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New Metal-Organic Frameworks with Large Cavities: Selective Sorption and Desorption of Solvent Molecules

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Abstract: Five novel transition metal complexes $[Cd^{II}_3(tpba\text{-}2)_2(SCN)_6]\cdot 6THF\cdot 3H_2O$ (**1**), $[Cu^{II}_3(tpba\text{-}2)_2(SCN)_6]\cdot 6THF\cdot 3H_2O$ (**2**), $[Ni^{II}_3(tpba\text{-}2)_2(SCN)_6]\cdot 6THF\cdot 3H_2O$ (**3**), $[Cd^{II}_2(tpba\text{-}2)(SCN)_3]ClO_4$ (**4**), $[Cu^{I}_3(SCN)_6(H_3tpba\text{-}2)]$ (**5**) [TPBA-2 = *N′*,*N″*,*N‴*-tris(pyrid-2-ylmethyl)-1,3,5-benzenetricarboxamide, THF = tetrahydrofuran] were obtained by reactions of the corresponding transition metal salts with TPBA-2 ligand in the presence of NH_4SCN using layering or solvothermal method, respectively. The results of X-ray crystallographic analysis showed that complexes **1**, **2** and **3** are isostructural and have the same 2D honeycomb network structure with Kagomé lattice, in which all the M^{II} (M = Cd, Cu, Ni) atoms are six-coordinated, and the TPBA-2 ligands adopt *cis,cis,cis* conformation while the thiocyanate anions act as terminal ligands. Capsule-like motifs are found in **1**, **2** and **3**, in which six THF molecules are hosted, and the results of XPRD and solid-state ^{13}C NMR spectral measurements showed that the compound **1** can selectively desorb and adsorb THF molecules occurring along with the re-establishment of its crystallinity. In contrast to **1**, **2** and **3**, complex **4** has different 2D network structure, resulting from TPBA-2 ligands with *cis,trans,trans* conformation, thiocyanate anions serving as end-to-end bridging ligands, and the incomplete replacement of perchlorate anions, which further link the 2D layers into 3D framework by the hydrogen bonds. In complex **5**, the Cu^{II} atoms are reduced to Cu^{I} during the process of solvothermal reaction, and the Cu^{I} atoms are connected by thiocyanate anions to form a 3D porous framework, in which the protonated TPBA-2 ligands are hosted in the cavities as templates.

Keywords: capsules · desorption · metal–organic frameworks · sorption · tripodal ligands

Introduction

During the past decades, a great deal of efforts have been devoted to the crystal engineering of supramolecular frameworks, especially with hollow structures (capsules, cages, polyhedra, etc.) by using transition-metal salts and organic ligands due to their unique properties such as encapsulation of guest molecules and molecular aggregates and potential applications in many fields including medicine, material science, and chemical technology.[1–3] On the other hand, the coordination polymers have been considered to be a new class of materials. Many research groups have devoted their efforts on the development, design, and synthesis of novel metal-organic frameworks (MOFs) and significant results have been achieved concerning on gas storage and host–guest chemistry.[4] For example, Rebek and his colleagues recently reported the hydrogen-bonded dimeric capsules by using spacers with different length, which increased the cavities' volume and length,[5a] and they found that the hydrogen bonds and curved surfaces should be able to favor the encapsulation.[5] In addition, magnificent architectures, so-called "encapsulation complexes", were designed and constructed by using three-connecting organic ligands and the encapsulated guests may have special chemical and physical properties, which are different from those in bulk phases, due to the constrained environments of the hollow structures.[6,7]

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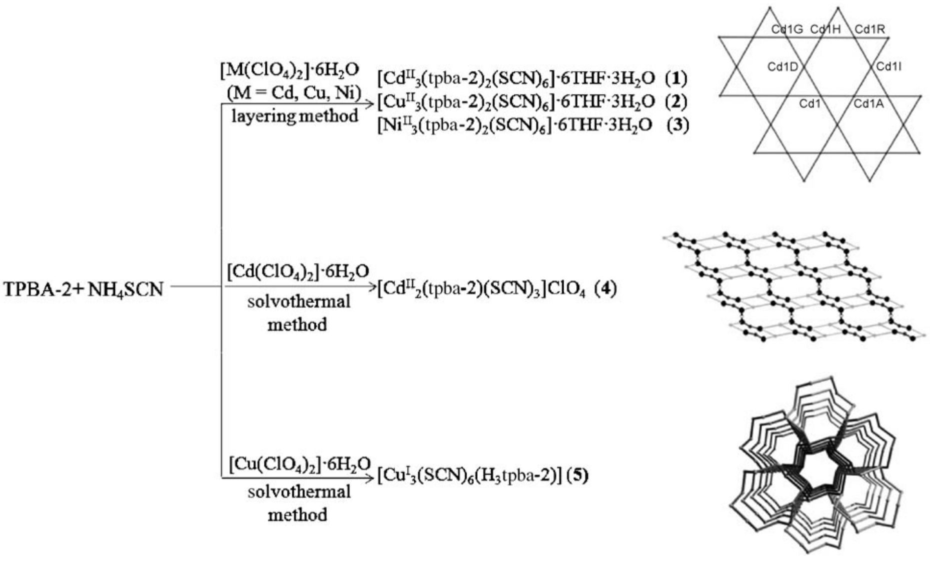
We concentrate our efforts on design and construction of MOFs with specific topologies and properties by using tripodal ligands with aromatic core, for instance, 1,3,5-tris(imidazol-1-ylmethyl)benzene (TIB), 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB), N',N'',N'''-tris(pyrid-3-ylmethyl)-1,3,5-benzenetricarboxamide (TPBA-3).[8,9] Cage-like complexes with encapsulation properties, for example, the M^3L_2 type cage-like complex $[Zn_3(tib)_2(OAc)_6]\cdot 4H_2O$ which shows guest-inclusion property of organic molecule like synthetic camphor in aqueous solution, and $[Ag(tpba\text{-}3)N_3]$ with twofold interpenetrated three-dimensional structure have been obtained.[8a,b] It is noteworthy that self-assembly using ligands containing carboxamide group, ubiquitous throughout nature for example in the primary structure of proteins, as construction unit has draw attentions of chemists during the past few years.[10] Due to the abilities of carboxamide groups as donors as well as acceptors of hydrogen bonds, ligands containing carboxamide group are widely used in research fields such as water clusters, gas storage, and molecular recognition.[11] In order to further investigate the self-assembly of flexible tripodal ligand with transition-metal salts and the encapsulation properties of MOFs, we designed and synthesized a new carboxamide-containing ligand N',N'',N'''-tris(pyrid-2-ylmethly)-1,3,5-benzenetricarboxamide (TPBA-2). The flexibility resulting from the methylene group can make TPBA-2 adopt varied conformations and result in different MOFs with novel structures. On the other hand, the existence of carboxamide groups can favor the investigations of encapsulation properties by forming hydrogen bonds between the host and guest molecules. In this paper, five supramolecular frameworks, namely $[Cd^{II}_3(tpba\text{-}2)_2(SCN)_6]\cdot 6THF\cdot 3H_2O$ (**1**), $[Cu^{II}_3(tpba\text{-}2)_2(SCN)_6]\cdot 6THF\cdot 3H_2O$ (**2**), $[Ni^{II}_3(tpba\text{-}2)_2(SCN)_6]\cdot 6THF\cdot 3H_2O$ (**3**), $[Cd^{II}_2(tpba\text{-}2)(SCN)_3]ClO_4$ (**4**), $[Cu^{I}_3(SCN)_6(h_3tpba\text{-}2)]$ (**5**) were obtained by assembly reactions between TPBA-2 and different metal salts in the presence of NH_4SCN, respectively (Scheme 1). Herein, we report the synthesis, crystal structures, sorption and desorption properties of the complexes.



