Syntheses, Structures, and Properties of Copper(II), Cobalt(II), and Cadmium(II) Complexes with Flexible Multicarboxylate Ligand

Xianrui Xu,^[a,b] Xiaobo Pan,^{*[a]} Sifu Tang,^[a] Xiaoxia Lv,^[a,b] Liangjun Li,^[a,b] and Xuebo Zhao^{*[a]}

Keywords: Crystal structure; Flexible ligand; Hydrothermal synthesis; Coordination polymers; Photoluminescence

Abstract. Three new coordination polymers, namely, $[\text{CuL}_{0.5}]$ (**1**), $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})_2][\text{H}_2\text{O}]$ (**2**), and $[(\text{CdCl})_{0.5}\text{Cd}_{0.25}(\text{H}_2\text{L})_{0.5}]$ (**3**) were synthesized under hydrothermal conditions from the corresponding Cu^{II} , Co^{II} , and Cd^{II} salts with a multidentate ligand of 2,2',2'',2'''-[2,3,5,6-tetramethyl-1,4-phenylenebis(methylenenitrilo)]tetraacetic acid (H_4L). The complexes were characterized by single-crystal X-ray diffraction, IR, thermogravimetric, and elemental analyses. Complex **1** crystallizes in the orthorhombic space group $Pbca$ and has a three-dimensional architecture with infinite two-dimensional networks linked together by weak Cu–O interactions. Complex **2** crystallizes in

the monoclinic space group $P2(1)$ and displays a 2D network. Complex **3** crystallizes in the tetragonal space group $P4(2)/ncm$ and exhibits an infinite 3D architecture that has unusual $[\text{Cd}_2(\text{CO}_2)_4\text{Cl}_2]$ dinuclear paddle-wheel units and $[\text{Cd}(\text{CO}_2)_4]$ dodecahedron units. The results showed that the coordination arrangement of central metal atoms and the conformation and coordination mode of organic ligands play an important role in determining the structure of the complexes. The luminescence property of complex **3** was studied in the solid state at room temperature.

Introduction

Recent years have witnessed intense research in the rational design and synthesis of metal-organic coordination polymers, not only due to their interesting topologies but also because of their potential applications as functional materials in fields such as molecular magnetism, catalysis, luminescence, gas adsorption, etc.^[1,2] Metal-organic complexes exhibit diversified structures because the coordination arrangement of the selected metal ions, the adopted bridging modes of the organic ligands, counterions, templates, and the reaction conditions such as temperature, solvent, pH value, and the ratio between metal salts and ligands exert crucial influences on the construction of the final results.^[3] However, it is still a great challenge to predict the exact structures and composition of the assembled products, and further studies are required to understand the assembly process of metal salts and organic linkers.

So far, most of research efforts have been devoted to rigid polycarboxylate ligands,^[4,5] such as 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid (H_3BTC), 1,3,5-benzenetricarboxylic acid (H_3BTA), 1,2,4,5-benzenetetracarboxylic acid

(H_4BTEC), and so on, owing to their rational synthesis of default structures and relative high thermal stability of the obtained materials. In our understanding, the rigidity of organic linker is a double-edged sword. On one hand, it can improve thermal stability, but it also somehow limits the coordination configuration around the central metal atom for the sake of unexpected steric hindrance. Therefore new synthesis strategy should be developed to consummate it. Comparing to rigid ligands, flexible ligands are not that extensively studied in the field of metal-organic complexes, suffering to low porosity and interpenetration. Actually, they have also achieved some successes^[6,7] and demonstrate that the flexibility of ligand plays an important role in the design and synthesis of metal-organic complexes, can be used as a complement to rigid ligands. Therefore, we decided to investigate some new multicarboxylate ligands, which combine both rigid and flexible moiety in it to explore new functional metal-organic complexes and which provide a deeper understanding of flexible ligands.

Flexible ligands can be obtained by doing some decorations to rigid ligands through the introduction of methylene, $-\text{CH}_2\text{O}-$, $-\text{CH}_2\text{S}-$, or imine group into the aromatic and coordination groups.^[7c,8] Until now, much of attention has been paid to ligands containing methylene and $-\text{CH}_2\text{O}-$ groups,^[8a,8b] whereas ligands decorated with imine group are less investigated.^[7c,8c] In our opinion, this kind of ligand could be interesting because of the imine group's coordinating nature and dual role (donor and acceptor) in hydrogen interactions. Therefore, we designed and synthesized a new tritopic carboxylic acid ligand, 2,2',2'',2'''-[2,3,5,6-tetramethyl-1,4-phenylenebis(methylenenitrilo)]tetraacetic acid (H_4L), from 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene and diethyl

