Synthesis, crystal structures and properties of three metal–organic supramolecular architectures based on mixed organic ligands†

Wentao Ai, Haiyan He, Longjie Liu, Qianjin Liu, Xiaoli Lv, Jing Li and Daofeng Sun*

Three metal–organic supramolecular architectures, $Co(H_2O)_2(H_2THFTCA)(4,4'-bpy)\cdot1/2H_2O$ (**1**), $Zn(H_2THFTCA)(phen)\cdot H_2O$ (**2**) and $Cd_3(H_2O)_2(HTHFTCA)_2(4,4'-bpy)_2\cdot4H_2O$ (**3**), constructed from mixed organic ligands of tetrahydrofuran-2,3,4,5-tetracarboxylic acid ($H_4THFTCA$) and 4,4'-bipyridine or 1,10-phenanthroline, have been synthesized and characterized. Complex **1** crystallizes in triclinic space group *P*-1 and has a discrete mononuclear structure. The multiple hydrogen bonding interactions connect **1** into a three-dimensional NaCl-like supramolecular architecture. Complex **2** crystallizes in monoclinic space group *P*21/*n* and possesses a one-dimensional helical chain structure. The $\pi\cdots\pi$ stacking between the chains further connects **2** into a two-dimensional layer architecture. Complex **3** crystallizes in monoclinic space group *C*2/*c* and has a rare three-dimensional 4,6-connected net. The THFTCA ligand connects the cadmium ions to form a two-dimensional layer, which is further connected by pillared 4,4'-bpy ligands to form the three-dimensional porous framework. The thermal stabilities of **1**, **2**, **3** and the photoluminescence properties of **2** and **3** have been studied.

Introduction

Metal–organic frameworks (MOF) have received much attention in recent years due to their potential applications in non-linear optics, magnetism, molecular recognition and gas storage.[1,2] In the past decades, many metal–organic frameworks with novel topologies and interesting properties constructed from carboxylate ligands, *e.g.*, terephthalic acid, benzene-1,3,5-tricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid, have been synthesized and reported.[3–5] By applying mixed organic ligands, several porous MOFs with 4,4'-bipyridine as the pillared ligand have also been documented.[6] Based on current research, to select a multi-functional organic ligand is crucial in an assembly of a MOF with a desired framework because the multi-functional organic ligands can provide not only versatile binding sites to connect metal ions but also hydrogen bond donor or acceptor to form supramolecular interactions.[7] As is known, hydrogen bonds and π–π interaction are powerful supramolecular interactions and they can connect the low-dimensional frameworks into high-dimensional supramolecular architectures.[8]

Very recently, with the development of supramolecular chemistry and crystal engineering, it is possible to predict the structure of the final product,[9] but it is limited to the specific classes of linkers. For the complex linker with large numbers of potential binding sites, for example, tetrahydrofuran-2,3,4,5-tetracarboxylic acid, it is difficult to predict the final structure. Research of these complex linkers may provide novel metal–organic frameworks with interesting structural topology. However, reports on tetrahydrofuran-2,3,4,5-tetracarboxylic acid are somewhat rare,[10] maybe due to its flexibility and difficulty in packing when forming crystals, although the rigid tetracarboxylate ligand, benzene-1,2,4,5-tetracarboxylic acid, has been widely researched.[5] We select tetrahydrofuran-2,3,4,5-tetracarboxylic acid as the assembly ligand considering its following several characteristics: (a) it has four carboxyl groups that provide rich coordination modes; (b) based on the number of deprotonated carboxyl groups, it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor; (c) the furan oxygen atom provides additional binding sites compared to benzene-1,2,4,5-tetracarboxylic acid, and it can chelate to the metal ions with two near carboxyl oxygen atoms; (d) all carboxyl groups do not lie in one plane, which allow it to connect the metal ions in different directions. In this paper, we report three novel metal–organic frameworks, $Co(H_2O)_2$ $(H_2THFTCA)(4,4'-bpy)\cdot1/2H_2O$ (**1**), $Zn(H_2THFTCA)(phen)\cdot$ H_2O (**2**) and $Cd_3(H_2O)_2(HTHFTCA)_2(4,4'-bpy)_2\cdot4H_2O$ (**3**) ($H_4THFTCA$ = tetrahydrofuran-2,3,4,5-tetracarboxylic acid, 4,4'-bpy = 4,4'-bipyridine, phen = 1,10-phenanthroline), based on tetrahydrofuran-2,3,4,5-tetracarboxylic acid and 1,10-phenanthroline or 4,4'-bipyridine ligands.

