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ARTICLE TYPE

Guest-induced single-crystal-to-single-crystal transformations of a new 4-connected 3D cadmium(II) metal–organic framework

Shi-Hui Li,[a] Min-Le Han,[a] Guang-Zhen Liu,[a] Lu-Fang Ma,*,[a] and Li-Ya Wang*,[a,b]

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Hydrothermal reaction of Cd(II) salt with 4-(pyridin-4-yl)-isophthalic acid (H_2pic) yields a new uninodal 4-connected 3D metal–organic framework [Cd(pic)(H_2O)]·H_2O (**1**) with Schläfli symbol of (4.6^5). **1** and [Cd(pic)] (**1a**) could occur single-crystal-to-single-crystal transformation (SC-SC) *via* reversible dehydration and rehydration.

Introduction

In recent years, the rational design and controlled synthesis of metal–organic frameworks (MOFs), also known as coordination polymers, has become an exciting field not only because of their interesting topological structures but also their properties and potential applications in the fields of luminescence, gas adsorption/separation, magnetism, catalysis and so on.[1-4] In this field, one of the possible strategies to this target is the utilization of multinuclear clusters as secondary building units (SBUs) for the synthesis of larger clusters or cluster-based networks, since such compounds may combine the novel architectures with interesting properties appearing in their SBUs.[5] Compared to single metal ions, SBUs usually have predefined and rigid coordination geometries, which is very critical for the achievement of MOFs with required properties, not only because the structural properties of SBUs have a significant influence on the topology and stability of MOFs, but also because the functional properties of SBUs can be imparted to the whole framework.[6] To data, numbers of defined metal carboxylate clusters, such as $Cu_2(CO_2)_4(H_2O)_2$, $Cr_3(CO_2)_6(H_2O)_3$, and $Zn_4O(CO_2)_6$ units, are potentially useful SBUs in the construction of MOFs with required properties.[7] Unfortunately, the discovery of new SBUs proves challenging and is usually through trial.

Meanwhile, several inorganic/organic framework materials can undergo reversible or irreversible structural transitions, but more often by the reversible removal of guest molecules—a process that can sometimes even involve the reabsorption of a different guest molecule. These types of transitions have been referred to as "dynamic structural changes" or, perhaps more commonly, as crystal-to-crystal transformations, when they can be carried out and observed on single crystals rather than powders.[8-10] Herein, we report the synthesis and characterization of a uninodal 4-connected 3D metal–organic framework [Cd(pic)(H_2O)]·H_2O (**1**, H_2pic = 4-pyridin-4-yl-isophthalic acid) with a wheel-type hexa-nuclear unit, and the desolvated crystal [Cd(pic)] (**1a**) after single-crystal-to-single-crystal transformations triggered by changes in temperature by the reversible removal of coordinated and free water molecules. It is worth noting that **1a** can be rehydrated in moist air to back **1**.

Experimental section

Materials and Physical Measurements

All reagents were commercially available and were used as received without further purification. Elemental analyses for C, H and N were performed on a Flash 2000 organic elemental analyzer. The infrared spectra (4000 ~ 600 cm^{-1}) were recorded on a NICOLET 6700 FT-IR spectrometer. Thermogravimetric analyses were performed on a SII EXStar6000 TG/DTA6300 analyzer heated from 30 to 800 °C under nitrogen. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8-ADVANCE X-ray diffractometer with Cu *Kα* radiation. Fluorescence spectra were performed on a FLS980 fluorescence spectrophotometer at room temperature and 77 K.

Preparation of Complexes 1 and 1a

[Cd(pic)(H_2O)]·H_2O (1). A mixture of H_2pic (0.1 mmol, 24.3 mg), $Cd(OAc)_2\cdot 2H_2O$ (0.1 mmol, 0.012 g), LiOH (0.1 mmol, 0.0042 g), and H_2O (6 mL) was placed in a Teflon-lined stainless steel vessel, heated to 130 °C for 4 days, and then cooled to room temperature over 24 h. Colorless crystals of **1** were obtained in 45% yield based on $Cd(OAc)_2\cdot 2H_2O$. Elemental analysis (%): calcd for $C_{13}H_{11}CdNO_6$ (M_r = 389.63) C 40.07, H 2.85, N 3.59; found C 40.00, H 2.95, N 3.51. IR (cm^{-1}): 3150 m, 1601 m, 1581 m, 1539 s, 1423 m, 1372 s, 834 s, 783 s, 765 s, 694 s.