* Dr. X. Pan
E-Mail: panxb05@hotmail.com

* Prof. Dr. X. Zhao
Fax: +86-532-80662729
E-Mail: zhaorb@qibebt.ac.cn

[a] Qingdao Institute of Bioenergy and Bioprocess Technology
Chinese Academy of Sciences
266101, Qingdao, P. R. China

[b] University of Chinese Academy of Sciences
100049, Beijing, P. R. China

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201300126> or from the author.

iminodiacetate. Using it as ligand, three new coordination complexes $[\text{CuL}_{0.5}]$ (**1**), $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})_2][\text{H}_2\text{O}]$ (**2**), and $[(\text{CdCl})_{0.5}\text{Cd}_{0.25}(\text{H}_2\text{L})_{0.5}]$ (**3**) were successfully obtained under hydrothermal conditions. All the compounds were characterized by general methods including elemental analysis, X-ray crystallography, IR, and thermogravimetric analysis.

Results and Discussion

Synthetic Analysis

Complexes **1–3** were successfully synthesized by reacting H_4L with the corresponding salts at 140 or 120 °C for 3 d under hydrothermal conditions. The reaction route of **1–3** is shown in Scheme 1. The conditions of the respective reactions were affected by pH value, reaction temperature, type of salts, and metal-ligand ratio. Complex **1** is a novel 3D framework, whose optimal conditions are 140 °C, pH value of 6.0, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}:\text{H}_4\text{L}$ ratio as 2:1. Complexes **2** and **3** were synthesized at 120 °C with different pH values and $M:\text{ligand}$ ratios. Different to $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$ and $-\text{CH}_2\text{S}-$, imine group can not only improve the flexibility of the ligand but also involve in the coordination with central metal atoms leading to new structures.

Scheme 1. Reaction routes of complexes **1–3**.

Description of the Structures

The coordination modes of H_4L ligand are shown in Scheme 2. The following structure discussion is based on CIF files of complexes **1–3** and the final formulas of complexes **1–3** are further determined by elemental analyses and thermogravimetric studies.

Scheme 2. Coordination modes of H_4L ligand in complexes **1–3**.

Description of $[\text{CuL}_{0.5}]$ (**1**)

X-ray crystallographic analysis revealed that complex **1** crystallizes in the orthorhombic space group $Pbca$. The asymmetric unit contains one coordinated Cu^{II} atom and half L^{4-} ligand (Figure 1). All carboxyl groups of H_4L are deprotonated, in agreement with the IR data, in which no characteristic absorption bands of the $-\text{COOH}$ group at $1700\text{--}1750\text{ cm}^{-1}$ are observed. The central Cu^{II} atom is five-coordinate and takes a distorted square pyramid arrangement. Each Cu^{II} atom is chelated by a L^{4-} ligand via its iminonitrogen (N1) and two oxygen atoms (O1 and O3) from the two iminocarboxylate arms, respectively. The remaining two face-related coordination sites are occupied by O2B and O4F (B: $2.5-x$; $0.5+y$; $+z$; F: $0.5+x$, y , $0.5-z$) from another two L^{4-} ligands. These four Cu1-O bonds around Cu^{2+} in complex **1** fall into two categories with bond lengths of Cu1-O1 1.926(5), Cu1-O2B 1.941(5), Cu1-O3 1.957(5), and Cu1-O4F 2.452 Å, respectively. The three short Cu1-O bonds distances [1.926(5)–1.957(5) Å] are in the normal range compared to the other similar Cu-O bonds in reported complexes.^[9] The Cu1 atom locates in the center of square-planar environment, which consists of three oxygen (O1, O2B, O3) atoms and one nitrogen (N1) atom (Figure 2a). The longer Cu-O bond [Cu1-O4F 2.45 Å] on the axial site, which completes the square pyramid arrangement around Cu1 in **1**, originates from the carboxylate group of the adjacent $\text{Cu}(\text{L})_{0.5}$ units. Thus, each iminodiacetate group of L^{4-} ligand functions as a chelating tridentate ligand to the first Cu^{2+} and as a monodentate bridging mode to another Cu^{2+} (Type A, Scheme 2), which, in turn, is responsible for the formation of building blocks (Figure 2a). These building blocks are further connected to form a 2D layer in bc plane (Figure 2b) through the aryl moieties of L^{4-} . Finally, such 2D layers are connected by weak Cu-O interactions to form a 3D architecture (Figure 2c).

Figure 1. The coordination environment of Cu^{II} ion in **1** with the thermal ellipsoid at the 50% probability level. Symmetry codes: (a) $2-x$, $1-y$, $1-z$; (b) $2.5-x$; $0.5+y$; $+z$; (c) $-0.5+x$, $0.5-y$, $1-z$; (d) $2.5-x$, $-0.5+y$, $+z$; (e) $-0.5+x$, $1.5-y$, $1-z$; (f) $0.5+x$, y , $0.5-z$; (g) $1.5-x$, $1-y$, $0.5+z$; (h) $-0.5+x$, y , $0.5-z$; (i) $2.5-x$, $1-y$, $0.5+z$.