Results and discussion

Synthesis

As known, hydrothermal synthesis is an effective technique for the preparation of inorganic solid, organic–inorganic hybrid material, and metal–organic frameworks with polycarboxylate as the ligand.[11] However, when we applied the hydrothermal reaction with the THFTCA as the ligand, only some unknown precipitates were obtained, which may arise from the flexibility of the ligand. Considering its solubility in water and common

Key Lab for Colloid and Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan, 250100, P. R. China. E-mail: dfsun@sdu.edu.cn; Fax: (86) 53188364218; Tel: (86) 53188364218
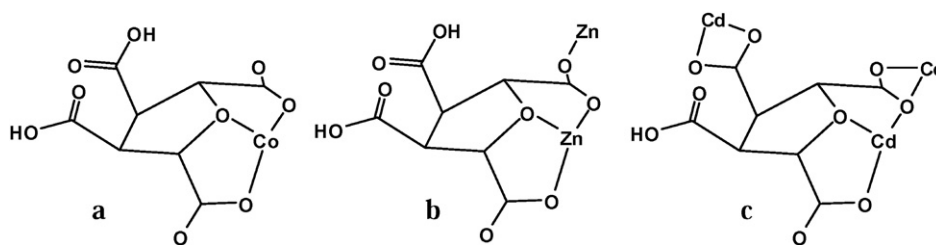
Scheme 1 Coordination modes of THFTCA in **1–3**.

organic solvents, we began work on the construction of metal–organic frameworks with THFTCA ligand using a conventional method. In our work, we introduced the phen or 4,4′-bpy as the second organic ligands to help crystallization due to their rigidity. Complexes **1–3** were synthesized in the mixed solvents of water and methanol. Crystals of **1–3** suitable for single crystal X-diffraction were obtained by slow evaporation of the reaction mixture at room temperature. The coordination modes of THFTCA in complexes **1–3** are shown in Scheme 1.

Crystal structure of $Co(H_2O)_2(H_2THFTCA)(4,4′-bpy) \cdot 1/2H_2O$ (1)

Single crystal X-ray diffraction reveals that complex **1** is a discrete structure. The THFTCA ligand adopts a chelating mode to chelate the cobalt ion with its furan oxygen atom and two adjacent carboxyl oxygen atoms, as shown in Fig. 1. The central cobalt ion in **1** is six-coordinated by three oxygen atoms from THFTCA ligands, two coordinated water molecules and one mono-dentate 4,4′-bpy molecule. The coordination environment of the central cobalt ion in **1** can be best described as an octahedral geometry. Two carboxyl oxygen atoms and two coordinated water molecules occupy the equatorial plane and the axial positions are occupied by the furan oxygen and the nitrogen atom from coordinated 4,4′-bpy with the average Co–O and Co–N distances being 2.105 and 2.114 Å, respectively. The two remaining carboxylate groups of the THFTCA ligand are protonated and do not take part in coordination which provides hydrogen-bond donors. The coordination mode of THFTCA in **1** is similar to that in $Ni(H_2THFTCA)(H_2O)_3 \cdot H_2O$, a previous reported mononuclear nickel compound.[12]

There are rich hydrogen-bond donors and acceptors existing in complex **1**. As shown in Scheme 2, the two protonated uncoordinated carboxylate groups of THFTCA and two coordinated water molecules provide the hydrogen-bond donors, while the
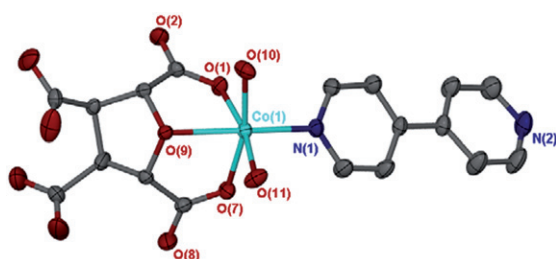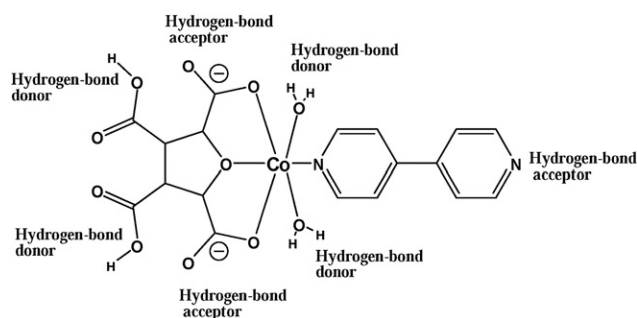

Scheme 2 Schematic representation of the hydrogen-bond donors and acceptors existing in **1**.

two deprotonated carboxylate groups and the uncoordinated nitrogen atom of 4,4′-bpy can act as hydrogen-bond acceptors.

