

Metal-organic frameworks derived from divalent metals and 4-(1H-1,2,4-triazol-1-yl)benzoic acid

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Received 24 March 2012; revised 25 April 2012; accepted 13 May 2012

ABSTRACT

Two inorganic-organic coordination polymers, $[\text{Cd}(\text{TBA})_2] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{TBA})_2] \cdot 2\text{H}_2\text{O}$ (**2**) have been synthesized by reaction of the metal ions of Cd(II) and Cu(II) with the ligand HTBA [HTBA = 4-(1H-1,2,4-triazol-1-yl)benzoic acid] under solvothermal condition. The compounds were characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy, X-ray powder diffraction (XRPD), and thermo gravimetric analysis (TGA). The structural analyses reveal the two independent polymers exhibit different structures. Complex **1** exhibits a 3D framework with 1D channels, and complex **2** shows a 2-fold interpenetrating 3D diamond net.

Keywords: Coordination Polymers; 4-(1H-1,2,4-triazol-1-yl)benzoic Acid; Crystal Structure; Cadmium; Copper

1. INTRODUCTION

The reticular design and synthesis of metal-organic frameworks (MOFs) are currently the hot topic for discovery of the materials with potential applications in magnetism [1-6], catalysis [7-10], luminescence and chemical sensing [11-15], as well as gas adsorption and/or separation [16-18]. However, any of a successful construction of the target MOFs shall practically depend on a deliberate design or a judicious selection of the organic ligand incorporating with a proper geometrical metal. For example, the MOFs with zeolitic or zeolite-like structures are constructed by using imidazole and its derivatives incorporating with tetrahedral coordinated metals [19-20]. To create novel MOFs having the 4-connected zeolitic structures, the MOFs based on imidazole derivative of 4-(1H-imidazol-1-yl)benzoic acid (HIBA) and divalent six-coordinated metals have been reported in our previous work [21,22], where the ligand presents two ((2.21)_{syn-syn}

and (2.11)_{syn}) of the several probable coordination models (**Scheme 1**).

The ligand of 4-(1H-1,2,4-triazol-1-yl)benzoic acid (HTBA) is structurally similar to HIBA and can be facilely prepared by the following procedure: So far we know that the use of 4-(1H-1,2,4-triazol-1-yl)benzoic acid (HTBA) to construct a coordination polymer remains still unexplored until this work. Compared with the ligand of HIBA, HTBA shows only small structural difference with one carbon being replaced by a nitrogen atom. Thus, HTBA shall also form the various probable coordination modes shown in **Scheme 1**. By virtue of this consideration, novel MOF structures of HTBA ligand were expected. In our current work, we successfully obtained two novel 3D coordination polymers formulated as $[\text{Cd}(\text{TBA})_2] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{TBA})_2] \cdot 2\text{H}_2\text{O}$ (**2**), which are characterized by X-ray single crystal analysis, elemental analysis, IR spectroscopy, X-ray powder diffraction (XRPD), and thermo gravimetric analysis (TGA).

2. EXPERIMENTAL SECTION

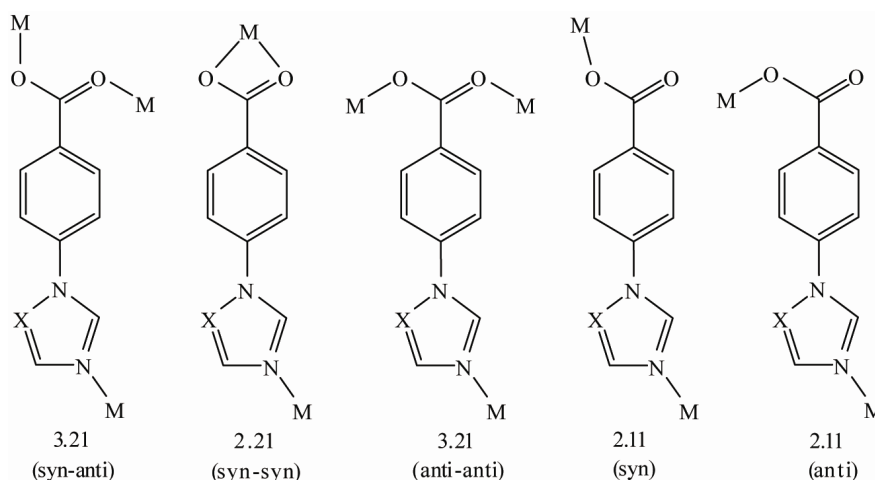
2.1. Materials and Methods

All chemicals and solvents used in the syntheses were commercially available and used without further purification. The elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer. The IR spectra were recorded (400 - 4000 cm^{-1}) on a FT-IR spectrometer Bruker TENSOR 27. X-ray powder diffraction (XRPD) analyses were carried out on a Bruker D8 Advance and thermal gravimetric analyses (TGA) was performed under static air atmosphere with a heating rate of 10°C/min by using a Perkin-Elmer Diamond thermo gravimetric analyzer.