Description of $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})_2][\text{H}_2\text{O}]$ (**2**)

Complex **2** crystallizes in the monoclinic $P2(1)$ space group. The asymmetric unit is composed of one independent central Co^{II} atom, one partly deprotonated H_2L^{2-} ligand, two aqua ligands, and one free water molecule in a crystal lattice (Fig-

Figure 2. View of 1D chain (a) 2D layer (b) and 3D architecture (c).

ure 3). The Co^{II} ion has a slightly distorted octahedral arrangement with four carboxyl oxygen atoms [O4, O5A, O2C, O7B] from four different H_2L^{2-} ligands, and two aqua ligands [O1W, O2W]. The Co–O bond lengths are in the range of 2.047(4)–2.146(4) Å and the O–Co–O bond angles vary from 84.13(16) to 176.06(15)°. The four carboxylic groups of the ligand are fully deprotonated with two protons transferred to the two nitrogen (N1 and N2) atoms, which is confirmed by crystallographic analysis as well as the IR spectroscopic data since a strong band at 3034 cm^{-1} was observed in the IR spectrum of **2**.^[10]

Figure 3. The coordination environment of Co^{II} ion in **2** with the thermal ellipsoid at the 40% probability level. Symmetry codes: (a) $1-x, 0.5+y, -z$; (b) $1-x, 0.5+y, 1-z$; (c) $+x, +y, 1+z$; (d) $+x, +y, -1+z$; (e) $1-x, -0.5+y, 1-z$; (f) $1-x, -0.5+y, -z$.

Each carboxylic group in H_2L^{2-} bridges one Co^{II} ion monodentately, the whole H_2L^{2-} ligand binds four Co^{II} atoms and behaves as a 4-connected node. Through the linkage of H_2L^{2-} , a 2D-network in bc plane is formed (Figure 4a). In addition,

there exist intramolecular hydrogen bonds ($\text{N2-H}\cdots\text{O1}$ and $\text{N1-H}\cdots\text{O8}$) and intermolecular hydrogen bonds ($\text{O2W-H}\cdots\text{O3W}$) (Table S2, Supporting Information). It is believed that the hydrogen-bonding interactions play an important role in stabilizing the 2D network (Figure 4b).

Figure 4. Two dimensional layer and pseudo three dimensional supramolecular structure of complex **2**. The CoO_6 octahedra are shaded in grey. Intramolecular and intermolecular hydrogen bonds are presented as dark grey dashed lines.

Description of $[(\text{CdCl})_{0.5}\text{Cd}_{0.25}(\text{H}_2\text{L})_{0.5}]$ (**3**)

Complex **3** crystallizes in the tetragonal $P4(2)/ncm$ space group and displays a three dimensional framework structure consisting of $[\text{Cd}_2(\text{CO}_2)_4\text{Cl}_2]$ paddle wheel units and distorted $[\text{CdO}_8]$ dodecahedra. In the asymmetrical unit, there are two crystallographic unique Cd^{2+} cations (Cd1 and Cd2), half chlorine anion and half H_2L^{2-} ligand, which corresponds to the formula $[(\text{CdCl})_{0.5}\text{Cd}_{0.25}(\text{H}_2\text{L})_{0.5}]$ (see Figure 5). Two symmetry-related Cd1^{II} ions are bridged by four carboxylate groups of two neighboring H_2L^{2-} ligands to form the paddle-wheel unit $[\text{Cd}_2(\text{CO}_2)_4\text{Cl}_2]$ with a Cd–Cd distance of 3.2130(15) Å. Since each Cd^{2+} ion has square-pyramidal coordination arrangement, its axial position is occupied by a Cl^- anion with Cd–Cl distance of 2.415(3) Å [$\text{Cl1}–\text{Cd1}–\text{O4}$ 102.84(15)°; $\text{Cl1B}–\text{Cd1B}–\text{O3}$ 102.10(15)°, see Table S1, Supporting Information]. The Cd1–O bond lengths are found in the range of 2.270(8)–2.282(5) Å, and the O–Cd1–O bond angles vary from 83.40(19) to 154.58 (19)°, which are all comparable to those of other reported cadmium carboxylates.^[11] It should be noticed that this kind of dinuclear Cd^{II} building unit is rare, only limited examples are known.^[11] Different from

Cd1, Cd2 is situated at a fourfold axis and eight coordinated by eight oxygen atoms (O1, O2; O1E, O2E; O1F, O2F; and O1G, O2G; operators: E $0.5-x, 1.5-y, +z$; F $0.5+y, 0.5+x, -z$; G $1-y, 1-x, -z$) of four carboxylic groups from four different LH_2^{2-} ligands, forming a slight distorted $[\text{CdO}_8]$ dodecahedron coordination sphere. The Cd2–O bond lengths extend from 2.369(6) to 2.573(6) Å and the O–Cd2–O bond angles vary from 88.2(3) to 176.5(3)°, which are all slight larger than those of Cd1 (see Table S1).