The strong hydrogen bonding interactions between the uncoordinated carboxylate group and the uncoordinated pyridyl nitrogen atom connect **1** into a one-dimensional chain with the O···O distance being 2.602 Å (Fig. 2); then the hydrogen bonding interactions between the coordinated water molecules and the two coordinated carboxyl oxygen atoms link the 1D chains to form a two-dimensional layer with a O···O distance of 2.731 Å (Fig. 2); the two-dimensional layers are further connected by the hydrogen bonding interactions between the uncoordinated carboxyl oxygen atoms and the coordinated water molecules with an average O···O distance of 2.760 Å, to give rise to a 3D supramolecular architecture (Fig. 3). The free water molecules reside in the lattice and form strong hydrogen bonds with the uncoordinated carboxyl oxygen atoms.
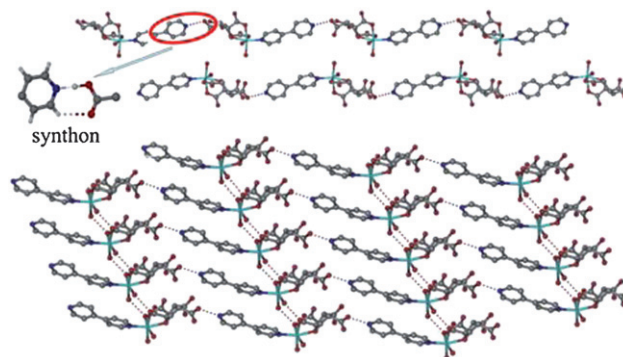

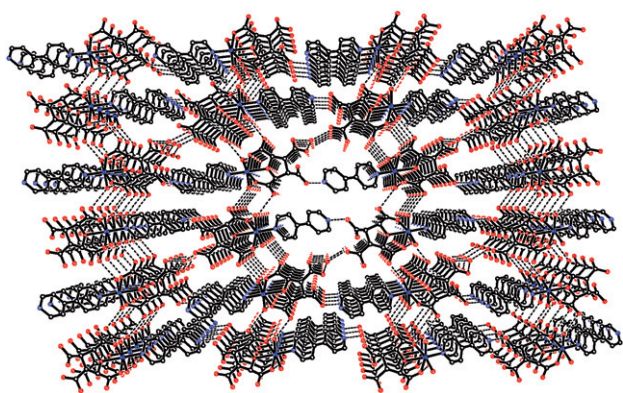**Fig. 2** A 1D chain (top) and a 2D layer (bottom) formed by hydrogen bonding interactions.

Fig. 1 Molecule structure of **1** (thermal ellipsoids: 50%).

Fig. 3 The 3D supramolecular architecture of **1** along the *c* axis formed by multiple hydrogen bonding interactions.
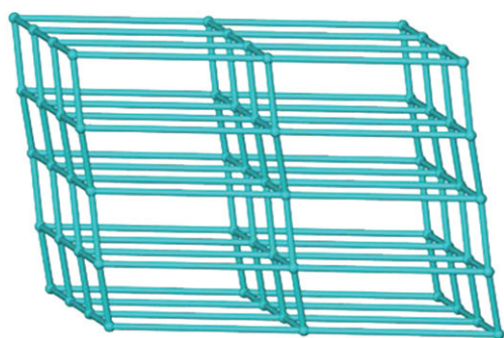

Fig. 4 The resulting NaCl-like topology of **1** after treating the supramolecular interactions as actual "bonds".

If we treat these supramolecular interactions as an actual "bond" and the cobalt ion as the single node, the 3D supramolecular architecture has a NaCl-like topology, as shown in Fig. 4.

Crystal structure of Zn(H$_2$THFTCA)(phen)·H$_2$O (2)

Complex **2** has a one-dimensional chain structure. As shown in Fig. 5, the central zinc ion is coordinated by two nitrogen atoms from the phen ligand, four oxygen atoms from two THFTCA ligands in a distorted octahedral geometry with an average Zn–O distance of 2.181 Å and a Zn–N distance of 2.238 Å. Two
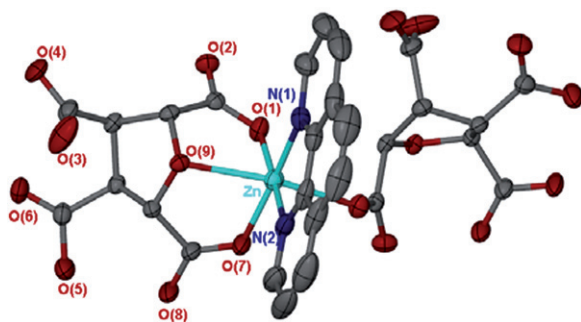
nitrogen atoms and two carboxyl oxygen atoms occupy the equatorial plane and the axial positions are occupied by the furan oxygen atom and the carboxyl oxygen atom from another THFTCA ligand. Two carboxylate groups of THFTCA are deprotonated during the reaction. Different from complex **1**, the THFTCA ligand in **2** adopts a chelate-bridging mode to connect two zinc ions by using one of two deprotonated carboxylate group (Scheme 1b). The coordination mode of THFTCA in **2** is quite different from the previously reported 3D zinc MOF,[10a] in which all the carboxylate groups are deprotonated and connect two metal ions. As shown in Fig. 6a and b, every THFTCA ligand connects two zinc ions to generate a 2_1 helical chain with the nearest Zn–Zn distance being 5.804 Å and the left- and right-handed helical chains equal in complex **2**, thus the whole structure is achiral.