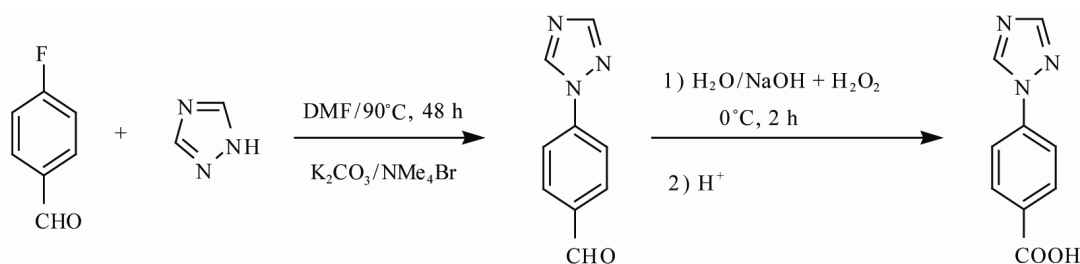
2.2. X-Ray Single-Crystal Structure Determination

Suitable single crystals of two complexes **1** and **2** were mounted on glass fibers for X-ray measurement. Crys-

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Scheme 1. The probable coordination modes of ligand (X=C or N atom).



Scheme 2. Synthesis pathway of the ligand.

tallographic measurements for **1** & **2** were carried out on a Bruker SMART-Apex-II CCD diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 293(2) K. All absorption corrections were performed using the SADABS program [23]. Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of carbon atoms were fixed at calculated positions with isotropic thermal parameters, while the free lattice water molecules were located by difference Fourier maps. All calculations were performed using the SHELX-97 program [24]. However, hydrogen atoms on O1W and O2W in **1** are refined isotropically and hydrogen atom of O1W, O2W in **2** could not be located. Crystal data and details of the data collection and the structure refinement are given in **Table 1**. The selected bond lengths and bond angles of complexes **1** and **2** are listed in **Table 2**.

2.3. Synthesis of the Organic Ligands

4-(1H-1,2,4-triazol-1-yl)-benzaldehyde: a mixture of 4-fluorobenzaldehyde (5.58 g, 45 mmol), 1,2,4-triazol (2.05 g, 30 mmol), anhydrous K₂CO₃ (4.14 g, 30 mmol) and tetramethylammonium bromide (0.159 g, 0.6 mmol) in anhydrous DMF (50 mL) was stirred under nitrogen atmosphere at 90°C for 48 h. After the reaction was completed, the solvent was removed by vacuum distillation.

Then, ice water was added into the residue and the white needle product was obtained by filtration. Yield: 4.2 g (96%).

4-(1H-1,2,4-triazol-1-yl)benzoic acid (HTBA): 4-(1H-1,2,4-triazol-1-yl)-benzaldehyde (3.46 g, 20 mmol) and 0.8 g NaOH (10 mmol) were placed in a 200 mL flask, stirred at 0°C, then 30% H₂O₂ was added dropwisely. After the mixture was stirred at 0°C for 2 h and refluxed for 12 h, it was filtrated. The filtrate was then adjusted to pH 6.0 with dilute hydrochloric acid to obtain solid product. The product was washed with water and dried to obtain a white solid of 4-(1H-1,2,4-triazol-1-yl)benzoic acid (**Scheme 2**). Yield: 3.02 g (80%).

2.4. Synthesis of the Two Complexes

[Cd(TBA)₂] \cdot 3H₂O (**1**): 0.0410 g (0.2 mmol) of HTBA was dissolved in 7 mL of DMF, and 0.0308 g (0.1 mmol) of Cd(NO₃)₂ \cdot 4H₂O was added and stirred at room temperature for 1 h. The reaction mixture was sealed in a 25 mL Teflon-lined stainless autoclave, heated at 120°C under autogenous pressure for 48 h, and then slowly cooled down to room temperature. The colorless block crystals formed were collected, washed with ethanol, and dried at room temperature; Yield, 0.0195 g; 36% (based on Cd). Formula of the compound (molecular mass): C 40.95 (calc. 41.88); H 3.45 (3.49); N 15.44 (16.29)%.

Table 1. Crystallographic data for complexes **1** and **2**.