Scheme 1. Schematic depiction of the reactions for preparing complexes **1**–**5**.

Results and Discussion

Structure descriptions of complexes 1–3: The structures of the complexes were determined by X-ray crystallography. The crystallographic data for all five complexes are summarized in Table 1 and selected bond lengths and bond angles are provided in Table S1, Supporting Information. Similar cell parameters with the same space group $R\bar{3}$ as listed in Table 1 and the results of crystallographic analysis indicate that complexes **1**, **2**, **3** are isomorphous and isostructural, and thus only the structure of **1** is presented here as an example. As shown in Figure 1, the Cd^{II} atom in complex **1** is six-coordinated with slightly distorted octahedral coordination environment, in which the equatorial plane consists of two N atoms and two O atoms from two different TPBA-2 ligands, while two N atoms from two different thiocyanate anions occupy the apical positions. The Cd1−N1 and Cd1−N3 bond lengths are 2.336(3) and 2.257(3) Å with the N-Cd-N bond angles varying from 89.25(13) and 180.0°, while the Cd−O bond length is 2.329(2) Å with the N-Cd-O bond angles in the range of 87.92(12) to 92.08(12)° (Table S1, Supporting Information). It is noteworthy that the carbonyl O atoms participate the coordination with the Cd^{II} atom in **1**, while in the case of complex $[Ag(tpba\text{-}3)N_3]$ with 3-pyridyl arms in the TPBA-3 ligand, the carbonyl O atoms did not take part in the coordination with the metal atoms.[8a] On the other hand, each TPBA-2 ligand connects three different Cd^{II} atoms through the chelate coordination of pyridyl N and carbonyl O atoms (Figure 1). The O and N atoms of each carboxamide group are out of the central benzene ring plane in the contrary directions with deviations of 0.78 and 1.05 Å, respectively. The combination of octahedral metal center with about 90 and 180° coordination angles and the three connecting TPBA-2 ligand with *cis*,*cis*,*cis* conformation results in the formation of an infinite 2D honeycomb network on the *ab* plane as illustrated in Figure 2.[12] In the 2D sheet, six TPBA-2 ligands and six Cd^{II} atoms form a 48-membered macrocycle with a large Cu_6 honeycomb hexagon of 19.75 Å diameter (Figure 2a), which is much larger than those reported previously.[13] In addition, three Cd^{II} atoms (e.g. Cd1D, Cd1H, Cd1G) are connected together by one TPBA-2 ligand to form a Cd_3 triangle, which are lateral-

Table 1. Crystal data and structure refinement parameters for complexes **1**–**5**.

	1	**2**	**3**	**4**	**5**
formula	$C_{84}H_{102}N_{18}O_{15}S_6Cd_3$	$C_{84}H_{102}N_{18}O_{15}S_6Cu_3$	$C_{84}H_{102}N_{18}O_{15}S_6Ni_3$	$C_{30}H_{24}N_9O_7S_3Cl_1Cd_2$	$C_{33}H_{27}Cu_3N_{12}O_3S_6$
M	2133.40	1986.82	1972.33	979.01	1022.65
crystal size [mm]	0.25×0.20×0.20	0.45×0.40×0.15	0.20×0.20×0.05	0.20×0.15×0.13	0.50×0.20×0.20
crystal system	trigonal	trigonal	trigonal	triclinic	trigonal
space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$P\bar{1}$	$R\bar{3}$
a [Å]	19.750(3)	20.126(6)	19.552(8)	10.4845(19)	21.713(2)
b [Å]	19.750(3)	20.126(6)	19.552(8)	13.174(2)	21.713(2)
c [Å]	21.590(4)	20.554(7)	21.204(10)	13.832(2)	14.998(2)
α [°]	90.00	90.00	90.00	78.042(3)	90.00
β [°]	90.00	90.00	90.00	75.359(3)	90.00
γ [°]	120.00	120.00	120.00	82.623(4)	120.00
V [Å^3]	7293(2)	7210(4)	7020(5)	1802.6(5)	6123.6(12)
Z	3	3	3	2	6
T [K]	173(2)	200(2)	200(2)	293(2)	293(2)
μ [mm^{-1}]	0.847	0.857	0.802	1.487	1.907
ρ_{calcd} [g cm^{-3}]	1.457	1.373	1.400	1.804	1.664
$F(000)$	3276	3105	3096	968	3096
reflections [$I>2\sigma(I)$]	3466	2817	1651	4860	2142
unique reflections	3714	3680	2750	6254	3128
measured reflections	18685	23701	18433	9066	12315
GOF	1.086	1.035	1.033	1.032	1.026
R_1 [$I>2\sigma(I)$][a]	0.0608	0.0482	0.0749	0.0629	0.0491
Rw [$I>2\sigma(I)$)][b]	0.1680	0.1194	0.1551	0.1377	0.1596
$\Delta\rho$ max/min [e Å^{-3}]	3.897, −0.859	0.553, −0.403	0.397, −0.415	0.953, −1.042	1.355, −0.312

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR = |\Sigma w(|F_o^2|-|F_o^2|)/\Sigma|wF_o^2|^{1/2}$.