[Cd(pic)] (1a). Colorless **1a** was obtained by exposing **1** to a dynamic vacuum at 180 °C for 10 h. The product was stored in sealed containers, as exposure to moist air for 12 h will result in rehydration and conversion of **1a** back to **1**. The single crystal habit was unchanged. It was confirmed by the single crystal X-ray diffraction. Elemental analysis (%): calcd for $C_{13}H_7CdNO_4$ (M_r = 353.60) C 44.16, H 2.00, N 3.96; found C 44.10, H 2.08, N 3.88. IR (cm^{-1}): 1602 m, 1582 s, 1532 s, 1418 s, 1363 s, 834 s, 783 s, 761 s, 687 s.

X-Ray Crystallography

Single crystal X-ray diffraction data for complexes **1** and **1a** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97),[11] and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-H atoms (SHELXL-97).[11] The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement with geometrical restrains. Further crystallographic data and selected bond parameters for 1 and 1a are listed in Table 1 and Table S1 (Electronic Supplementary Information). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 1038718 for **1** and 1038719 for **1a**.

Results and Discussion

Description of Crystal Structures

[Cd(pic)(H_2O)]·H_2O (1). Single crystal X-ray analysis revealed that **1** crystallizes in trigonal space group $R\bar{3}$ and its framework demonstrates a new zeolite-like topology with a (4.6^5) topology. The fundamental building unit of **1** contains one cadmium center, one pic, one coordinated H_2O and one guest H_2O molecule. In **1**, each Cd(II) atom adopts the distorted octahedral geometry, which is coordinated by one nitrogen atom from one pic, four carboxyl oxygen atoms from three different pic, and one water molecule (Fig. S1a, ESI). The Cd–N bond distance is 2.508(13) Å, and the Cd–O distances are in the range 1.95(3)–2.500(12) Å. The pic ligand coordinates to four different Cd(II) atoms through one bidentate carboxylate, one chelating carboxylate, and a pyridyl nitrogen atom (Fig. S1b).

In the framework of **1**, six Cd(II) atoms are held together by six bidentate carboxylate groups to form a puckered wheel-type [$Cd_6(COO)_6$] unit (Fig. 1a) with Cd···Cd separation of 5.162 Å. Each Cd_6 unit is extended by eighteen pic ligands to generate a neutral 3D framework with two types of channels (Fig. 1c, 1d and Fig. S2), star-like channel of 7.4 × 7.4 Å (Fig. 1b and Fig. S3), and trigonal four-fold helical channel of 4.0 × 4.0 Å (Fig. S4), viewed along the [001] direction. Since the coordinated water molecules are directed inside the channels, these channels are hydrophilic. Without guest molecules, the effective free volume of **1** is calculated by PLATON[12] analysis to be 10.0% of the crystal volume (611.8 Å^3 of the 6108.0 Å^3 unit cell volumes). Free water molecules are located in the channels by hydrogen bonds among free water molecules, coordinated water molecules (Table S2 for details, ESI).

Table 1. Crystallographic Data and Structure Refinement Details for **1** and **1a**.

Compounds	1	1a
Formula	$C_{13}H_{11}CdNO_6$	$C_{13}H_7CdNO_4$
Formula weight	389.63	353.60
Temperature	296(2)	296(2)
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}$
a (Å)	30.515(5)	30.00(3)
b (Å)	30.515(5)	30.00(3)
c (Å)	7.574(2)	7.554(13)
V (Å^3)	6108(2)	5889(13)
Z	18	18
ρ (g cm^{-3})	1.907	1.795
F (000)	3456	3096
Reflns. collected	14670	11031
Independent reflns.	2475	2358
R_{int}	0.0799	0.2114
Data/restraints/parameters	2475 / 190 / 37	2358 / 148 / 299
R_1,wR_2 [I>2σ (I)]	0.0739, 0.1607	0.0982, 0.2360
R_1,wR_2 (all data)	0.1265, 0.2041	0.2849, 0.3685
GOOF	1.081	0.963