Complex	1	2
Formula	C ₁₈ H ₁₈ CdN ₆ O ₇	C ₁₈ H ₁₆ CuN ₆ O ₆
<i>M</i> (g·mol ⁻¹)	515.76	475.91
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pnna</i>
<i>a</i> (Å)	15.629(3)	13.063(2)
<i>b</i> (Å)	15.991(3)	9.9017(18)
<i>c</i> (Å)	9.2343(19)	17.472(3)
α (deg)	90	90
β (deg)	102.774(2)	90
γ (deg)	90	90
<i>V</i> (Å ³)	2250.6(8)	2260.0(7)
<i>Z</i>	4	4
<i>D</i> _{calc} (Mg/m ³)	1.602	1.399
Temperature (K)	293(2)	293(2)
Crystal size (mm)	0.53 × 0.35 × 0.21	0.56 × 0.32 × 0.20
<i>F</i> (000)	1088	972
μ (Mo-K α)/mm ⁻¹	1.021	1.011
Theta range for data collection (deg)	2.55 - 25.00	1.95 - 26.00
Reflections collected	5526	9407
Independent reflections	1980	2231
Parameters	151	140
$\Delta(\rho)$ (e·Å ⁻³)	0.825 and -0.266	0.796 and -0.419
Goodness of fit	1.037	1.130
Final R indices [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	R1 = 0.0335, wR2 = 0.1047	R1 = 0.0707, wR2 = 0.2010
R indices (all data) ^[b]	R1 = 0.0420, wR2 = 0.1114	R1 = 0.1269, wR2 = 0.2413

^a[a] $R = \sum \|F_o| - |F_c|\| / \sum |F_o|$, $wR_2 = \sum w(F_o^2 - F_c^2)^2 / \sum (w(F_o^2)^2)^{1/2}$; [*F*_o > 4 σ (*F*_o)]; [b] Based on all data.

IR spectrum (KBr, cm⁻¹): 3415(s), 3117(s), 1602(s), 1535(vs), 1381(vs), 1278(w), 1148(w), 974(w), 787(m). (see **Figure S5** in supporting information).

[Cu(TBA)₂]₂·2H₂O (**2**): 0.0410 g (0.2 mmol) of HTBA was dissolved in 7 mL of DMF, and 0.02625 g (0.1 mmol) of Cu(ClO₄)₂·6H₂O was added and stirred at room temperature for 1 h. The reaction mixture was sealed in a 25 mL Teflon-lined stainless autoclave, heated at 100°C for 48 h under autogenous pressure, and slowly cooled to room temperature. The blue block crystals formed were collected, washed with ethanol, and dried at room temperature; Yield, 0.0216 g; 43.7% (based on Cu). Formula of the compound (molecular mass): C 45.64 (calc.45.39); H 3.71 (3.36); N 16.91 (17.65)%.

IR spectrum (KBr, cm⁻¹): 3428(m), 3098(m), 1673(m), 1609(s), 1552(vs), 1393(vs), 1281(m), 980(m), 850(m), 779(m), 669(w) (see **Figure S6** in supporting information).

3. RESULTS AND DISCUSSION

3.1. Synthesis of the Compounds of **1** and **2**

The two compounds were prepared under solvothermal conditions in DMF. The metal ions employed in the synthesis are divalent six-coordinated transition metal cations because we hope that they can incorporate with the ligands of HTBA just as with the ligand of HIBA to form the neutral four-connected frameworks. So far, only two MOFs of **1** and **2**, representing two different structural types, have been obtained by reaction of Cd(II) and Cu(II) with the ligand of HTBA. Their crystal structures are determined and their X-ray powder diffraction patterns on the bulk samples were experimentally obtained that were in agreement with those simulated from their X-ray single-crystal data, revealing that the structures of the single crystal **1** and **2** represent those of the bulk samples.

However, the other Cd and Cu group compounds

failed to obtain, such as Zn and Ag.

3.2. Structural Description of Complexes 1 and 2

The complex **1** crystallizes in monoclinic, space group C2/c. The asymmetry unit of **1** contains half a cadmium ion, one TBA[−] ligand and one highly disordered lattice

water molecule. The coordination environment of the cadmium ion (Cd) is depicted in **Figure 1**. In the structure of **1**, each of the metal Cd(II) ion is six-coordinated by two nitrogen atoms (N1 and N1#3) from two different TBA[−] ligands and four carboxylate oxygen atoms (O1#4, O1#5, O2#1, O2#2) from another four different TBA[−]

Table 2. Selected bond distances (Å) and angles (deg) of complexes **1** and **2**.