Figure 5. The coordination environment of Cd^{II} ion in **3** with the thermal ellipsoid at the 40% probability level. Symmetry codes: (a) $1.5-y, 1.5-x, +z$; (b) $1-x, 2-y, 1-z$; (c) $-0.5+y, 0.5+x, 1-z$; (d) $1-x, 2-y, -z$; (e) $0.5-x, 1.5-y, +z$; (f) $0.5+y, 0.5+x, -z$; (g) $1-y, 1-x, -z$.

The flexible multicarboxylate H_2L^{2-} ligand in complex **3** is fully deprotonated and two protons transferred to the two imine groups, which is confirmed by the IR spectrum.^[12] Two of the four carboxylic groups bend to the middle of the ligand and bridge two Cd^{II} ions forming the above mentioned $[\text{Cd}_2(\text{CO}_2)_4\text{Cl}_2]$ paddle-wheel unit, whereas another two chelate two Cd^{II} ions forming the distorted $[\text{CdO}_8]$ dodecahedra (Type C, Scheme 2). Consequently, these H_2L^{2-} ligands bridge the $[\text{Cd}_2(\text{CO}_2)_4\text{Cl}_2]$ units and distorted $[\text{CdO}_8]$ dodecahedra into a complicated three-dimensional compact architecture (see Figure 6).

The Effect of Flexibility of the Tetracarboxylic Ligand on Crystal Structure

Compounds **1–3** were obtained under similar reaction conditions, but display totally different structures, suggesting that their structures are mainly metal-dependent. The flexibility of the ligand allows the four carboxylic groups coordinate to different metal ions with different conformations and coordination modes. From the structure analyses it is clear that the two iminoacetic acid moieties in compounds **1** and **2** exhibit *trans* conformation, whereas in compound **3** *cis* conformation is observed. With the changing of metal ions, the coordination modes of the tetracarboxylic ligand changes also. In compound **1** the four carboxylic groups all adopt *anti-anti* double monodentate coordination modes. But only monodentate coordination mode is found in compound **2**, and both chelating and double monodentate *syn-syn* bridging coordination modes are formed in compound **3**. The flexibility of the tetracarboxylic

Figure 6. View of the structure of **3** down the *c* axis. The $[\text{Cd}(\text{I})\text{ClO}_4]_2$ paddle-wheel units and $[\text{Cd}(\text{II})\text{O}_8]$ dodecahedron are shaded in grey (all hydrogen atoms are omitted for clarity).

ligand can also be intuitively embodied by the dihedral angles between the carboxylic groups and the central aromatic ring (38.970, 38.970, 53.085, 53.085° for **1**; 13.552, 22.932, 88.097, 88.830° for **2**; 18.251, 18.251, 48.440, 48.440° for **3**). Obviously, the employment of flexible ligands can greatly enrich the structures of coordination compounds.

IR, Powder XRD Analysis, and Photoluminescence Property

The measurements of IR spectra of **1**, **2**, and **3** confirm the presence of the organic ligands used in the syntheses through the characteristic bands of aromatic and carboxylate groups (see Figure S2, Supporting Information). The broad absorption bands of the asymmetric and symmetric stretching vibrations of water appear at 3700–2700 cm^{-1} .^[13] The bands at 1676–1560 cm^{-1} and 1408–1334 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the bound carboxylate groups ($-\text{CO}_2\text{M}$), respectively. In the high-frequency region, the sharp bands are observed in the 3034 cm^{-1} and 3157 cm^{-1} range for complexes **2** and **3** due to $\nu(\text{N-H})$ vibration of the ligand.^[9] Figures S3–S5 (Supporting Information) show the powder XRD patterns of the title compounds. The experimental XRD pattern for each compound is in accordance with the simulated one generated on the basis of structural data, confirming that the as-synthesized products are pure phase. The solid state emission spectra of compound **3** and ligand H_4L were measured at room temperature. Under excitation of 250 nm, both compound **3** and ligand H_4L show a broad featureless band with a maximum of about 396 nm (Figure 7), suggesting the emission of **3** might be assigned to the intraligand fluorescent emission. Comparing with the free H_4L ligand, the enhancement of luminescence of compound **3** might be attributed to ligand chelation to the central metal atom, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.^[13]

Figure 7. The emission spectra in the solid state at room temperature: free H_4L ligand ($\lambda_{ex} = 250$ nm, dot line); complex **3** ($\lambda_{ex} = 250$ nm, solid line).