The 1D helical chain is further stabilized by the strong intra-molecular hydrogen bonding interactions in the helical chain between the oxygen atom in the uncoordinated carboxylate group and the oxygen atom in the coordinated carboxylate group with a O···O distance of 2.680 Å. The π···π stacking (3.506 Å) between the phen in the chain with the adjacent chain further links the one-dimensional helical chain into a two-dimensional layer. The left- and right-handed helical chains in the layer (Fig. 6c) are alternate. The free water molecules fill between the layers and form hydrogen bonds (2.902 Å) with the uncoordinated carboxylate groups.

Crystal structure of Cd$_3$(H$_2$O)$_2$(HTHFTCA)$_2$(4,4′-bpy)$_2$·4H$_2$O (3)

Single-crystal X-ray diffraction reveals that complex **3** has a three-dimensional porous framework pillared by 4,4′-bpy. There are one-and-a-half crystallogrophically independent cadmium atoms (Cd1, Cd2) in the structure: Cd1 lies on a twofold axis and is eight-coordinated by six oxygen atoms and two coordinated water molecules with an average Cd–O distance of 2.413 Å; Cd2 is seven-coordinated by five oxygen atoms from three different THFTCA ligands and two nitrogen atoms from different 4,4′-bpy with an average Cd–O distance of 2.404 Å and a Cd–N distance of 2.302 Å (Fig. 7). Three carboxylate groups of THFTCA are deprotonated during the reaction. The

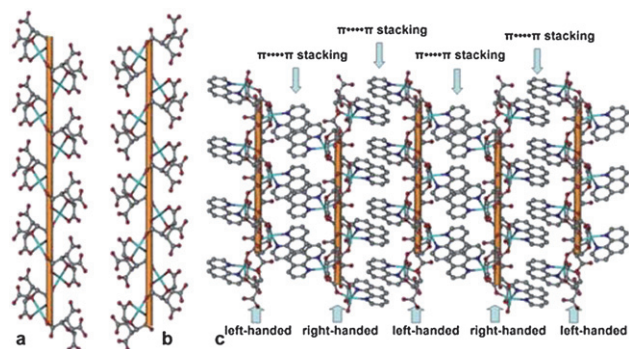**Fig. 5** The coordination environment of zinc ion in complex **2** (thermal ellipsoids: 50%).

Fig. 6 Left- (a) and right-handed (b) helical chains (coordinated phen ligands are omitted for clarity) and (c) the 2D layer formed by π···π stacking between the chains in **2**.
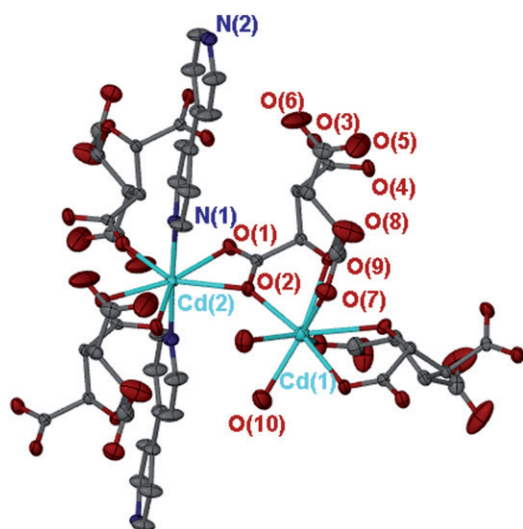
Fig. 7 The coordination environment of cadmium ions in **3** (thermal ellipsoids: 50%).

Fig. 9 3D porous framework of **3** pillared by 4,4′-bpy along the *b* axis.

THFTCA ligand adopts a chelate-bridging mode to connect the three cadmium ions as shown in Scheme 1c. The coordination mode is quite different from those in **1** and **2**.