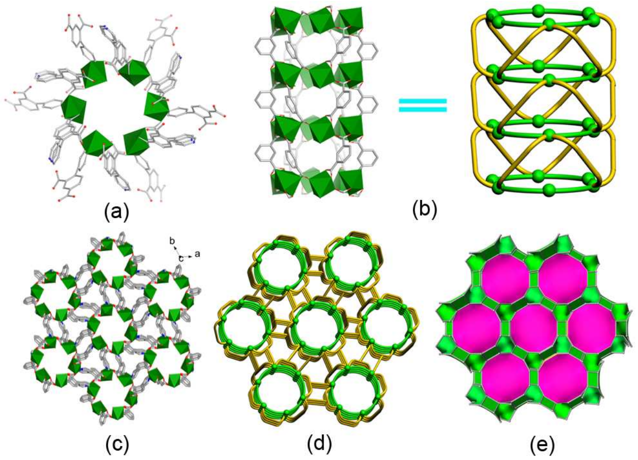

Fig. 1 View of (a) the wheel-type Cd_6 unit which is coordinated by 18 pic ligands. (b) Perspective and schematic views of the 1D star-like channel (The pyridine motifs of the pic ligand are omitted for clarity). Perspective (c) and schematic (d) view of the 3D network. (e) Nature tiling view of the zeolite-like framework of **1**. Color code: Cd, green; O, red; C, gray; N, blue.

From the view of topological point, the assembly of the 4-connected inorganic cadmium and organic pic nodes results in the generation of two new cages, the ($6^3.12^2$) cage (Fig. S5a) consisting of 12 tetrahedrally coordinated atoms (T-atoms) and the ($4.6.8^3$) cage (Fig. S5b) containing 14 T-atoms. Each ($6^3.12^2$) cage shares its twelve-membered rings with two neighboring ones above and below, and six-membered rings with three neighboring ($4.6.8^3$) cages in the plane, while each ($4.6.8^3$) cage shares its six-membered ring with one neighboring ($6^3.12^2$) cage, four- and eight-membered rings with four ($4.6.8^3$) cages. In this way, the interconnection of these cages gives rise to the 3D network (Fig. 1e) with a new zeolite-like topology with Schläfli symbol of (4.6^5). To our knowledge, these two cages ($6^3.12^2$) and ($4.6.8^3$) as well as the (4.6^5) net have not been observed in MOFs and zeolite-related materials.

[Cd(pic)] (1a). The crystal of **1a** maintains the original space group and zeolite-like topology of **1**. The asymmetric unit consists of one Cd(II) atom and one pic ligand. Compared to that in **1**, the coordination environment around the Cd(II) center is changed significantly. Each Cd(II) center in **1a** is coordinated by one N atom from pic ligand [Cd–N 2.547(17) Å] and four O atoms from three different pic ligands [Cd–O 2.298(18), 2.431(15), 2.435(18), and 2.597(13) Å], furnishing a distorted {$CdNO_4$} trigonal bipyramidal geometry (Fig. S6). The Cd–O and Cd–N bond lengths are longer than that in **1**. The pic keeps the same coordination mode. Another significant change is the channel of **1a**. Due to the remove of the coordinated and guest H_2O molecules, the channel in **1a** shows a dimension of 8.8 × 8.8 Å (Fig. S7).

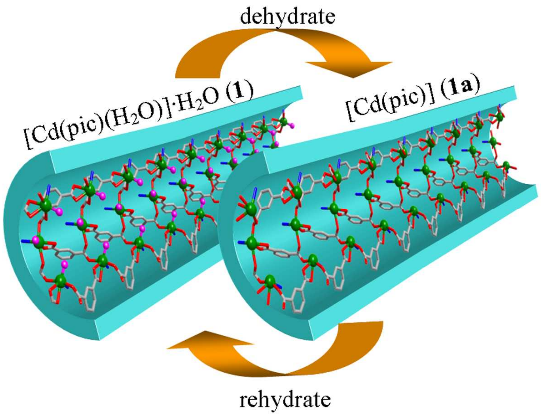

Fig. 2 View of the pore walls in **1** and **1a** (the coordinated water molecules in **1** are highlighted in purple).