Thermal Stabilities of Complexes 1–3

Thermogravimetric analyses (TGA) were carried out in a nitrogen atmosphere to examine the thermal stability of complexes **1–3** and the results are shown in Figure 8. Complex **1** is stable up to about 240 °C, and decomposes rapidly on further heating. For complex **2**, the weight loss in the range of 50–225 °C corresponds to the departure of one lattice water molecule and two coordinated aqua molecules (calcd. 10.10%, found 9.75%), and the framework undergoes decomposition in the range of 225–420 °C. There is no obvious weight loss before 310 °C for complex **3**, indicating no solvent molecules accommodated in the structure and good stability. Finally, it decomposes rapidly till 600 °C.

Figure 8. Thermal gravimetric curves of complexes **1–3**.

Conclusions

Three new metal-organic coordination polymers based on flexible multicarboxylate ligand were synthesized and thor-

oughly characterized using IR, EA, powder and single-crystal X-ray diffraction, TGA, and luminescence measurements. The structure measurements indicate that the multicarboxylate ligand in complexes **1–3** shows varied coordination modes to different transition metals and results in three different types of structures. The imine groups exhibit affinity to copper ions since only in the copper compound they are involved in the coordination, whereas central Cd^{II} atoms are more propitious to form paddle-wheel units under synthesis conditions used in this research. The structure results also indicated that the introduction of imine groups and methyl groups to multicarboxylate ligand is a promising strategy to fabricate new MOFs with a specific structure.

Experimental Section

General: All solvents and reagents for the syntheses were of analytical grade and were used as received from commercial sources without further purification. 1,4-Bis(bromomethyl)-2,3,5,6-tetramethylbenzene was prepared as described in the literature.^[14] Diethyl iminodiacetate was purchased from Aldrich. Elemental analyses for C, H, and N were carried out with a German Elementary Vario EL cube instrument. The IR spectra were performed with a Nicolet 6700 FTIR spectrometer in the region 4000–400 cm^{-1} using KBr pellets. Thermogravimetric analyses were recorded with a NETZSCH STA 449C unit at a heating rate of 10 °C·min⁻¹ in a nitrogen atmosphere. The powder X-ray diffraction (XRD) patterns were collected with a D8 Advance X-ray diffractometer using $Cu-K\alpha$ radiation ($\lambda = 0.154$ nm). Fluorescent analysis of the complexes was performed with a Fluoromax-4. In the measurements of emission and excitation spectra the pass width is 5 nm, and all the measurements were carried out under the same experimental conditions.

Synthesis of H_4L : 2,2',2'',2'''-[2,3,5,6-Tetramethyl-1,4-phenylenebis(methylenenitrilo)]tetraacetic acid (H_4L) (see Scheme S1, Supporting Information) was synthesized according to the literature.^[7a] **1H NMR** (600 MHz, $[D_6]DMSO$, ppm) (see Figure S1): $\delta = 12.30$ (s, 4 H, $-COOH$), 3.92 (s, 4 H, $Ar-CH_2$); 3.37 (s, 8 H, $N-CH_2-COOH$); 2.22 (s, 12 H, $Ar-CH_3$) ppm. $C_{20}H_{28}N_2O_8$: calcd. C 56.59; H 6.65; N 6.60%; found: C 56.41; H 6.78; N 6.30%. **IR** (KBr, selected data): $\tilde{\nu} = 3431$ (br), 1686 (s), 1540 (vs), 1461 (w), 1424 (s), 1369 (vs), 1316 (vs), 1256 (w), 1190 (w), 1003 (vs), 955 (vs), 843 (vs), 793 (vs), 698 (vs) cm^{-1} (see Figure S2).

Synthesis of $[CuL_{0.5}]$ (1**):** A mixture of H_4L (0.17 g, 0.4 mmol) and $CuSO_4 \cdot 5H_2O$ (0.20 g, 0.8 mmol) was dissolved in distilled water (15 mL) and stirred for 15 min. The pH value of the obtained mixture was adjusted to ca. 6.0 with NaOH. Afterwards, the solution was transferred into a 25 mL Teflon-lined container. The container containing the above solution was placed in an autoclave and heated at 140 °C for 3 d. The autoclave was allowed to cool to 30 °C in 24 h. Blue block crystals of complex **1** were collected in 58% yield based on H_4L . $C_{20}H_{24}N_2O_8Cu_2$ (547.51): calcd. C 43.87; H 4.42; N 5.12%; found: C 43.25; H 4.09; N 5.03%. **IR** (KBr, selected data): $\tilde{\nu} = 3431$ (br), 1627 (s), 1560 (s), 1404 (vs), 1334 (w), 1309 (w), 1117 (w), 999 (w), 887 (vs), 748 (vs) cm^{-1} (see Figure S2).