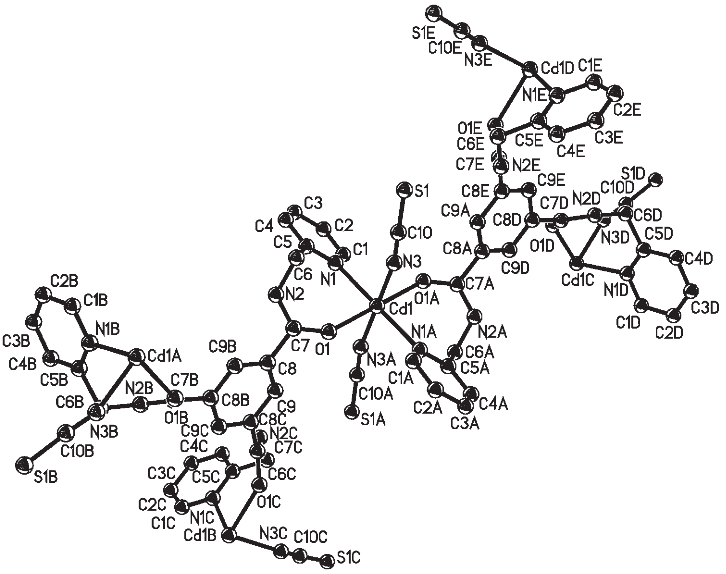


Figure 1. ORTEP plot of **1** showing local coordination environment of Cd^{II} with thermal ellipsoids at 30% probability. The uncoordinated solvent molecules and hydrogen atoms were omitted for clarity.

shared with the three circumjacent Cd_6 hexagons to generate a geometrical topology of Kagomé lattice as simplified in Figure 2b. Furthermore, all the TPBA-2 ligands with alternating "up" and "down" orientations look like "bowls" and upside down "bowls", respectively (Figure 2c, d).[12] The depth of the bowl, defined by the distance between the C atom at the *para*-position of the pyridyl N atom (e.g. C3 in Figure 1) and the central benzene ring plane, is 4.35 Å. The back-to-back benzene ring planes of the TPBA-2 ligands with "up" and "down" orientations are strictly parallel each other with a distance of 0.98 Å between the two benzene ring planes, and the plane containing Cd^{II} atoms is at the middle of the two benzene ring planes, namely, each Cd^{II} atom is out of the benzene ring plane by distance of 0.49 Å (Figure 2c).

The packing arrangement of the 2D sheets is shown in Figure 3. The layers repeat in an -ABCABC- stacking sequence along the *c* axis. The salient structure feature is the formation of capsules through the layer stacking. It can be seen from Figure 3a that a upside down "bowl" of the TPBA-2 ligand from layer A and "bowl" from layer C adopt a face-to-face orientation to generate a large capsule-like motif with a distance of 13.42 Å between two benzene planes (Figure 3b). Each capsule accommodates six THF molecules through the formation of N2-H2A···O2 hydrogen bond. The hydrogen-bonding data of **1**–**3** are summarized in Table S2, Supporting Information. The THF molecules just locate through the Cd_6 hexagon hole of layer B, which also serves as the border of the capsule-like motif to make it a closed one (Figure 3b).

It is noteworthy that the same result was achieved by using nitrate salts instead of perchlorate salts due to the complete replacement of nitrate or perchlorate by thiocyanate. The similar structures of **1**, **2**, and **3** may suggest that the structures of the complexes are mainly depending on the coordination geometry requirement of the metal ions but not influenced significantly by the metal atoms in this system.

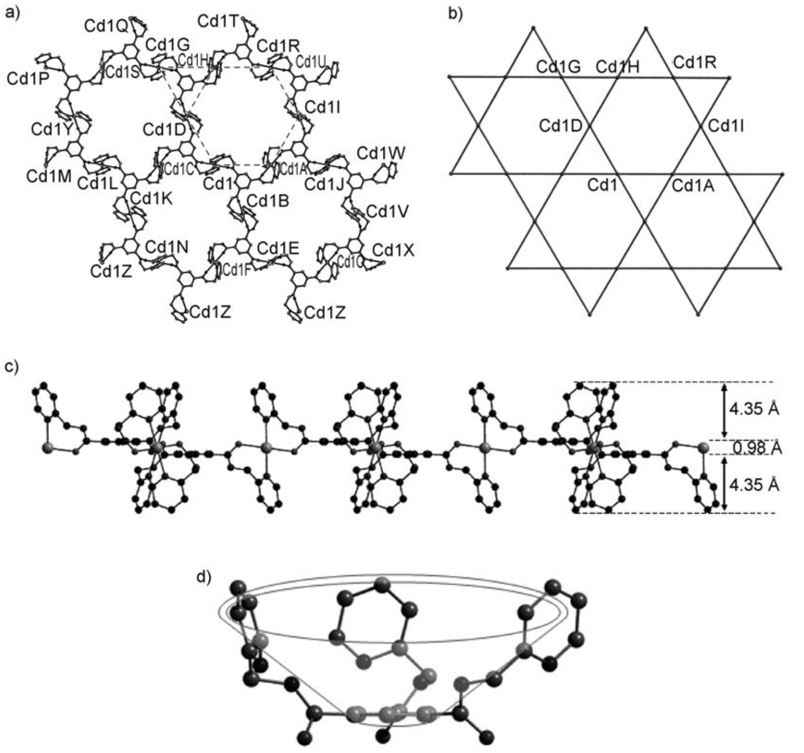


Figure 2. a) Top view of 2D layer of complex **1** with a Cd_6 hexagon and a Cd_3 triangle indicated by dashed lines, in which the THF, water and coordinated SCN^- were omitted for clarity. b) Schematic drawing of Kagomé lattice of **1** where only the cadmium(II) atoms are presented. c) Side view of 2D layer of **1** along the *b* axis with distances marked, where the THF, water and coordinated SCN^- were omitted for clarity. d) Schematic drawing of the TPBA-2 in bowl shape.