Complex 1					
Cd-O2 ^{#1}	2.303(3)	Cd-O2 ^{#2}	2.303(3)	Cd-N1 ^{#3}	2.342(3)
Cd-N1	2.342(3)	Cd-O1 ^{#4}	2.343(2)	Cd-O1 ^{#5}	2.343(2)
O2 ^{#1} -Cd-O2 ^{#2}	180.00(15)	O2 ^{#1} -Cd-N1 ^{#3}	89.39(9)	O2 ^{#2} -Cd-N1 ^{#3}	90.61(9)
O2 ^{#1} -Cd-N1	90.61(9)	O2 ^{#2} -Cd-N1	89.39(9)	N1 ^{#3} -Cd-N1	180.00(16)
O2 ^{#1} -Cd-O1 ^{#4}	97.23(11)	O2 ^{#2} -Cd-O1 ^{#4}	82.77(11)	N1 ^{#3} -Cd-O1 ^{#4}	101.13(9)
N1-Cd-O1 ^{#4}	78.87(9)	O2 ^{#1} -Cd-O1 ^{#5}	82.77(11)	O2 ^{#2} -Cd-O1 ^{#5}	97.23(11)
N1 ^{#3} -Cd-O1 ^{#5}	78.87(9)	N1-Cd-O1 ^{#5}	101.13(9)	O1 ^{#4} -Cd-O1 ^{#5}	180.00(15)
Complex 2					
Cu-O1 ^{#1}	1.975(4)	Cu-O1 ^{#2}	1.975(4)	Cu-N1 ^{#3}	1.994(5)
Cu-N1	1.994(5)				
O1 ^{#1} -Cu-O1 ^{#2}	90.6(3)	O1 ^{#1} -Cu-N1 ^{#3}	165.53(19)	O1 ^{#2} -Cu-N1 ^{#3}	89.3(2)
O1 ^{#1} -Cu-N1	89.3(2)	O1 ^{#2} -Cu-N1	165.53(19)	N1 ^{#3} -Cu-N1	94.3(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2, -y + 3/2, -z + 2$; #2 $x - 1/2, y + 1/2, z$; #3 $-x + 1, -y + 2, -z + 2$; #4 $-x + 3/2, y + 1/2, -z + 3/2$; #5 $x - 1/2, -y + 3/2, z + 1/2$ for complex 1; #1 $x - 1/2, -y + 1/2, z + 1/2$; #2 $-x, y + 1/2, z + 1/2$; #3 $-x - 1/2, -y + 1, z$ for complex 2.

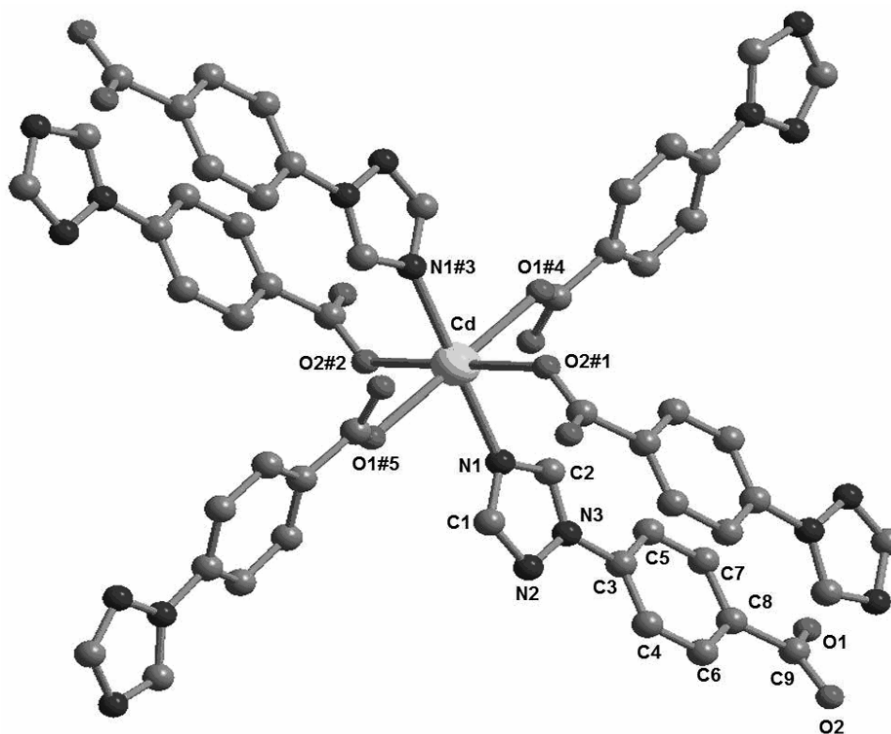


Figure 1. The coordination environment of Cd(II) in complex **1** (The lattice water molecules and hydrogen atoms have been omitted for clarity. Symmetry codes: #1 $-x + 3/2, -y + 3/2, -z + 2$; #2 $x - 1/2, y + 1/2, z$; #3 $-x + 1, -y + 2, -z + 2$; #4 $-x + 3/2, y + 1/2, -z + 3/2$; #5 $x - 1/2, -y + 3/2, z + 1/2$).

ligands; Each TBA^- ligand shows a dihedral angle of 16.8° between triazole and benzoyl rings and bridges three Cd(II) ions, adopting the $(3.21)_{\text{syn-anti}}$ coordination mode (**Scheme 1**). Therefore, all the metal ions in the structure exhibit distorted octahedral coordination geometry with the equatorial positions occupied by the carboxylate oxygens donors and the apical positions taken up by the nitrogen atoms.

