

# 1*H*-3-(3-吡啶基)-5-(3'-吡啶基)-1,2,4-三唑的钴(II)配合物的合成、晶体结构、热稳定性及配体的 DFT 计算

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**摘要:** 合成了一个多功能的配体 1*H*-3-(3-吡啶基)-5-(3'-吡啶基)-1,2,4-三唑(3,3'-Hbpt, **1**)并得到了配体的晶体结构, 运用 DFT 理论计算了配体的最优构型、优势构象和电荷分布。在此基础上, 水热合成了一个配位化合物: [Co(3,3'-Hbpt)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·(ad)·6H<sub>2</sub>O(**2**) (ad=己二酸), 结构分析表明配合物 **2** 是零维单核化合物, 它的三维超分子结构是由分子间氢键连接而成, 其中包含着由游离的己二酸分子填充的矩形孔道。值得注意的是, 配体在配合物中的几何结构和构象与理论计算的结果一致。另外, 利用热重分析研究了配合物 **2** 的热稳定性。

**关键词:** 1*H*-3-(3-吡啶基)-5-(3'-吡啶基)-1,2,4-三唑; 理论计算; 配位化合物; 晶体结构; 热稳定性

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## A Cobalt(II) Coordination Compound with 1*H*-3-(3-Pyridyl)-5-(3'-pyridyl)-1,2,4-triazole: Synthesis, Crystal Structure, Thermostability and DFT Calculation of Ligand

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**Abstract:** Based on the versatile ligand 1*H*-3-(3-pyridyl)-5-(3'-pyridyl)-1,2,4-triazole (3,3'-Hbpt, **1**), a coordination polymer, [Co(3,3'-Hbpt)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·(ad)·6H<sub>2</sub>O (**2**), has been hydrothermally isolated (ad=adipate). The crystal structure of ligand has been investigated. Density functional theory (DFT) is employed to explicate the optimized geometry, preferred conformation and electronic properties of 3,3'-Hbpt ligand. Structural analysis reveals that compound **2** is a zero-dimensional mononuclear molecule, and the 3D supramolecular network is constructed through hydrogen-bonding interactions, in which the rectangular channels are filled by free adipate anions. Notably, the geometry and conformation of the ligand in compound **2** are corresponding with the calculated results. In addition, thermostability of compound **2** is investigated by TG. CCDC: 1028283, **1**; 1002548, **2**.

**Key words:** 1*H*-3-(3-pyridyl)-5-(3'-pyridyl)-1,2,4-triazole; theoretical calculation; coordination compound; crystal structure; thermostability

## 0 Introduction

The design and construction of coordination polymers (CPs) are of great interest in the field of

crystal engineering, for their intriguing variety of architectures and tremendous potential applications in non-linear optics, catalysis, gas absorption, luminescence, magnetism and medicine<sup>[1-5]</sup>. However, it

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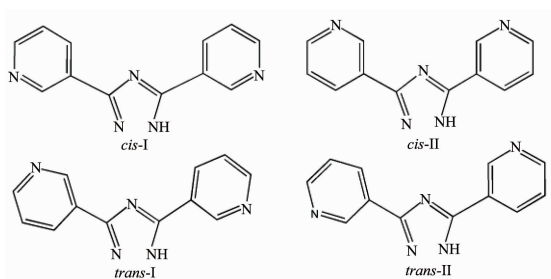
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is still a great challenge to rationally predict and control their exact structures of CPs because the structural natures are diverse depending on various factors such as the metal ions, pH values, solvents, the ligands and/or co-ligands, synthetic methods, etc<sup>[6-12]</sup>. Selecting appropriate organic ligands to construct expected CPs is still a committed step with a long-term issue in the field of coordination chemistry<sup>[13-20]</sup>. As we all known, pyridine-based triazole ligands have been proved as a type of excellent connector to engender a wide range of CPs resulting from the several advantages below: (i) The abundant nitrogen electron-donating atoms in the molecule could selectively coordinate to metal ions, facilitating the generation of CPs<sup>[21]</sup>. (ii) The ligand indicates various coordination fashions, such as multidentate or bridging building modes, offering the possibility to obtain the fascinating CPs<sup>[22-25]</sup>. In this work, we adopt 1*H*-3-(3-

pyridyl)-5-(3'-pyridyl)-1,2,4-triazole (3,3'-Hbpt) as ligand to assemble the target supramolecular architectures.

One thing to note is that 3,3'-Hbpt has potential tendency to show four typical conformations under different surroundings (Scheme 1). Therefore, it is an efficient strategy to conduct research on the reaction systems in the basic of the combination of theory and experiment, which is conducive to forming the structural model and revealing the preferred geometry, and even estimating the coordination mode of the compounds, especially in the application of non-metal organic compounds<sup>[26-27]</sup>. Whats more, it has long been a target for scientists to control the reaction conditions and use theoretical calculations to guide and verify experimental results<sup>[28-32]</sup>. It is tantalizing to introduce the theoretical calculation into the investigation of CPs.



Scheme 1 Four typical conformations of 3,3'-Hbpt

Based on the considerations above, we have synthesized the 3,3'-Hbpt·2H<sub>2</sub>O (**1**) ligand of which the crystal structure is determined and the optimized structure and preferred conformation are inferred by using DFT method<sup>[33]</sup>. Then, a coordination compound, namely [Co(3,3'-Hbpt)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](ad)·6H<sub>2</sub>O (ad= adipate) (**2**), has been obtained under hydrothermal condition and structurally characterized in detail, in which the structure and conformation of the ligand are comparable with the calculated results. The thermo stability of **2** is tested and discussed as well.