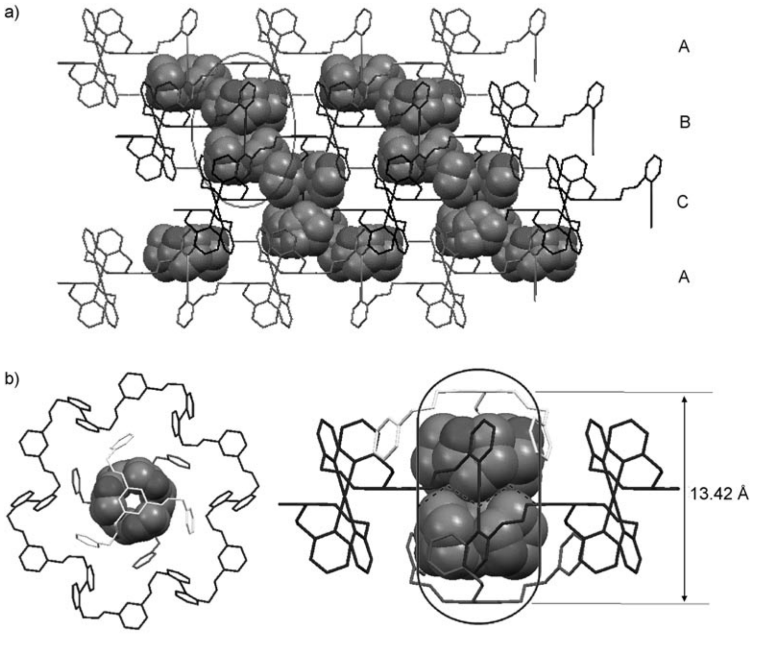


Figure 3. a) The stacking mode of complex **1** along *a* axis, b) top (left) and side (right) views of the capsule-like moiety in **1**. The O atom of the carboxamide group, water molecules and thiocyanate anions are omitted for clarity.

Complex $[Cd_2(tpba\text{-}2)(SCN)_3]ClO_4$ (4): In order to further investigate the influence of reaction conditions on the structure of the complexes, solvothermal method was used for the reactions of TPBA-2 ligand with perchlorate salts in the presence of thiocyanate anions, respectively. Inspiringly, MOFs **4** and **5** with different structures were successfully isolated and they will be discussed below.

The X-ray diffraction analysis revealed that, in contrast to terminal coordination of the thiocyanate anions in complexes **1**–**3**, the thiocyanate anions served as end-to-end bridging ligands to link two Cd^{II} atoms, which may contribute to the totally different structure of **4**. The compound **4** crystallizes in triclinic with $P\bar{1}$ space group; the coordination environment around the Cd^{II} centers in complex **4** is shown in Figure 4a. It is obvious that there are two distinct Cd^{II} atoms in the asymmetry unit: the Cd1 and Cd2 atoms are both six-coordinated but in different coordination environment. Three of the six sites of Cd1 are coordinated by two N atoms from two different thiocyanate anions and one pyridyl N atom with Cd−N bond lengths varying from 2.295(7) to 2.379(6) Å, and the remaining three sites are occupied by one O atom from one TPBA-2 ligand and two S atoms from two different thiocyanate anions with the Cd−O bond length of 2.380(5) Å while the Cd−S bond lengths are 2.636(2) and 2.708(2) Å, respectively (Table S1, Supporting Information). The N-Cd1-N, N-Cd1-S, N-Cd-O, O-Cd1-S and S-Cd1−S bond angles around Cd1 are in the range of 82.4(2) to 174.96(17)°. Thus, the coordination geometry of the Cd1

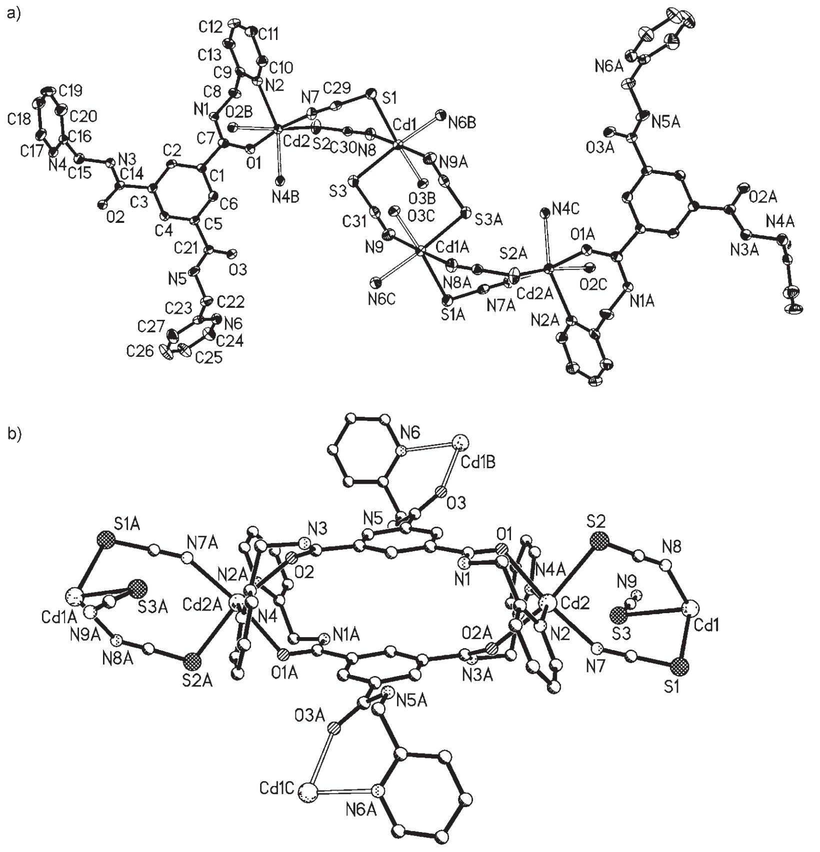


Figure 4. a) ORTEP plot of complex **4** showing local coordination environment of Cd^{II}, the thermal ellipsoids were drawn at 30% probability. b) The coordination mode of the TPBA-2 ligands with M_2L_2 macrocycle. The uncoordinated perchlorate anions and hydrogen atoms were omitted for clarity.

