-$\mathbf{L^{II}}$ ligands and twelve μ_6-$\mathbf{L^{III}}$ ligands. Two symmetry-related $Cd(1)_6(\mu_6\text{-}\mathbf{L^{II}})$ motifs and twelve symmetry-related $Cd(1)_6(\mu_6\text{-}\mathbf{L^{III}})$ motifs compose the basal planes and the six side walls of each hexagonal prism, respectively, *via* sharing some of the Cd atoms. The Na(I) ions are immobilized on the surfaces of the cages and coordinated in irregular geometries by the carboxylates and ordered/disordered water molecules (Na–$O_{carboxylato}$ = 2.344(5)–2.958(13), Na–O_{water} = 2.339(4)–2.804(11) Å). The V_{void} of **2** without water guests is 23.1% per unit volume calculated by PLATON.[9] It should be noted that decoration of alkali cations on the surface of a porous coordination polymer is an ongoing challenge in the field of materials chemistry.[10] Therefore, the 3D MOF of nanoscale cages in **2** represents a new contribution to this field. Topologically, the anionic network of **2** is a rare 3D (4,6)-connected net with four-connected nodes and two types of six-connected nodes by simplifying the Cd(II) atoms as the 4-coordinate nodes and the $\mathbf{L^{II}}$ and $\mathbf{L^{III}}$ ligands as the six-coordinate nodes.

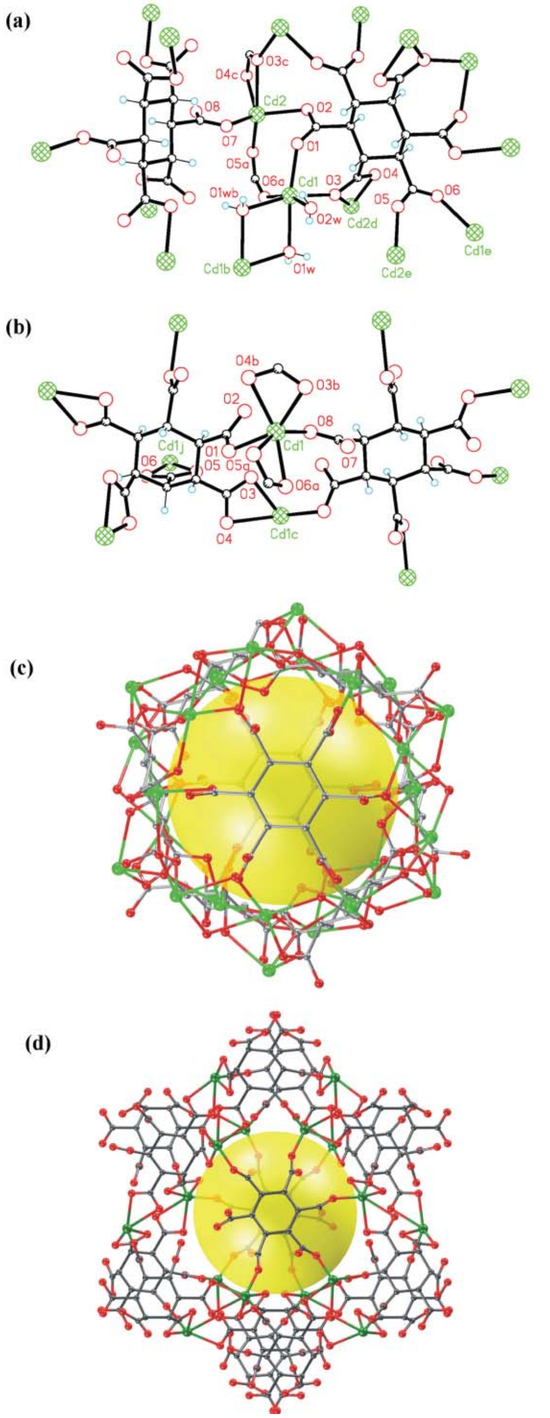

Fig. 1 Perspective views of the coordination geometries of Cd(II), bridging modes of $\mathbf{L}^{6-}$ ligands (**1**: a, **2**: b) and nanoscale cages along the *c*-axis (**1**: c, **2**: d). Symmetry codes used to generate equivalent atoms: (a) $-x + y + 1/3, -x + 2/3, z - 1/3$; (b) $-x + 1, -y + 1, -z$; (c) $y, -x + y, -z$; (d) $x - y, x, -z$; (e) $-y + 2/3, x - y + 1/3, z + 1/3$ for **1**; (a) $-x + y + 1/3, -x + 5/3, z - 1/3$; (b) $x - y + 1, x, -z$; (c) $y, -x + y + 1, -z$; (j) $-y + 5/3, x - y + 4/3, z + 1/3$ for **2**.