PXRD and TGA Results

In order to check the phase purity of these complexes, the powder X-ray diffraction (PXRD) patterns of complexes **1** and **1a** were checked at room temperature. As shown in Fig. S8, ESI, the peak positions of the simulated and experimental PXRD patterns are in agreement with each other, demonstrating the good phase purity of the compounds. The differences in intensity may be due to the preferred orientation of the crystalline powder samples.

TGA curve (Fig. S9, ESI) reveals that **1** could lose all H_2O molecules above 125 °C and the resulting open framework starts to decompose after ca. 350°C. In order to completely remove the guest H_2O molecules located in the channels of the framework structure, a single crystal of **1** was heated at 180 °C under vacuum for 3 h and a desolvated crystal [Cd(pic)] (**1a**) was obtained, as indicated by single crystal X-ray diffraction and TGA. Furthermore, **1a** can be rehydrated in moist air to back **1** (Fig. 2), confirmed by single crystal X-ray diffraction.

Luminescent Property

The luminescent properties of compounds containing d^{10} metal centers have been attracting more interest because of their potential applications in chemical sensors, photochemistry and electroluminescent display. To examine the luminescent properties of the d^{10} metal complex, the luminescence spectra of solid **1** has been measured at room temperature and 77 K (Fig. 3). Complex **1** displays emission peak at 440 nm with a shoulder peak at 547 nm upon excitation at $\lambda_{ex} = 370$ nm. When frozen to 77 K, the emission of **1** shifts to shorter wavelength at about 437 nm and with only one peak, and the intensity is enhanced. This might be attributable to ligand-to-metal charge transfer (LMCT). The solid-state lifetime at 298 and 10 K is in the range of nanoseconds (Fig. S10 and Table S2) revealing that the emission is fluorescence.[13] Complex **1a** also shows emission peak at 440 nm with a shoulder peak at 547 nm upon excitation at $\lambda_{ex} = 370$ nm (Fig. S11). This indicates that the luminescence band gaps between the highest occupied molecular orbitals (HOMOs) and the lower unoccupied molecular orbitals (LUMOs) could not be altered by removing the coordinated and free water molecules.

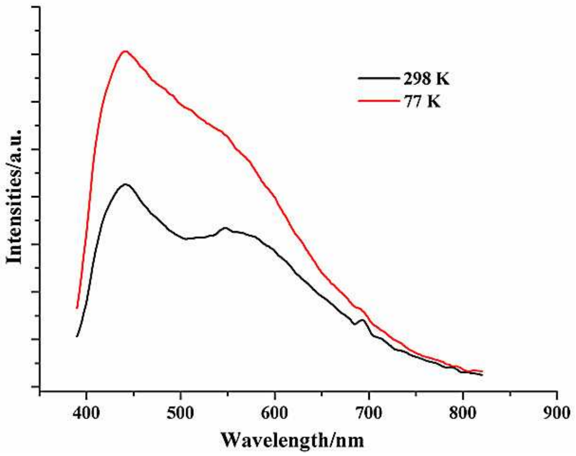

Fig. 3 Emission spectrum for solid **1** at 298 K ($\lambda_{ex} = 370$ nm) and 77 K ($\lambda_{ex} = 370$ nm).

Conclusions

In summary, one uninodal 4-connected metal–organic framework [Cd(pic)(H_2O)]·H_2O (**1**) containing wheel-type hexanuclear unit has been synthesized under hydrothermal conditions. Guest-induced single-crystal-to-single-crystal reversible transformations occurred between **1** and the desolvated crystal [Cd(pic)] (**1a**).

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Notes and references

[a] *College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, P. R. China. Fax: +86-379-65511205; Tel: +86-379-65526089; E-mail: mazhuxp@126.com (L. F. Ma).*

[b] *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, P. R. China. wlya@lynu.edu.cn (L. Y. Wang)*

†Electronic Supplementary Information (ESI) available: [X-ray crystallographic information for complex **1** and **1a** in CIF format. Selected bond lengths and angles for **1** and **1a**. Distance (Å) and angles (°) of hydrogen bonding for **1**. Supplementary structural graphics for **1** and **1a**. The PXRD patterns and TGA plots for complexes **1** and **1a**. 1038718 for **1** and 1038719 for **1a** contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]. See DOI: 10.1039/c0xx000x/

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