The N-Cd-O angles slightly deviate from 90° , revealing the nearly regular octahedron with the equatorial Cd-O distances ranging from 2.303(3) to 2.343(2) Å and the two apical Cd-N distances are identical of 2.343(3) Å. The Cd-N and Cd-O bond distances are similar to that observed in other Cd(II) octahedral coordination polymer [25].

In order to understand the structure thoroughly, the coordinate relationship between the metals and the ligands of complex **1** are analyzed further as follows: We regard that the structure are composed of Cd(II) chains, which are bridged by carboxylate groups of TBA^- ligands along [001] direction ($\text{Cd}\cdots\text{Cd}$ distance of 4.617(1) Å

(**Figure 2(b)**). And then, these chains are linked by the connected six-five-rings of TBA^- ligands into a 3D network with 1D channels. ($\text{Cd}\cdots\text{Cd}$ contact of 12.738(6) Å, Cd-Cd-Cd angle of $102.24(0)^\circ$ and $77.76(0)^\circ$ respectively) (**Figures 2(a), (c)**).

The complex **2** crystallizes in orthorhombic, space group Pnna . The asymmetric unit of complex **2** consists of half a copper atom, one TBA^- ligand and a free water molecule. In the structure of complex **2**, each of Cu(II) ions is six-coordinated by four oxygen atoms and two nitrogen atoms from four different TBA^- ligands. Due to Jahn-Teller effect, the Cu(II) ions display a distorted octahedral coordination geometry (**Figure 3**) with Cu-O1 bond distance of 1.975(4) Å, Cu-O2 bond distance of 2.516(0) Å and Cu-N bond distance of 1.994(5) Å, which are close to those reported in literature [21,22]. Each TBA^- ligand in complex **2** links two Cu(II) and shows dihedral angle of 18.7° between triazole and phenyl rings, adopting $(2.11)_{\text{syn}}$ coordination mode (**Scheme 1**).

Thus, each metal center is coordinated by four TBA^- ligands and each ligand in turn links two Cu(II) ions,

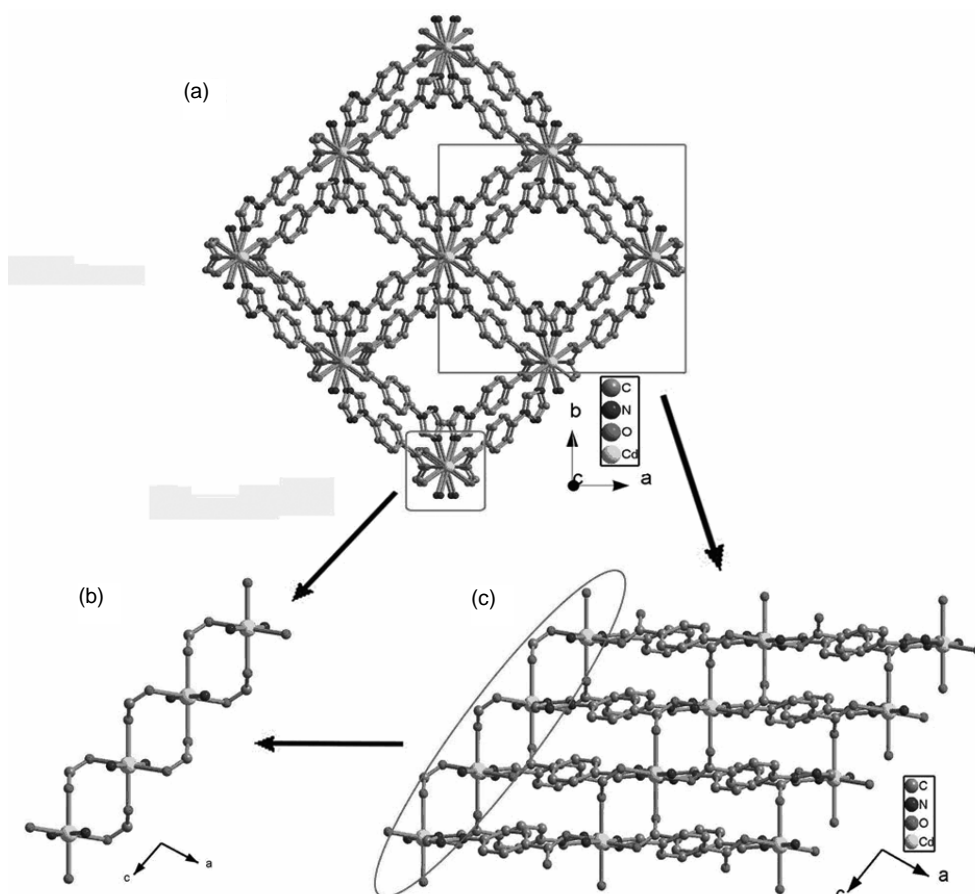


Figure 2. The framework structure of complex **1**: (a) View the whole structure along [001] to show the 1D channels; (b) The Cd(II) chains bridged by carboxylate groups oriented along [010]; (c) View the whole structure along [010] to show the connectivity of the chains with the six-five-rings of the TBA^- ligands.