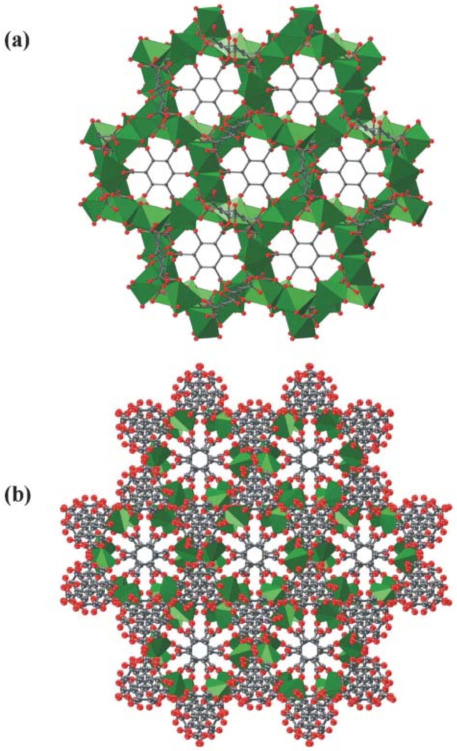

Fig. 2 The 3D MOFs viewed along the *c*-axis in **1** (a) and **2** (b). The guest molecules are omitted for clarity.

Thermogravimetric analysis (TGA) of **1** shows all the lattice water molecules are removed in two steps (Fig. S2a†). The first weight loss of 5.4% from 20 to 120 °C corresponds to ten lattice water molecules (calculated: 5.6%), and the second 4.0% weight loss from 120 to 170 °C corresponds to the remaining 6.5 lattice water molecules (calculated: 3.9%). The twelve coordinated water molecules are gradually removed between 170 and 400 °C (found: 6.5%, calculated: 6.4%). The MOF starts to decompose at 400 °C. The thermal stability was also confirmed by variable-temperature XRPD measurements (Fig. S3a†). From 70 to 170 °C, most of the peaks are weakened but still unaltered on the gradual release of the guest water molecules, illustrating that the framework remains crystalline. In comparison, the TGA curve of **2** (Fig. S2b†) indicates that the ordered/disordered water molecules coordinated to Na(I) were step by step removed before 415 °C, and the MOF began to decompose at 460 °C. The variable-temperature XRPD measurements (Fig. S3b†) show that an apparent shift was observed for the sharp diffraction peaks ($10\bar{2}$) to higher angles, with the removal of about seven water molecules at 100 °C, which may be attributed to the local deformation of the coordination environments of the Cd atoms which resulted from the enhanced Na–carboxylate coordination when the water ligands coordinated to Na(I) were gradually released from the cages. That most diffraction peaks could be observed up to 280 °C indicates the main framework retains crystallinity.

In summary, we have successfully obtained two novel 3D MOFs with nanoscale cages from the hydrothermal reactions of $Cd(NO_3)_2{\cdot}4H_2O$ with conformationally-flexible $H_6\mathbf{L}^{\mathbf{I}}$, during which the $\mathbf{L}^{\mathbf{I}}$ ligand transforms its conformation to e,e,e,e,e,e form and to a mixture of e,e,e,e,e,e and unprecedented e,e,e,e,a,a forms tuned by the auxiliary Na(I) as the template. Moreover, the stable MOF of **2** represents a new porous coordination polymer decorated by alkali cations on the pore surfaces. We are exploring the porosity of both compounds in selective gas adsorption.

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Notes and references

‡ Elemental analysis calcd (%) for **1**: C, 17.84; H, 2.53. Found: C, 18.49; H, 2.41. IR data (KBr) (400–4000 cm^{-1}): 3419s, 2972w, 1608vs, 1402vs, 1333m, 1278w, 1204vw, 1082vw, 1039w, 936w, 794w, 739w, 579w, 524w, 493w.

Elemental analysis calcd (%) for **2**: C, 20.55; H, 2.80. Found: C, 20.48; H, 2.66. IR data (KBr) (400–4000 cm^{-1}): 3415s, 1593vs, 1399vs, 1305s, 1221w, 1192w, 1150w, 1073vw, 1029w, 943w, 903w, 841m, 742w, 694w, 619w, 520w, 482w.

§ Crystal structure refinement parameters. Crystal data for **1** (293 K): $C_{48}H_{81}O_{76.5}Cd_{12}$, M = 3230.93, trigonal, space group $R\bar{3}$ (no. 148), a = 17.7971(14), c = 22.961(4) Å, U = 6298.2(12) $Å^3$, Z = 3, ρ_{calcd} = 2.556 g cm^{-3}, μ(Mo Kα) = 3.108 mm^{-1}. A total of 5450 reflections collected, 2707 independent reflections (R_{int} = 0.0391) with 2193 [$I > 2\sigma(I)$] observed data. R_1 = 0.0615, wR_2 = 0.1049 (for all data). **2** (123 K): $C_{48}H_{78}Cd_6Na_{12}O_{75}$, M = 2805.38, trigonal, space group $R\bar{3}c$ (no. 167), a = 26.010(1), c = 20.854(2) Å, U = 12217.9(11) $Å^3$, Z = 6, ρ_{calcd} = 2.288 g cm^{-3}, μ(Mo Kα) = 1.744 mm^{-1}. A total of 16061 reflections collected, 3049 independent reflections (R_{int} = 0.0298) with 2830 [$I > 2\sigma(I)$] observed data. R_1 = 0.0466, wR_2 = 0.1194 (for all data). Data were collected on a Bruker SMART Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and all non-H atoms were subjected to anisotropic refinement by full-matrix least-squares refinement on F^2 using SHELXTL.[11] Several restraints were employed to fix the geometries of water molecules in the refinement of compounds **1** and **2**. CCDC 603913 (**1**) and CCDC 603914 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604584g

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