The cadmium ions are first connected by the THFTCA ligands in a chelate-bridging mode to generate a two-dimensional layer (Fig. 8) containing a one-dimensional infinite Cd(COO) chain with the nearest Cd–Cd distance in the chain and between the chain being 3.782 and 6.888 Å, respectively. All the uncoordinated carboxylate groups point out of the layer. The thickness of the layer is about 8.159 Å. The Cd2 ion is surrounded by oxygen atoms from THFTCA ligands and coordinated water molecules, while Cd1 ion is coordinated by 4,4′-bpy ligands from an axial position. Thus, the two-dimensional layer is further linked by pillared 4,4′-bpy ligands to give rise to a three-dimensional
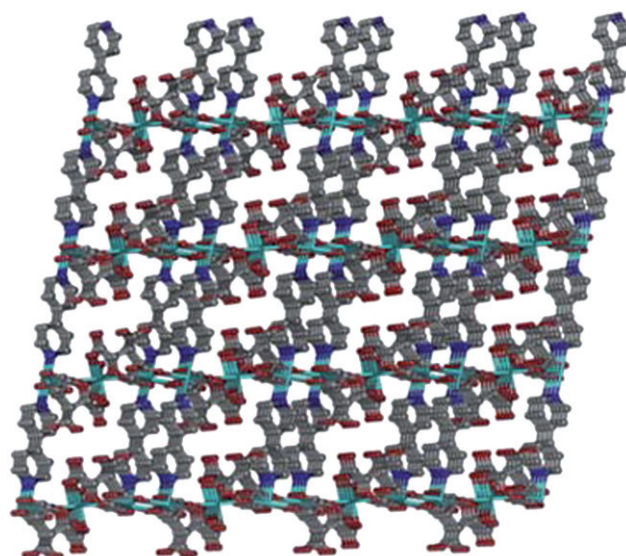

Fig. 10 The 4,6-connected net of **3**.

porous framework with a layer-to-layer distance of 9.897 Å (Fig. 9). The resulting dimensions of the channel are about 2.6 × 7.5 Å. The uncoordinated water molecules reside in the channels and form strong hydrogen bonds (2.626–2.934 Å) with the uncoordinated carboxyl oxygen atoms. The solvent accessible volume in the desolvated structure is 11.1% calculated from PLATON/SOLV.[13]

In order to analyze the topology of complex **3**, it is necessary to predigest the structure. Indeed, the dinuclear Cd2 unit can be treated as a single node which is surrounded by four Cd1 nodes in the Cd-HTHFTCA layer and connected by two other Cd2 nodes through 4,4′-bpy between layers. Thus, the dinuclear Cd2 unit can be considered as a 6-connecting node and the Cd1 atom as a 4-connected node, which makes complex **3** a 4,6-connected net, as shown in Fig. 10. The Schäfli notation is $(4^4.6^2)$ for the Cd1 node and $(4^4.6^{10}.8)$ for Cd2 node, giving the net the symbol $(4^4.6^2)(4^4.6^{10}.8)$. In the literature, only a few MOFs possessing a 4,6-connected net have been reported.[14] Although the type of pillared connection between (4,4)-nets has been documented,[6] reports on 4,6-connected net in pillared frameworks like complex **3** are quite rare.[15]

Fig. 8 2D Cd-THFTCA layer in **3** along the *b* (a) and *a* (b) axis.

Thermal stability of complexes 1, 2 and 3

The thermal stabilities of complexes **1**, **2** and **3** have been measured. For complex **1**, there are two weight loss steps from 100 to 360 °C. The first weight loss of 10.0% from 100 to 235 °C corresponds to the loss of 0.5 uncoordinated and two coordinated water molecules (calculated: 8.9%), the second weight loss of 29% from 240 to 335 °C corresponds to the loss of the coordinated bpy molecule (calculated: 30.8%), and after 340 °C, THFTCA ligand starts to decompose. The uncoordinated and coordinated water molecules were lost at higher temperature in **1**, which derives from the existence of strong hydrogen bonding interactions between the water molecules with the uncoordinated carboxylate groups. For complex **2**, we did not find the loss of the uncoordinated water molecule in the lattice, which may result from the fact that the methanol molecule had been lost when we dried the sample in the air. There is no weight loss from 50 to 260 °C and after 260 °C **2** starts to decompose. For complex **3**, the weight loss of 7.5% from 50 to 190 °C corresponds to the loss of three uncoordinated and two coordinated water molecules (calculated: 8.6%), and there is no weight loss from 190 to 320 °C. After 320 °C, **3** starts to decompose.