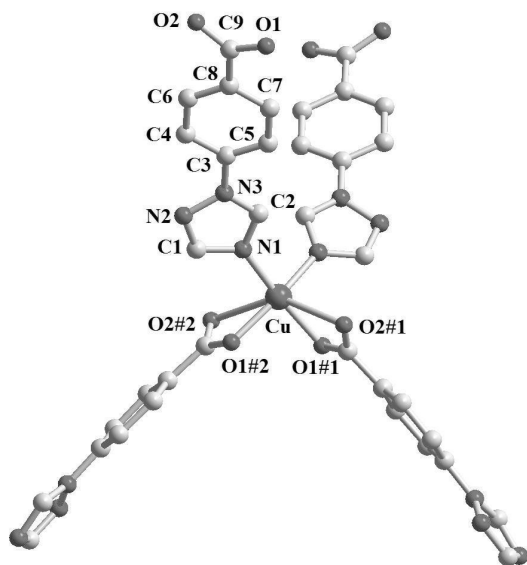


Figure 3. The coordination environment of the Cu(II) in complex **2** (The lattice water molecules and hydrogen atoms have been omitted for clarity. Symmetry codes: #1 $x - 1/2, -y + 1/2, z + 1/2$; #2 $-x, y + 1/2, z + 1/2$; #3 $-x - 1/2, -y + 1, z$ for 2).

which shows a 4-connected net with diamondoid structure with the adjacent $\text{Cu} \cdots \text{Cu}$ distance of 11.979(1) Å and the Cu-Cu-Cu angles ranging from 86.35° to 131.18°, deviating significantly from the standard value of 109.5° for diamond network (**Figure 4(a)**). Two set of such nets interpenetrate and form the structures of compound **2** (**Figure 4(b)**), which show 1D channels of 6.0×3.0 Å window (Van der Waals radii was considered) (**Figure 4(c)**).

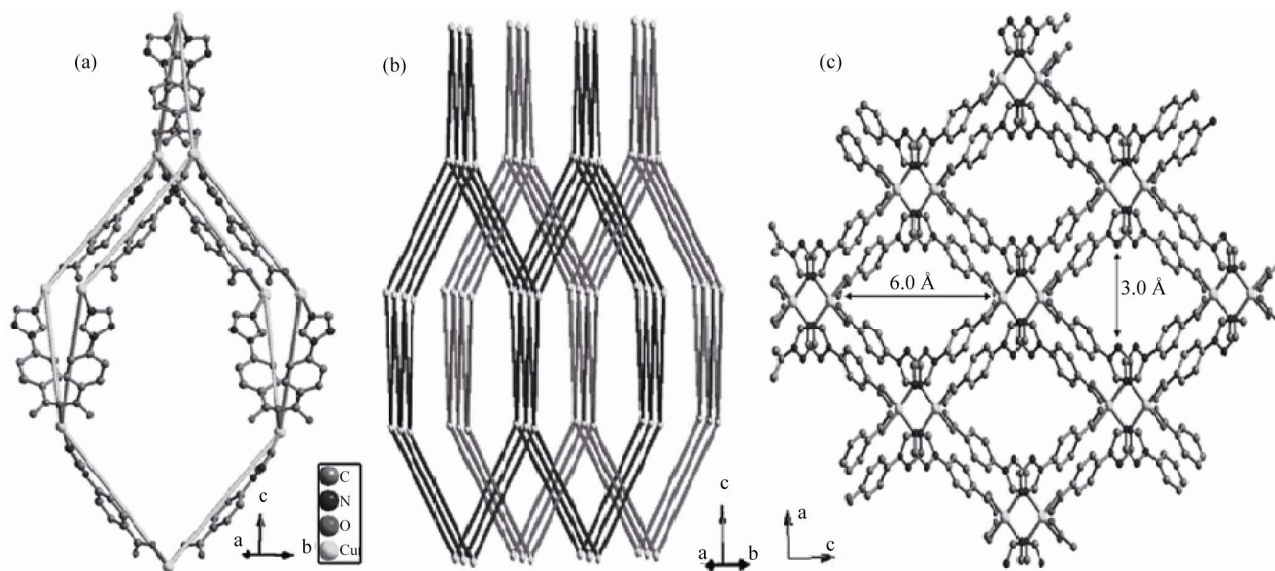


Figure 4. The structure of compound **2**: (a) A diamondane unit of the diamond network; (b) The ball-and-stick diagram to display the 2-fold interpenetrating diamondoid net (balls: metals, sticks: TBA^- ligands); (c) View the structure along [010] to show the 1D channels.