Synthesis of $[Co(H_2L)(H_2O)_2][H_2O]$ (2**):** Complex **2** was synthesized in an analogous procedure to **1** except that 0.095 g (0.4 mmol) $CoCl_2 \cdot 6H_2O$ was used instead of $CuSO_4 \cdot 5H_2O$ and heated at 120 °C. The reactant mixture was cooled to lead to the formation of pink needle crystals of **2**. $C_{20}H_{32}N_2O_8Co$ (535.41): calcd. C 44.87; H 6.02;

Table 1. Crystal data and structure refinements for complexes **1–3**.

	1	2	3
Formula	C ₁₀ H ₁₂ NO ₄ Cu	C ₂₀ H ₃₂ N ₂ O ₁₁ Co	C ₁₀ H ₁₂ NO ₄ Cl _{0.5} Cd _{0.75}
Mol. weight /g	273.75	535.41	313.24
Crystal system	orthorhombic	monoclinic	tetragonal
Space group	<i>Pbca</i>	<i>P2(1)</i>	<i>P4(2)/ncm</i>
<i>a</i> /Å	9.1648(11)	5.2091(12)	19.0440(6)
<i>b</i> /Å	9.2984(11)	24.732(6)	19.0440(6)
<i>c</i> /Å	22.768(3)	8.933(2)	11.8804(8)
<i>a</i> /°	90.00	90.00	90.00
<i>β</i> /°	90.00	99.068(3)	90.00
<i>γ</i> /°	90.00	90.00	90.00
<i>Z</i>	8	2	16
<i>V</i> /Å ³	1940.3(4)	1136.5(4)	4308.7(3)
Density /g·cm ⁻³	1.874	1.559	1.932
<i>μ</i> /mm ⁻¹	2.248	0.819	1.670
<i>F</i> (000)	1120	558	2504
Reflections collected/unique	6846/1711/0.0917	7854/4507/0.0474	20750/1982/0.1378
Data / restraints / parameters	1711 / 0 / 147	4507 / 7 / 312	1982 / 18 / 194
Final <i>R</i> indices [<i>R</i> ₁ > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0626, <i>wR</i> ₂ = 0.1593	<i>R</i> ₁ = 0.0510, <i>wR</i> ₂ = 0.1048	<i>R</i> ₁ = 0.0510, <i>wR</i> ₂ = 0.1310
GOF on <i>F</i> ²	1.049	1.019	1.139
Largest diff. peak and hole /e·Å ⁻³	0.791 and -0.726	0.547 and -0.444	0.983 and -0.774

N 5.23 %; found: C 44.65; H 5.96; N 5.26 %. **IR** (KBr, selected data): $\tilde{\nu}$ = 3409 (br), 3034 (s), 3020 (s), 2977 (vs), 1676 (vs), 1635 (s), 1408 (s), 1369 (s), 1315 (vs), 1251 (w), 1186 (w), 916 (vs), 715 (vs), 676 (vs) cm⁻¹ (see Figure S2).

Synthesis of [(CdCl)_{0.5}Cd_{0.25}(H₂L)_{0.5}] (3): Complex **3** was prepared by a procedure similar to that used for the preparation of **1** except for using CdCl₂·0.5H₂O (0.14 g, 0.6 mmol) instead of CuSO₄·5H₂O and being synthesized at 120 °C. Colorless needle crystals of complex **3** were collected in 59 % yield based on H₄L. C₂₀H₃₂N₂O₈ClCd_{1.5} (626.50): calcd. C 38.34; H 4.18; N 4.47 %; found: C 38.18; H 4.02; N 4.51 %. **IR** (KBr, selected data): $\tilde{\nu}$ = 3440 (br), 3157 (w), 1657 (s), 1628 (s), 1399 (vs), 1344 (vs), 1269 (w), 913 (w), 860 (w), 723 (vs) cm⁻¹ (see Figure S2).

X-ray Crystallography: All the structure data of complexes **1–3** were collected with a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) at room temperature. All of the structures were resolved by the direct method and refined by full-matrix least-squares fitting on *F*² by SHELX-97.^[15] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the water molecules were found in the electron density map and refined by riding except that belonging to free water molecule (O3W) atom in **2**, which cannot be found. The other hydrogen atoms were located at geometrically calculated positions and refined by riding. Six carbon atoms (C5, C6, C7, C8, C9, C10) in complex **3** are disordered and are refined using carbon atoms split over two equivalent sites with a total occupancy of 1. Crystallographic data and structure refinement results are summarized in Table 1. Selected bond lengths and bond angles are listed in Table S1 (Supporting Information). More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-871654 (**1**), CCDC-871653 (**2**), and CCDC-871652 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Results of the TG/DTA measurements, Raman- and UV/Vis spectra, XRPD patterns, results of the Rietveld refinements as well as the ORTEP presentations.