Photoluminescence properties of 2 and 3

On the basis of the current research of luminescent MOFs, the emission of coordination networks can be assigned to a ligand-to-metal charge transfer (LMCT),[16] metal-to-ligand charge transfer (MLCT)[17] or to an intraligand $\pi \rightarrow \pi^*$ transition. In general, metal coordination significantly influences the fluorescence properties in MOFs (compared to organic ligands), an important property to consider when trying to synthesize new luminescent materials. The fluorescence properties of **2** and **3** were measured at room temperature, and the fluorescent spectra are displayed in Fig. 11. Complexes **2** and **3** exhibit similar luminescence at λ_{max} = 420 and 435 nm, upon excitation at 387 and 375 nm, respectively. The emissions of **2** and **3** can probably be assigned to an intraligand $\pi \rightarrow \pi^*$ transition,[18] as free $H_4THFTCA$ possesses similar emission in the solid state. These results imply that the coordination of the THFTCA ligand with the zinc and cadmium ions, although yielding different topological structures, has no influence on the emission mechanism of the metal–organic frameworks.[19]
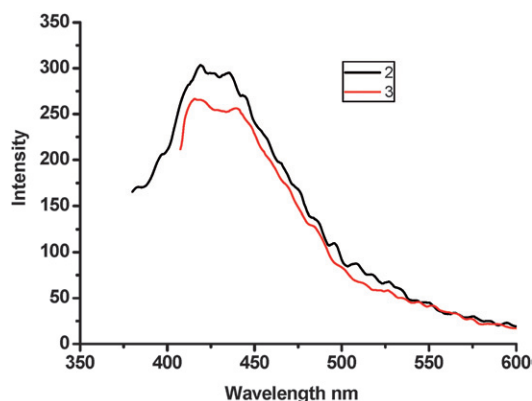

Fig. 11 Solid-state emission spectra of **2** and **3** at room temperature.

Conclusions

In summary, three metal–organic supramolecular architectures have been synthesized and characterized based on a tetra-carboxylate ligand, THFTCA. Although many metal–organic frameworks constructed from 1,2,4,5-benzenetetracarboxylic acid (BTEC) have been widely reported, MOFs based on THFTCA are quite rare due to its flexibility compared to that of BTEC. The introduction of rigid 4,4′-bpy or phen in our work is important in the formation of **1**, **2** and **3**. Complex **3** possesses a rare 4,6-connected net. In complex **1**, two carboxylate groups of THFTCA and one nitrogen atom of 4,4′-bpy did not take part in the coordination, which can act as an intermediate to further connect other metal ions in the reaction. Further studies on this subject are currently underway.

Experimental

Materials and physical measurements

All chemicals used are as purchased without purification. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate of 10 °C min^{-1}, nitrogen stream). Elementary analyses were carried out in the elementary analysis group of this department.

Preparation

Synthesis of Co(H$_2$O)$_2$(H$_2$THFTCA)(4,4′-bpy)·1/2H$_2$O (1). Co(NO$_3$)$_2$·6H$_2$O (0.03 g, 0.1 mmol) and H$_4$THFTCA (0.01 g, 0.04 mmol) were dissolved in 15 mL distilled water. The solution was heated to boiling for 15 min, then cooled to room temperature, to which 15 mL MeOH solution containing 4,4′-bpyridine (0.01 g, 0.05 mmol) was added. After the pH value was adjusted to about 7 by adding 0.1 M NaOH solution, the reaction mixture was filtered and the filtrate was allowed to evaporate at room temperature. Pink prism-like crystals of **1** were formed after two days. (yield: 40%). Elemental anal. Calcd for **1**: C, 42.70; H, 3.78; N, 5.53%. Found: C, 41.87; H, 3.74; N, 5.39%

Synthesis of Zn(H$_2$THFTCA)(phen)·H$_2$O (2). Zn(NO$_3$)$_2$·6H$_2$O (0.02 g, 0.067 mmol) and H$_4$THFTCA (0.01 g, 0.04 mmol) were dissolved in 15 mL distilled water. The mixture was heated to boiling for 15 min, then cooled to room temperature, to which 15 mL MeOH containing 1,10-pentathroline (0.01 g, 0.055 mmol) was added. The reaction mixture was filtered and the filtrate was allowed to evaporate at room temperature. Colorless block crystals of **2** were formed after three days. (yield: 35 %). Elemental anal. Calcd for **2**: C, 47.13; H, 3.16; N, 5.50%. Found: C, 47.05; H, 3.10; N, 5.48%.

Synthesis of Cd$_3$(H$_2$O)$_2$(HTHFTCA)$_2$(4,4′-bpy)$_2$·4H$_2$O (3). Cd(NO$_3$)$_2$·4H$_2$O (0.03 g, 0.097 mmol) and H$_4$THFTCA (0.01 g, 0.04 mmol) were dissolved in 15 mL distilled water. The mixture was heated to boiling for 15 min, then cooled to room temperature, to which 15 mL MeOH containing 4,4′-bipyridine (0.01 g, 0.05 mmol) was added. After the pH value was adjusted to about 7 by adding 0.1 M NaOH solution, the reaction mixture was filtered and the filtrate was allowed to evaporate at room temperature. Colorless block crystals of **3** were formed after two

days. (yield: 45 %). Elemental anal. Calcd for **2**: C, 34.65; H, 3.07; N, 4.49%. Found: C, 34.47; H, 2.92; N, 4.49%

Crystal structure determinations

Crystallographic data for **1–3** were collected on a Bruker Smart 1000 CCD diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at room temperature. All structures were solved by the direct method using the SHELXS program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL.[20] The metal atoms in each complex were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å).