3.3. Thermogravimetric and X-Ray Powder Diffraction Analysis

Thermo gravimetric analysis (TGA) was carried out for investigating the thermal stabilities of the coordination polymers. TGA curve of complex **1** exhibits three main steps of weight losses (see **Figure S1** in supporting information). The first weight loss starts at 42°C and completes at 175°C, which corresponds to the release of three free water molecule per molecule of complex. The observed weight loss of 9.7% is close to the calculated value (9.9%). The second weight loss region occurs in the range of 175°C - 430°C. The weight loss is about 33.5% that is corresponding to the decomposition of the framework into CdCO_3 and TBA^- ligands (calculated 31.77%). The third weight loss region occurs in the range of 520°C - 630°C. The weight loss is about 33.5% that is corresponding to the complete decomposition of the TBA^- ligands and CdCO_3 . The final residue is CdO because the TGA curve does not change with the temperature increase above 630°C (34.67%).

The TGA data of complex **2** indicates three steps of weight lost (See **Figure S2** in supporting information). It firstly loses one and a half of crystalline water molecules and two free water molecule per molecule of complex, the in the temperature range of 50°C - 190°C (observed 15.2%); Then, the second weight loss occurs at the range of 248°C - 300°C. The weight loss is about 14.65% that is corresponding to the decomposition of the framework 480°C. The weight loss is about 54.5% that is corresponding to the complete decomposition of the TBA^- ligands and CuCO_3 . The final residue is CuO because the

into CuCO_3 and TBA^- ligands (calculated 14.58%). The third weight loss region occurs in the range of 350°C —TGA curve does not change with the temperature increase above 480°C (56.67%).

The Powder X-ray diffraction (PXRD) was used to confirm the phase purity of the bulk samples of complexes **1** and **2** (see **Figures S3** and **S4** in the supporting information). All the peaks presented in the measured patterns closely match with the simulated patterns generated from single crystal diffraction data.

4. CONCLUSIONS

In conclusion, by use of 4-(1H-1,2,4-triazol-1-yl) benzoic acid (HTBA), two novel 3D coordination polymers of $[\text{Cd}(\text{TBA})_2] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{TBA})_2] \cdot 2\text{H}_2\text{O}$ (**2**) have been successfully synthesized for the first time under solvothermal conditions. The TBA^- ligand exhibits two different coordination modes in the two compounds. Compound **1** has a tubular net consisting of metal-carboxylate chains linked by TBA^- ligands, which presents $(3.21)_{\text{syn-anti}}$ coordination mode that was not seen in the MOFs constructed by HIBA. Compound **2** demonstrates a 4-connected diamond net of 2-fold interpenetrating structure where the metals serve as the nodes and the TBA^- as linkers, which demonstrates $(2.11)_{\text{syn}}$ coordination mode that also exists in the MOF constructed by HIBA, but with a two dimensional (4, 4)-network [21,22]. Compared with the numbers of the MOFs constructed by the ligand HIBA, why only two of MOFs could have been produced for the ligand of HTBA is till an open question.

5. SUPPORTING INFORMATION AVAILABLE

TGA, XRD, IR and CIF files for compounds **1** and **2** are available on the <http://www.scirp.org/journal/ojic> or from the author. The atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. CCDC Nos. 859904 (**1**) and 859905 (**2**) contain the supplementary crystallographic data for **1** - **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; E-mail: deposit@ccdc.cam.ac.uk).

6. ACKNOWLEDGEMENTS

We are thankful for financial support from the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (FANEDD)

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Supporting Information

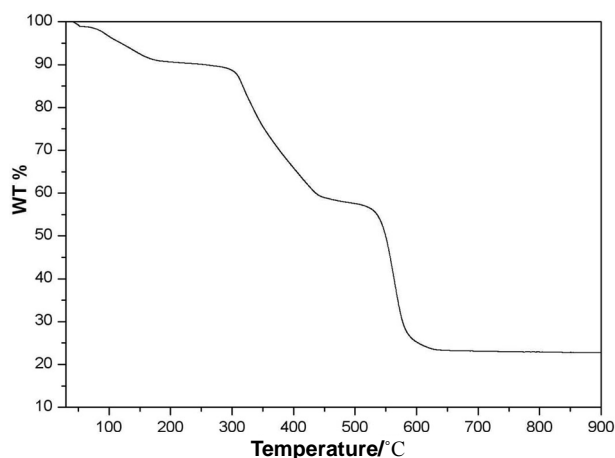


Figure S1. Thermogravimetric analysis curve of compound **1**.