Acknowledgements

We thank the National Natural Science Foundation of China (21073216, 21171173 and 21173246) and the “Hundred-talent Project” (KJCX2-YW-W34) of the Chinese Academy of Sciences for the financial support. We also acknowledge Mr. Anthony S. Hall for the help with editing English.

References

- a) M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O' Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522; c) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288; d) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248–1256; e) M. Kurmoo, *Chem. Soc. Rev.* **2009**, *38*, 1353–1379; f) J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417; g) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477–1504; h) D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* **2009**, *48*, 7502–7513.
- a) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem. Int. Ed.* **2004**, *43*, 3644–3662; b) M.-H. Zeng, W.-X. Zhang, X.-Z. Sun, X.-M. Chen, *Angew. Chem. Int. Ed.* **2005**, *44*, 3079–3082; c) Y.-F. Zhou, M.-C. Hong, X.-T. Wu, *Chem. Commun.* **2006**, 135–143; d) M. Du, X.-J. Jiang, X.-J. Zhao, H. Cai, J. Ribas, *Eur. J. Inorg. Chem.* **2006**, 1245–1254; e) K. Oisaki, Q. Li, H. Furukawa, A. U. Czaja, O. M. Yaghi, *J. Am. Chem. Soc.* **2010**, *132*, 9262–9264; f) R. Thakuria, B. Sarma, A. Nangia, *New J. Chem.* **2010**, *34*, 623–636.
- a) J. Zhang, Y. G. Yao, X. H. Bu, *Chem. Mater.* **2007**, *19*, 5083–5089; b) L. F. Ma, L. Y. Wang, X. K. Huo, Y. Y. Wang, Y. T. Fan, J. G. Wang, S. H. Chen, *Cryst. Growth Des.* **2008**, *8*, 620–628; c) S. L. Li, Y. Q. Lan, J. S. Qin, J. F. Ma, J. Liu, J. Yang, *Cryst. Growth Des.* **2009**, *9*, 4142–4146; d) Q. Gao, F. L. Jiang, M. Y. Wu, Y. G. Huang, W. Wei, M. C. Hong, *Cryst. Growth Des.* **2010**, *10*, 184–190; e) S. R. Batten, *J. Solid State Chem.* **2005**, *178*, 2475–2579.