Crystal data of **1**: $C_{18}H_{19}CoN_2O_{11.5}$, $M = 506.28$, triclinic, space group $P\text{-}1$, $a = 5.1928(5)$, $b = 12.7800(14)$, $c = 15.3165(15)$ Å, $\alpha = 82.143(6)$, $\beta = 80.888(6)$, $\gamma = 87.501(6)°$, $U = 993.96(17)$ Å^3, $Z = 1$, $D_c = 1.692$ Mg m^{-3}, μ(Mo Kα) $= 0.934$ mm^{-1}, $T = 273$ K, 9571 reflections collected. Refinement of 4783 reflections (330 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0404$ ($R1$ all data $= 0.0523$), $wR2 = 0.1040$ ($wR2$ all data $= 0.1121$), gof $= 1.104$. Crystal data for **2**: $C_{20}H_{16}N_2O_{10}Zn$, $M = 509.72$, monoclinic, space group $P2_1/n$, $a = 13.1282(3)$, $b = 8.5385(2)$, $c = 17.7763(4)$ Å, $\beta = 91.9390(10)°$, $U = 1991.50(8)$ Å^3, $Z = 4$, $D_c = 1.700$ Mg m^{-3}, μ(Mo Kα) $= 1.298$ mm^{-1}, $T = 273$ K, 24533 reflections collected. Refinement of 4444 reflections (306 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0382$ ($R1$ all data $= 0.0437$), $wR2 = 0.1182$ ($wR2$ all data $= 0.1236$), gof $= 1.060$. Crystal data for **3**: $C_{36}H_{38}Cd_3N_4O_{24}$, $M = 1247.90$, monoclinic, space group $C2/c$, $a = 21.693(4)$, $b = 8.5861(18)$, $c = 22.878(5)$ Å, $\beta = 100.686(12)°$, $U = 4187.2(15)$ Å^3, $Z = 4$, $D_c = 1.980$ Mg m^{-3}, μ(Mo Kα) $= 1.608$ mm^{-1}, $T = 273$ K, 26220 reflections collected. Refinement of 6860 reflections (320 parameters) with $I > 1.5\sigma(I)$ converged at final $R1 = 0.0325$ ($R1$ all data $= 0.0398$), $wR2 = 0.0871$ ($wR2$ all data $= 0.0915$), gof $= 1.073$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 682754 for **1**, 682755 for **2** and 682756 for **3**.†

References

1 (*a*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefee and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*b*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*c*) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040; (*d*) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012; (*e*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.

2 (*a*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*b*) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, Y. Wei, S. L. Qiu and R. R. Xu, *Angew. Chem., Int. Ed.*, 2005, **44**, 3845; (*c*) L. Pan, H. M. Liu, X. G. Lei, X. Y. Huang, D. H. Olson, N. J. Turro and J. Li, *Angew. Chem., Int. Ed.*, 2003, **42**, 542; (*d*) J. S. Seo, D. Whang, H. Lee, S. I. Jun,

J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (*e*) W. B. Lin, *J. Solid State Chem.*, 2005, **178**, 2486; (*f*) R. Xiong, X. You, B. F. Abrahams, Z. Xue and C. Che, *Angew. Chem., Int. Ed.*, 2001, **40**, 4422.

3 (*a*) A. C. Sudik, A. P. Cote and O. M. Yaghi, *Inorg. Chem.*, 2005, **44**, 2998; (*b*) W. Chen, J. Y. Wang, C. Chen, Q. Yue, H. M. Yuan, J. S. Chen and S. N. Wang, *Inorg. Chem.*, 2003, **42**, 944; (*c*) B. H. Ye, B. B. Ding, Y. Q. Weng and X. M. Chen, *Cryst. Growth Des.*, 2005, **5**, 801; (*d*) N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504; (*e*) C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer and G. Ferey, *J. Am. Chem. Soc.*, 2002, **124**, 13519.

4 (*a*) S. S. -Y. Chui, S. M. -F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (*b*) D. P. Cheng, M. A. Khan and R. P. Houser, *Cryst. Growth Des.*, 2004, **4**, 599; (*c*) Z. Shi, G. H. Li, L. Wang, L. Gao, X. B. Chen, J. Hua and S. H. Feng, *Cryst. Growth Des.*, 2004, **4**, 25; (*d*) H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 2004, **126**, 15844; (*e*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*f*) Z. Q. Wang, V. Ch, Kravtsov and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2005, **44**, 2877.