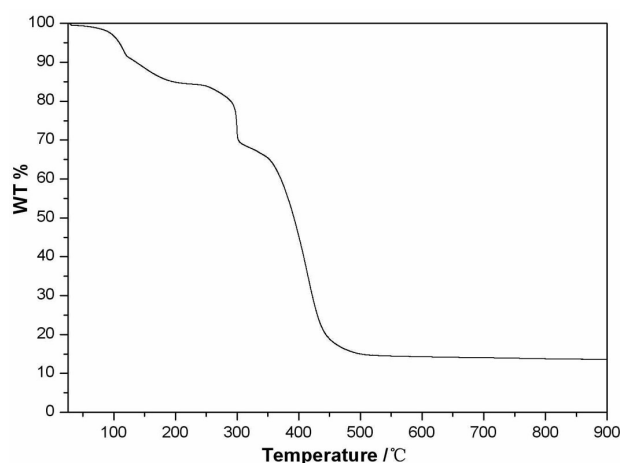


Figure S2. Thermogravimetric analysis curve of compound **2**.

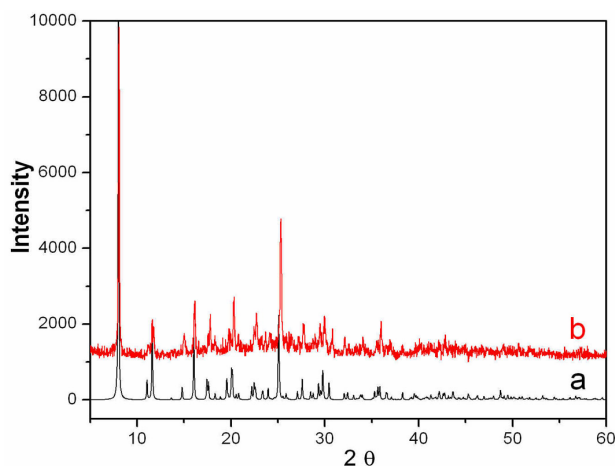


Figure S3. XRD powder patterns: (a) The simulated XPRD pattern calculated from single-crystal structure of complex **1**; (b) Experimental XPRD for complex **1**.

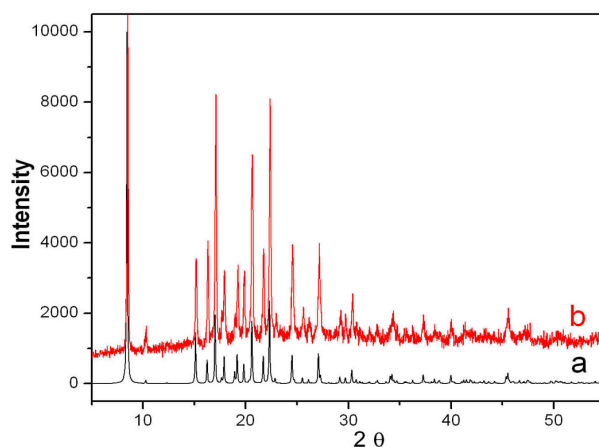


Figure S4. XRD powder patterns: (a) The simulated XPRD pattern calculated from single-crystal structure of complex **2**; (b) Experimental XPRD for complex **2**.

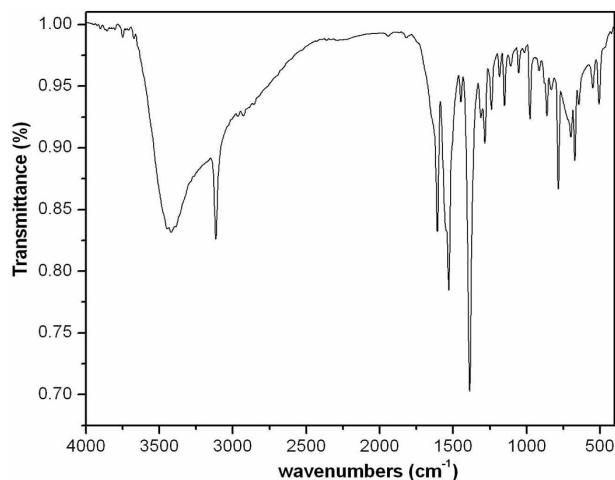


Figure S5. The infrared spectra for as-synthesized **1**.

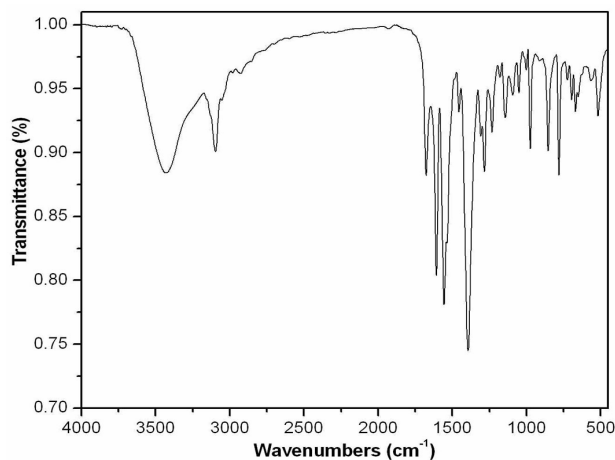


Figure S6. The infrared spectra for as-synthesized **2**.