center can be regarded as a slightly distorted octahedral with $N_3O_1S_2$ donor set. On the other hand, four of the six sites of the Cd2 are coordinated by two N atoms and two O atoms from two different TPBA-2 ligands with the Cd–N bond lengths of 2.355(6) and 2.357(6) Å, and the Cd–O bond lengths of 2.334(6) and 2.369(5) Å, respectively. The remaining two sites are occupied by one S atom (S2) and one N atom (N7) from two different thiocyanate anions with the Cd–S and Cd–N bond lengths of 2.666(2) and 2.265(7) Å, respectively. The bond angles around Cd2 vary from 74.11(19) to 171.7(2)° (Table S1, Supporting Information). Therefore, the coordination geometry of octahedron around the Cd2 center with $N_3O_2S_1$ donor set is more distorted than that around the Cd1. It is interesting that there is a Cd2-Cd1-Cd1-Cd2 tetranuclear unit in **4** which is double bridged by two thiocyanate anions between each two adjacent metal atoms as illustrated in Figure 4a.

On the other hand, each TPBA-2 ligand coordinates with two Cd2 and one Cd1 atoms, and furthermore two TPBA-2 ligands and two Cd2 atoms form a M_2L_2 macrocycle (Figure 4b), in which the two central benzene ring planes of the TPBA-2 are parallel with a centroid–centroid distance of 4.35 Å. It is noteworthy that in contrast to the *cis,cis,cis* conformation of TPBA-2 in complexes **1**–**3**, the TPBA-2 ligands adopt *cis,trans,trans* conformation in complex **4**, in which the three arms of the TPBA-2 ligand occurs at different torsions (Figure 4b). Each carbonyl O atom lies in the same direction of the pyridine ring it attached to with deviation of 0.71, 0.14, and 0.36 Å out of the benzene ring plane, respectively. The dihedral angles between the benzene ring plane and the pyridine ring planes are 70.4, 63.2, and 73.7°, respectively.

When the thiocyanate anions bridging the two Cd1 atoms are ignored, the four-coordinated Cd1, six-coordinated Cd2 atoms and the three-connecting TPBA-2 ligand result in formation of an infinite 1D chain as shown in Figure 5a and b. The adjacent 1D chains are further bridged by another thiocyanate anions (e.g. N9-C31-S3 in Figure 4a) to generate a 2D-network structure as schematically shown in Figure 5c.

It is interesting that although the starting materials for the synthesis of complex **4** are the same as those used in preparation of **1**, the perchlorate anions are not completely replaced by the thiocyanate anions under the solvothermal reaction, and there is still one remaining in each asymmetric unit of **4**. The perchlorate anions occupy the voids between the 2D layers and form C-H···O and N-H···O (C8-H8B···O8, N1-H1A···O6B, as listed in Table S2, Supporting Information) hydrogen bonds with the ligands from the adjacent layers to link the 2D networks to generate the 3D framework.

Complex $[Cu_3^I(SCN)_6]_3(h_3tpba\text{-}2)$ (5): The yellow crystal of complex **5** and the result of X-ray crystallographic analysis revealed that the Cu^{II} was reduced to Cu^I under the solvothermal process. The Cu^I in **5** was also confirmed by EPR spectral measurements. It has been reported that the Cu^{II} could be reduced to Cu^I under the solvothermal conditions.[14] The coordination environment around the Cu^I was shown in Figure 6a. It can be clearly seen that the TPBA-2 ligand did not participate in the coordination with the metal atoms and all the Cu^I atoms are four-coordinated with two N atoms from two thiocyanate anions and two S atoms from another two thiocyanate anions, in which the Cu–N bond lengths are 1.960(4) and 1.970(4) Å, and the Cu–S bond lengths are 2.2991(12) to 2.4440(14) Å (Table S1, Supporting Information), respectively. The N-Cu-S, N-Cu-N and S-Cu-S coordination angles vary from 100.94(5) to 116.48(13)°, and thus the Cu^I atoms can be regarded as distorted tetrahedral

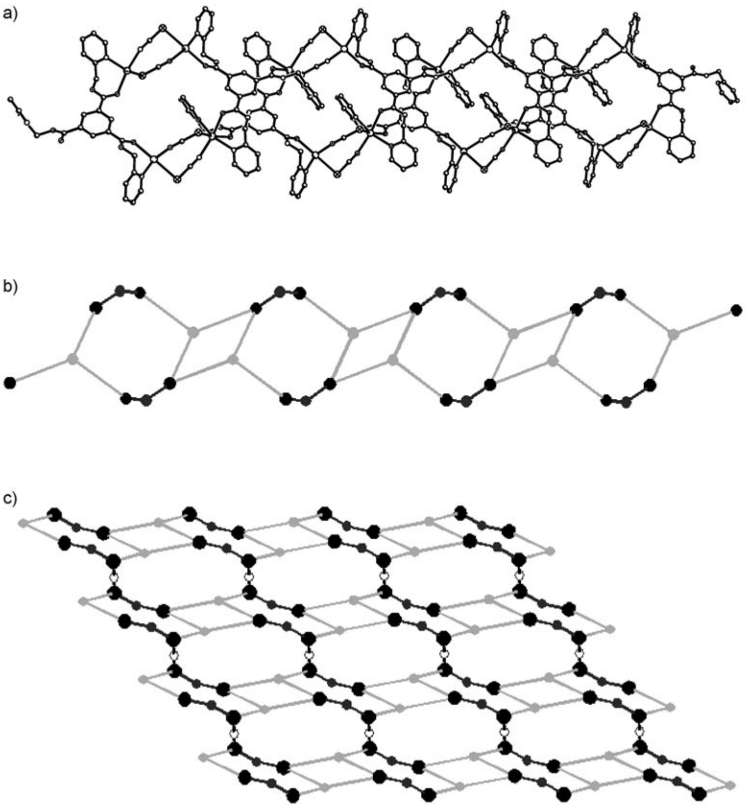


Figure 5. a) 1D chain structure and b) schematic drawing of the 1D chain of complex **4**, in which the three-connecting TPBA-2 ligand and two-connected SCN^- are represented by three (light gray) and two (dark black) spokes radiation from a solid point, respectively, and the Cd^{II} by solid black ball. The ClO_4^- and SCN^- that bridged Cd1 atoms were omitted. c) Schematic drawing of the 2D network of **4**, in which the three-connecting ligand and two-connected thiocyanate anions are represented by three (light gray) and two (dark black) spokes radiation from a solid point, respectively, the Cd^{II} by solid black ball, and the SCN^- that bridged Cd1 atoms by two (dark black) spokes radiation from a open point.