5 (*a*) D. F. Sun, R. Cao, Y. Q. Sun, W. H. Bi, X. J. Li, Y. Q. Wang, Q. Shi and X. Li, *Inorg. Chem.*, 2003, **42**, 7512; (*b*) R. Cao, Q. Shi, D. F. Sun, M. C. Hong, W. H. Bi and Y. J. Zhao, *Inorg. Chem.*, 2002, **41**, 6161; (*c*) H. Kumagai, C. J. Kepert and M. Kumoo, *Inorg. Chem.*, 2002, **41**, 3410; (*d*) S. V. Ganesan and S. Natarajan, *Inorg. Chem.*, 2004, **43**, 198.

6 (*a*) D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033; (*b*) B. Q. Ma, K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2005, **44**, 4912; (*c*) H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem.–Eur. J.*, 2005, **11**, 3521.

7 R. Cao, D. F. Sun, Y. C. Liang, M. C. Hong, K. Tatsumi and Q. Shi, *Inorg. Chem.*, 2002, **41**, 2087.

8 (*a*) C. M. R. Juan and B. Lee, *Coord. Chem. Rev.*, 1999, **183**, 43; (*b*) M. -C. Tse, K. -K. Cheung, M. C. -W. Chan and C. -M. Che, *Chem. Commun.*, 1998, 3245; (*c*) M. Tadokoro, S. Isobe, H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro and K. Nakasujhi, *Angew. Chem., Int. Ed.*, 1999, **38**, 95; (*d*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (*e*) D. F. Sun, R. Cao, Y. Q. Sun, X. Li, W. H. Bi, M. C. Hong and Y. J. Zhao, *Eur. J. Inorg. Chem.*, 2003, 94; (*f*) M. L. Tong, H. K. Lee, X. M. Chen, R. B. Huang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1999, 3657.

9 (*a*) G. Ferey, *Chem. Mater.*, 2001, **13**, 3084; (*b*) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; (*c*) M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2000, **39**, 3052.

10 (*a*) K. Hanson, N. Calin, D. Bugaris, M. Scancella and S. C. Sevov, *J. Am. Chem. Soc.*, 2004, **126**, 10502; (*b*) P. Thuery, C. VILLERS, j. Jaud, M. Ephritikhine and B. Masci, *J. Am. Chem. Soc.*, 2004, **126**, 6838.

11 (*a*) R. M. Barrer, *The Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982; (*b*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638.

12 M. C. Guillem, J. Latorre, R. Martinez-Manez, J. Paya, S. Gatcia-Granda, E. Perez-Carreno and F. Gomez-Beltran, *Polyhedron*, 1993, **12**, 1681.

13 (*a*) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (*b*) (b)A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2006; available via http://www.cryst.chem.uu.nl/platon (for unix) and http://www.chem.gla.ac.uk/~louis/software/platon/ (for MS Windows).

14 (*a*) A. M. Kutasi, A. R. Harris, S. R. Batten, B. Moubaraki and K. S. Murray, *Cryst. Growth Des.*, 2004, **4**, 605; (*b*) P. K. Chen, Y. X. Che and J. M. Zheng, *Inorg. Chem. Commun.*, 2007, **10**, 187.

15 S. L. Li, Y. Q. Lan, J. F. Ma, J. Yang, G. H. Wei, L. P. Zhang and Z. M. Su, *Cryst. Growth Des.*, 2008, **8**, 675.

16 Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu, W.-X. Du, H.-H. Zhang and R.-Q. Sun, *Eur. J. Inorg. Chem.*, 2002, 2730.

17 (*a*) Z. Abedin-Siddique, T. Ohno, K. Nozaki and T. Tsubomura, *Inorg. Chem.*, 2004, **43**, 663; (*b*) S. J. A. Pope, B. J. Coe, S. Faulkner, E. V. Bichenkova, X. Yu and K. T. Douglas, *J. Am. Chem. Soc.*, 2004, **126**, 9490.

18 (a) S. T. Wang, Y. Hou, E. B. Wang, Y. G. Li, L. Xu, J. Peng, S. X. Liu and C. W. Hu, *New J. Chem.*, 2003, **27**, 1144; (b) X. D. Chen, M. Du and T. C. W. Mak, *Chem. Commun.*, 2005, 4417–4419.

19 (a) M. P. Clares, J. Aguilar, R. Aucejo, C. Lodeiro, M. T. Albelda, F. Pina, J. C. Lima, A. J. Parola, J. Pina, S. de Melo, C. Soriano and E. García-España, *Inorg. Chem.*, 2004, **43**, 6114; (b) F. Bolletta, I. Costa, L. Fabbrizzi, M. Licchelli, M. Montalti, P. Pallavicini, L. Prodi and N. Zaccheroni, *J. Chem. Soc., Dalton Trans.*, 1999, 1381; (c) S. A. Zabin and C. R. Jejurkar, *J. Polym. Mater.*, 1997, **14**, 239.

20 (a) G. M. Sheldrick, SHELXS-97, *Program for Crystal Structure Solution*, Göttingen University, Germany, 1997; (b) (b)G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, Göttingen University, Germany, 1997.