- [4] a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217–225; b) M. L. Tong, S. Kitagawa, H. C. Chang, M. Ohba, *Chem. Commun.* **2004**, 418–419; c) F. Y. Lian, F. L. Jiang, D. Q. Yuan, J. T. Chen, M. Y. Wu, M. C. Hong, *CrystEngComm* **2008**, *10*, 905–914.
- [5] a) S. R. Batten, *CrystEngComm* **2001**, *18*, 1–7; b) N. W. Ockwig, O. Delgado-Friedrichs, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182; c) C. N. R. Rao, S. Natarajan, R. Vaidyanathan, *Angew. Chem. Int. Ed.* **2004**, *43*, 1466–1496; d) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; e) M. Du, X. J. Jiang, X. J. Zhao, *Inorg. Chem.* **2006**, *45*, 3998–4006; f) F. A. A. Paz, J. Klinowski, *Inorg. Chem.* **2004**, *43*, 3882–3893; g) H. Abourahma, B. Moulton, V. Kravtsov, M. J. Zaworotko, *J. Am. Chem. Soc.* **2002**, *124*, 9990–9991; h) R. Wang, M. Hong, J. Luo, R. Cao, Q. Shi, J. Weng, *Eur. J. Inorg. Chem.* **2002**, 2904–2912.
- [6] a) G. L. Zhuang, X. J. Sun, L. S. Long, R. B. Huang, L. S. Zheng, *Dalton Trans.* **2009**, 38, 4640–4642; b) Q. D. Liu, J. R. Li, S. Gao, B. Q. Ma, H. Z. Kou, L. Ouyang, R. L. Huang, X. X. Zhang, K. B. Yu, *Chem. Eur. J.* **2003**, *9*, 731–736; c) B. Zhai, L. Yi, H. S. Wang, B. Zhao, P. Cheng, D. Z. Liao, S. P. Yan, *Inorg. Chem.* **2006**, *45*, 8471–8473; d) H. B. Cui, B. Zhou, L. S. Long, Y. Okano, H. Kobayashi, A. Kobayashi, *Angew. Chem. Int. Ed.* **2008**, *47*, 3376–3380.
- [7] a) J. X. Ma, X. Q. Song, W. Dou, X. F. Huang, W. S. Liu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2008**, *38*, 721–726; b) J. Ma, F. L. Jiang, L. Chen, M. Y. Wu, S. Q. Zhang, D. Han, R. Feng, M. C. Hong, *Cryst. Growth Des.* **2011**, *11*, 3273–3281; c) Y. Q. Xu, D. Q. Yuan, B. L. Wu, L. Han, M. Y. Wu, F. L. Jiang, M. C. Hong, *Cryst. Growth Des.* **2006**, *6*, 1168–1174; d) C. Drouza, A. D. Keramidias, *Inorg. Chem.* **2008**, *47*, 7211–7224; e) L. S. Natrajan, P. L. Timmins, M. Lunn, S. L. Heath, *Inorg. Chem.* **2007**, *46*, 10877–10886; f) M. L. Liu, W. Shi, H. B. Song, P. Cheng, D. Z. Liao, S. P. Yan, *CrystEngComm* **2009**, *11*, 102–108; g) D. P. Walsh, R. Clérac, N. G. Hearn, P. E. Kruger, W. Schmitt, *CrystEngComm* **2009**, *11*, 1666–1673.
- [8] a) H. F. Zhu, W. Y. Sun, T. A. Okamura, N. Ueyama, *Inorg. Chem. Commun.* **2003**, *6*, 168–173; b) Z. R. Pan, H. G. Zheng, T. W. Wang, Y. Song, Y. Z. Li, Z. J. Guo, S. R. Batten, *Inorg. Chem.* **2008**, *47*, 9528–9536; c) Y. M. Zhao, S. R. Zhu, M. Shao, X. He, M. X. Li, W. C. Lu, *Inorg. Chem. Commun.* **2008**, *11*, 239–242.
- [9] a) S. L. Laborda, R. Clerac, C. E. Anson, A. K. Powell, *Inorg. Chem.* **2004**, *43*, 5931–5943; b) Y. M. Zhao, S. R. Zhu, M. Shao, T. T. Jia, M. X. Li, W. C. Lu, W. J. He, *Inorg. Chem. Commun.* **2008**, *11*, 925–928; c) J. Fielden, K. Quasdorf, A. Ellern, P. Kögerler, *Eur. J. Inorg. Chem.* **2009**, 717–720.
- [10] a) S. Mukhopadhyay, P. B. Chatterjee, D. Mandal, G. Mostafa, A. Caneschi, J. Van Slageren, T. J. R. Weakley, M. Chaudhury, *Inorg. Chem.* **2004**, *43*, 3413–3420; b) J. A. Gould, J. Bacsá, H. Park, J. B. Claridge, A. M. Mogg, V. Ramanathan, J. E. Warren, M. J. Rosseinsky, *Cryst. Growth Des.* **2010**, *10*, 2977–2982.
- [11] a) T. Allman, R. C. Goel, N. K. Jha, A. L. Beauchamp, *Inorg. Chem.* **1984**, *23*, 914–918; b) S.-L. Li, T. C. W. Mak, *J. Chem. Soc. Dalton Trans.* **1995**, 1519–1524; c) J. P. Li, L. K. Li, H. W. Hou, Y. T. Fan, L. H. Gao, *Inorg. Chim. Acta* **2009**, *362*, 4671–4677; d) A. D. Burrows, C. G. Frost, M. Kandiah, L. L. Keenan, M. F. Mahon, T. L. Savarese, J. E. Warren, *Inorg. Chim. Acta* **2011**, *366*, 303–309.
- [12] a) O. M. Yaghi, H. L. Li, T. L. Groy, *J. Am. Chem. Soc.* **1996**, *118*, 9096–9101; b) R. Lyszczyk, *J. Therm. Anal. Calorim.* **2008**, *91*, 595–599; c) Z. H. Sun, W. T. Yu, X. F. Cheng, X. Q. Wang, G. H. Zhang, G. Yu, H. L. Fan, D. Xu, *Opt. Mater.* **2008**, *30*, 1001–1006; d) J. H. He, Y. T. Zhang, Q. H. Pan, J. H. Yu, H. Ding, R. R. Xu, *Microporous Mesoporous Mater.* **2006**, *90*, 145–152.
- [13] a) X.-R. Hao, X.-L. Wang, Z.-M. Su, K.-Z. Shao, Y.-H. Zhao, Y.-Q. Lan, Y.-M. Fu, *Dalton Trans.* **2009**, 8562–8566; b) S. L. Zheng, X. M. Chen, *Aust. J. Chem.* **2004**, *57*, 703–712; c) *Photochemistry and Photophysics of Coordination Compounds* (Eds.: H. Yersin, A. Vogler), Springer, Berlin, **1987**; d) B. Valeur, *Molecular Fluorescence: Principles and Application*, Wiley-VCH, Weinheim, **2002**.
- [14] A. W. van der Made, R. H. van der Made, *J. Org. Chem.* **1993**, *58*, 1262–1263.
- [15] G. M. Sheldrick, *SHELXS-97*, Programs for X-ray Crystal Structure Solution; University of Göttingen, Germany, **1997**.

Received: February 28, 2013
Published Online: April 26, 2013