coordination geometry with a N_2S_2 donor set. There are two bridge modes of the thiocyanate anions in complex **5**. As shown in Figure 6a, the Cu1 and Cu1A are double bridged by two different thiocyanate anions while the Cu1 and Cu1B (or Cu1C) are bridged by only one, and we define them as double-bridging and single-bridging modes with the Cu–Cu distances of 5.01 and 5.78 Å, respectively. Furthermore, twelve Cu^I atoms are linked together by eighteen thiocyanate anions to form a 48-membered macrocyclic ring which stacks along the *c* axis with a distance of 14.9980(22) Å between two adjacent rings and result in a pipeline motif as shown in Figure 6b. Each 48-membered macrocycle is lateral-shared using its double-bridging sides with the circumjacent six macrocycles from different pipelines, which also serve as the border of the central pipe by using their single-bridging sides to make it a closed one. Thus, the combination of the staggered arrangement of pipelines and the lateral-sharing mode among the different pipes make a novel 3D porous framework of complex **5** with large cavities of 13.1848(16) Å in diameters (Figure 6b). The another feature in complex **5** is the protonation of the TPBA-2 ligands occurred along with the reduction of Cu^{II}. Two protonated TPBA-2 ligands stack in pairs occupying the cavitiy between the adjacent macrocyclic rings in the same pipeline (Figure 6c), which is stabilized by the N-H···O hydrogen bond where the N atom is of the protonated pyridine (Table S2, Supporting Information) and strong π···π interactions between the benzene ring planes of the two TPBA-2 ligands with a distance of 3.42 Å (Figure 6d and e). The pairs of TPBA-2 ligands are further stabilized in the cavities by N-H···S hydrogen bonds (Table S2, Supporting Information). The occupation of the protonated ligand pair in the cavitiy may act template effect during the self-assembly of the complex **5**. It is noteworthy that the reactions of TPBA-3 and *N′*,*N″*,*N‴*-tris(pyrid-4-ylmethyl)-1,3,5-benzenetricarboxamide with Cu^{II} salt in the presence of NH_4SCN, were also studied, respectively, but no such result was obtained probably due to the different position of N atom in the pyridine ring. The different structure of complexes **1** and **4** provides a nice example that the reaction method determines the topology and structure of the complexes.

Selective desorption and sorption of THF by complex 1: As discussed above complex **1** has large capsule-like cavity with encapsulation of THF molecules. Further investigations on the desorption and sorption properties of complex **1** were carried out. The TGA data of complex **1** showed that the loss of the uncoordinated solvents occurred from 60 to 190 °C and the desolvated species is stable up to about 250 °C. The results of X-ray powder diffraction (XPRD) analysis (Figure 7) and solid state ^{13}C NMR spectral measurements (Figure 8) showed that complex **1** can selectively desorb and adsorb THF molecules. The XPRD pattern shows that complex **1** lost its crystallinity (Figure 7c) after being heated at 150 °C for 24 h, probably due to the collapse of the layer structure. However, the crystallinity can be recovered upon immersing the desolvated species in THF for one day and as indicated by the XPRD pattern shown in Figure 7d. While in the most cases the reconstruction of the crystallinity occurs with more or less modification, the complete reestablishment of crystallinity is rarely reported.[15] In order to further investigate whether the desolvated species had selectivity for sorption of THF to reconstruct its crystal-

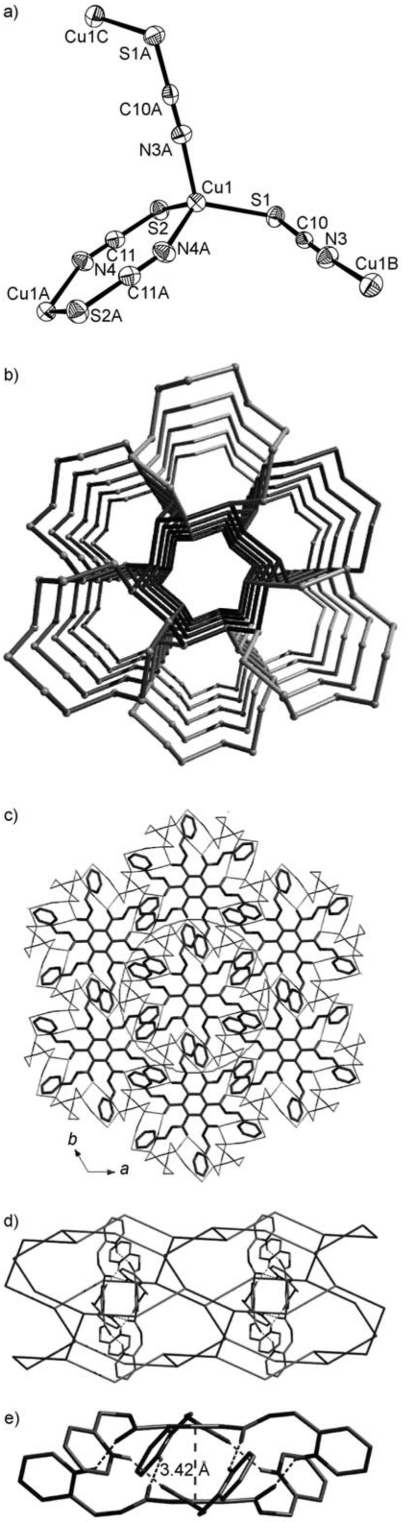


Figure 6. a) ORTEP plot of complex **5** showing coordination environment of Cu^{I} and the thermal ellipsoids were drawn at 30% probability. The uncoordinated TPBA-2 ligands were omitted for clarity. The 3D framework of complex **5** b) the protonated TPBA-2 ligands were omitted to show the empty cavity of **5**, where only the Cu^{I} atoms are presented, c) showing that the protonated TPBA-2 ligand pairs occupying the cavitiy of **5**, d) showing the highlight pipeline part in **5**, where only the Cu^{I} atoms and ligand pairs are presented, and the macrocycles are shown by black while the border by gray. The hydrogen bonds are indicated by dashed lines. e) The ligands pair in complex **5** with distance marked and the hydrogen bonds are shown by dashed lines.

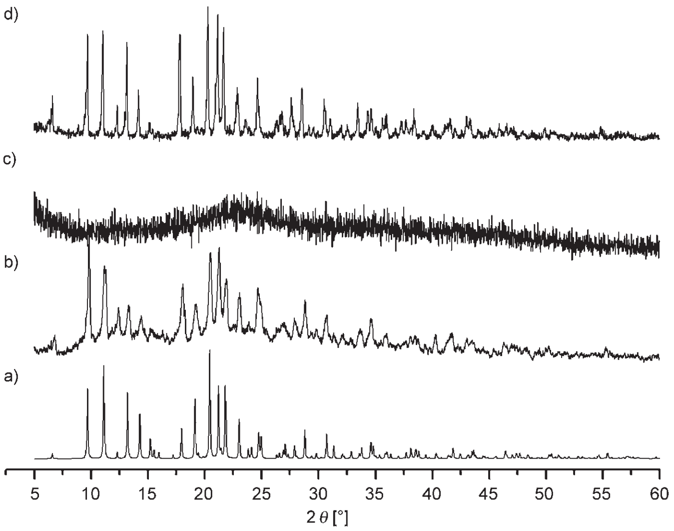


Figure 7. XPRD patterns monitoring the desolvation/resolvation for compound **1**. a) Calculated from single crystal data; b) experimental; c) after the removal of solvent molecules from sample **1**; d) after immersion of the desolvated sample in THF for one day.

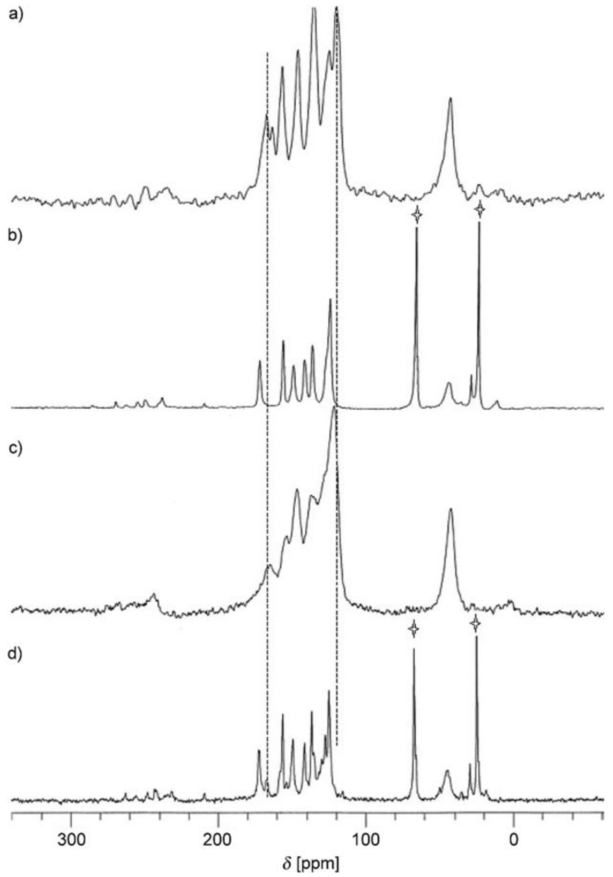


Figure 8. The solid state ^{13}C NMR spectrum of complex **1**. a) Ligand TPBA-2; b) as-synthesized sample; c) desolvated sample; d) re-adsorbed sample.

linity or not, several other solvents including benzene, 1,4-dioxane, 1,3,5-trimethylbenzene, methylbenzene, pyridine, acetone, were tested and no reconstruction its crystallinity was observed after immersing the desolvated samples in such solvents, respectively for even one week, which confirmed that the complex **1** has selectivity for sorption of the THF molecules.

The desorption and sorption was also verified by the solid state ^{13}C NMR spectral measurements. Figure 8 shows the natural abundance solid state ^{13}C NMR spectra of TPBA-2 ligand (Figure 8a) and the samples of complex **1** (as-synthesized, desolvated and re-adsorbed samples in Figure 8b, c and d, respectively). The two signals with star label in Figure 8b are from the guest THF molecules, which disappeared after the removal of the guest THF molecules in complex **1**, and the remaining peaks are highly broadened as shown in Figure 8c, but are much similar to those of TPBA-2 ligand shown in Figure 8a.[16] However, it can be seen from Figure 8d, after immersing the desolvated sample in THF for one day, the re-adsorbed sample has almost identical pattern as that of original sample of **1** shown in Figure 8b. The results of ^{13}C NMR are consistent with those of XPRD analysis. It is considered that the carboxamide group in TPBA-2 may play an important role for the selective sorption of THF through the formation of N-H···O hydrogen bond between the N atoms of the carboxamide groups and the O atoms of THF, which stabilizes the guest molecules in the cavity in complex **1**.

Conclusion

Five new coordination polymers with *N*′,*N*′′,*N*′′′-tris(pyrid-2-ylmethly)-1,3,5-benzenetricarboxamide (TPBA-2) and thiocyanate ligands have been prepared and structurally characterized (Scheme 1). The complexes **1**–**3** were synthesized by layering method and have the same 2D honeycomb framework structure with Kagomé lattice, in which the TPBA-2 ligands adopt *cis*,*cis*,*cis* conformation and thiocyanate anions serve as monodentate terminal ligands rather than bridging ones. Capsule-like motif is formed in **1**–**3**, in which six THF molecules are encapsulated. The selective and reversible desorption/sorption of THF occurring along with the reconstruction of the crystallinity of complex **1** was studied and examined by powder X-ray diffraction pattern and solid state ^{13}C NMR spectroscopy. The compounds **4** and **5** were synthesized by solvothermal method. In **4**, the TPBA-2 ligands adopt *cis*,*trans*,*trans* conformation, and the thiocyanate anions act as end-to-end bridging ligands, which result in a totally different 2D network structure. The 2D layers are further linked to 3D framework by the hydrogen bonds formed between the TPBA-2 and perchlorate anions. Reduction of Cu^{II} to Cu^{I} and protonation of TPBA-2 ligands occurred in the self-assembly of complex **5** under solvothermal conditions. The backbone of **5** is a porous 3D framework accommodating the protonated TPBA-2 ligand pairs which may exert template effect on the self-assembly of **5**. The results show that the reaction conditions have a great influence on the self-assembly process of supramolecular frameworks.

Experimental Section

Materials and measurements: All commercially available chemicals are of reagent grade and used as received without further purification. The ligand TPBA-2 was prepared by the same procedures reported previously for the preparation of TPBA-3.[8a] The C, H, and N microanalyses were carried out on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. Solid state ^{13}C NMR spectra were measured on a JNM-CMX300W spectrometer. Thermogravimetric analyses (TGA) were carried out on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with heating rate of $10\,^{\circ}C\,min^{-1}$ between ambient temperature and 800 °C. Powder X-ray diffraction patterns were recorded on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite monochromatic $Cu_{K\alpha}$ ($\lambda = 1.542$ Å) radiation at room temperature.

$[Cd_3(TPBA\text{-}2)_2(SCN)_6]\cdot 6\,THF\cdot 3\,H_2O$ (1): The compound was prepared by layering method. A buffer layer of a THF/acetone 1:1 solution (5 mL) containing NH_4SCN (7.6 mg, 0.1 mmol) was carefully layered over a solution of TPBA-2 (24.0 mg, 0.05 mmol) in THF (3 mL). Then a solution of $[Cd(ClO_4)_2]\cdot 6\,H_2O$ (20.9 mg, 0.05 mmol) in acetone (3 mL) was layered over the buffer layer. Single crystals appeared after one week in 61 % yield (21.7 mg). Elemental analysis calcd (%) for $C_{84}H_{102}N_{18}O_{15}S_6Cd_3$: C 47.29, H 4.82, N 11.82; found: C 47.21, H 4.84, N 11.81.

$[Cu_3(TPBA\text{-}2)_2(SCN)_6]\cdot 6\,THF\cdot 3\,H_2O$ (2): The complex was prepared by similar method to that used for preparation of complex **1**. A buffer layer of a solution (5 mL) of THF/ethanol 1:1 containing NH_4SCN (7.6 mg, 0.1 mmol) was carefully layered over a solution of TPBA-2 (24.0 mg, 0.05 mmol) in THF (3 mL). Then a solution of $[Cu(ClO_4)_2]\cdot 6\,H_2O$ (18.5 mg, 0.05 mmol) in ethanol (3 mL) was layered over the buffer layer. The crystalline product appeared after one week in 70 % yield (23.2 mg). Elemental analysis calcd (%) for $C_{84}H_{102}N_{18}O_{15}S_6Cu_3$: C 50.78, H 5.18, N 12.69; found: C 50.55, H 5.02, N 12.36.

$[Ni_3(TPBA\text{-}2)_2(SCN)_6]\cdot 6\,THF\cdot 3\,H_2O$ (3): The complex was prepared by the same method used for synthesis of **2** using $[Ni(ClO_4)_2]\cdot 6\,H_2O$ instead of $[Cd(ClO_4)_2]\cdot 6\,H_2O$ in 32 % yield (10.5 mg). Elemental analysis calcd (%) for $C_{84}H_{102}N_{18}O_{15}S_6Ni_3$: C 51.16, H 5.21, N 12.78; found: C 51.06, H 5.05, N 12.82.

$[Cd_2(TPBA\text{-}2)(SCN)_3]ClO_4$ (4): The complex was prepared by solvothermal method. A mixture of $[Cd(ClO_4)_2]\cdot 6\,H_2O$ (21.0 mg, 0.05 mmol), TPBA-2 (24.0 mg, 0.05 mmol), NH_4SCN (7.6 mg, 0.1 mmol), and ethanol (10 mL) was heated in a 20 mL stainless steel reactor with a Teflon liner at 80 °C for 3 d. The colorless crystalline product was filtered and washed with ethanol in 57 % yield (14.0 mg). Elemental analysis calcd (%) for $C_{30}H_{24}N_9O_7S_3Cl_1Cd_2$: C 36.80, H 2.47, N 12.88; found: C 36.79, H 2.53, N 12.68.

$[Cu_3^{I}(SCN)_6](H_3TPBA\text{-}2)$ (5): The complex was synthesized by the same method used for preparation of **4** except that $[Cd(ClO_4)_2]\cdot 6\,H_2O$ was replaced by $[Cu(ClO_4)_2]\cdot 6\,H_2O$. The yellow crystalline product was filtered and washed with ethanol in 40 % yield (6.8 mg). Elemental analysis calcd (%) for $C_{33}H_{27}Cu_3N_{12}O_3S_6$: C 38.76, H 2.66, N 16.44; found: C 38.58, H 2.52, N 16.50.

CAUTION: *Perchlorate salts of metal complex with organic ligands are potentially explosive and should be handled with care.*

X-ray crystallography: Colorless single crystal of **1** was mounted and data collection was carried out on a Rigaku Saturn diffractometer at 173 K, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), while the data collections for complexes **4** and **5** were made on a Bruker Smart Apex CCD with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods using SHELX-97[17] and refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms except for the perchlorate anions in complex **4**. Calculations were performed on a personal computer with the

Siemens SHELXTL program package.[18] In complex **1**, the THF molecules are disordered: the atoms C11, C12, C13, C14 of THF are disordered into two positions with site occupancy factors of 0.519(12) and 0.481(12), respectively. In complex **4**, two O atoms of the perchlorate anions (O6 and O7) are disordered into two positions with site occupancy factors of 0.381(18) and 0.619(18), respectively.

Single crystals of **2**, **3** were mounted and data collections were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å). The structures were solved by direct method using SHELX-97[17] and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms except for those of water molecules were generated geometrically. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package of the Molecular Structure Corporation.[19] In complexes **2** and **3**, the THF molecules are disordered: the atoms C21, C22, C23, C24 of THF are disordered into two positions with site occupancy factors of 0.618(18), 0.382(18) for **2** and 0.588(13), 0.412(13) for **3**, respectively. The details of the crystal parameters, data collection and refinement for the compounds are summarized in Table 1. The selected bond lengths and angels with their estimated standard deviations and the hydrogen bonds data are listed in Table S1 and Table S2, respectively, which can be obtained in the Supporting Information.

CCDC-634757 to -634761 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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