## 1 Experimental

### 1.1 Materials

Commercially available reagents were used as received without further purification. <sup>1</sup>H NMR spectra

were taken with a Varian 400 spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses (C, H and N) were performed on a Vario EL III analyzer. Infrared spectra were obtained from KBr pellets on a BEQ VZNDX 550 FTIR instrument within the 400~4 000 cm<sup>-1</sup> region. Thermal analysis was performed on Netzsch STA 449C microanalyzer under flowing N<sub>2</sub> atmosphere at a heating rate of 10 °C·min<sup>-1</sup>. X-ray powder diffractometer were received on a Bruker Advanced-D8 instrument at room temperature. The calculations have been carried out using Gaussian03 program<sup>[34]</sup>, at the B3LYP<sup>[35-36]</sup> level of theory with 6-31G(d, p) basis set.

### 1.2 Synthesis of 3, 3'-Hbpt·2H<sub>2</sub>O (**1**)

3,3'-Hbpt·2H<sub>2</sub>O was synthesized through advan-

ced methods reported<sup>[37]</sup>. A mixture of magnesium (0.6 g) and iodine (0.2 g) in methanol (110 mL) was refluxed for 0.5 h to prepare dry methanol (50 mL). Later a mixture of sodium (0.1 g) and 3-cyanopyridine (2.1 g) was added with stirring for 1 h, then 3-pyridyl carbonyl hydrazide (2.1 g) was added followed by glacial acetic acid (0.1 g). The resulting yellow precipitate was filtered off and washed thoroughly with boiling ethanol. Drying *in vacuo* gave 1.8 g (75%) of analytically pure 3,3'-Hbpt as a white powder. The product (10 mmol) was dissolved in the mixed solution of H<sub>2</sub>O (2 mL) and MeOH (20 mL), and the resulting solution was placed in a silicagel desiccator at room temperature for several weeks to give colorless crystals as compound **1**. Anal. Calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub> (%): C, 55.54; H, 5.01; N, 27.01. Found (%): C, 55.69; H, 5.10; N, 27.08. m.p.: 509~510 K; IR (cm<sup>-1</sup>, KBr): 3 327(s), 3 156(s), 3 048(m), 2 843(m), 1 620(s), 1 594(s), 1 482(w), 1 406(s), 1 308(s), 1 196(w), 1 051(m), 821(m), 709(m), 625(w). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 7.534~7.552 (2H, m), 8.408~8.427 (2H, d, *J*=7.6 Hz), 8.723~8.743 (2H, dd, *J*=8.0 Hz), 9.272 (2H, s), 14.926 (1H, s, Triazole-H).

### 1.3 Synthesis of [Co(3,3'-Hbpt)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](ad)6H<sub>2</sub>O (**2**)

A mixture containing Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (7.5 mg, 0.03 mmol), 3,3'-Hbpt (6.6 mg, 0.03 mmol), adipic acid (8.8 mg, 0.06 mmol) and water (6 mL) was sealed in a 15 mL Teflon-lined stainless steel vessel and

heated at 150 °C for 3 days, and then cooled to room temperature at a rate of 5 °C·h<sup>-1</sup>. Pink plate-like crystals of **2** were collected in a yield of 30% (based on Co). Anal. Calcd. for (CoC<sub>30</sub>N<sub>10</sub>O<sub>14</sub>H<sub>42</sub>)(%): C, 43.64; H, 5.13; N, 16.96. Found (%): C, 43.72; H, 5.15; N, 16.99. IR (cm<sup>-1</sup>, KBr): 3 208(s), 3 057(m), 2 964(w), 2 941(w), 2 643(w), 1 692(m), 1 550(s), 1 483(m), 1 450(m), 1 402(s), 1 292(m), 1 186(m), 1 146(m), 1 127(m), 1 048(w), 986(m), 952(w), 821(w), 748(m), 703(s), 695(s), 475(w).

### 1.4 Crystallographic data collection and structure determination

All diffraction data of compounds were collected on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo *K*α radiation (λ=0.071 073 nm) at 293(2) K. Absorption corrections were applied using SADABS<sup>[38]</sup>. All structures were solved by the direct methods using the SHELXS program of the SHELXTL-97 package and refined with SHELXL-97<sup>[39-40]</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. Crystallographic details are summarized in Table 1. Selected bond (nm) and bond angles (°) of compound **2** are shown in Table S1. Hydrogen bond geometries in compounds **1** and **2** are listed in Table S2 and Table S3, respectively.

CCDC: 1028283, **1**; 1002548, **2**.

Table 1 Crystal data and structure refinement details for compounds **1** and **2**

Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>12</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub>	C <sub>30</sub> H <sub>42</sub> CoN <sub>10</sub> O <sub>14</sub>
Formula weight	259.27	825.67
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.767 8(2)	0.777 37(15)
<i>b</i> / nm	2.034 5(6)	0.936 89(17)
<i>c</i> / nm	0.870 5(2)	1.315 5(2)
α / (°)	90	95.334(3)
β / (°)	113.420(5)	96.714(4)
γ / (°)	90	90.459(4)
<i>V</i> / nm <sup>3</sup>	1.247 7(6)	0.947 2(3)
<i>Z</i>	4	1
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.380	1.447

Continued Table 1

Absorption coefficient / $\text{mm}^{-1}$	0.099	0.529
$F(000)$	544	390
$\theta$ range for data collection / ( $^\circ$ )	2.74~26.98	2.18~26.52
Reflections collected / unique	6 922/2 670	5858/3906
$R_{\text{int}}$	0.047 2	0.018 3
Data / restraints / parameters	2 670/0/192	3 906/1/334
Goodness of fit on $F^2$	1.000	0.872
Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.057\ 3$ , $wR_2=0.138\ 7$	$R_1=0.047\ 5$ , $wR_2=0.130\ 2$
$R$ indices (all data)	$R_1=0.104\ 6$ , $wR_2=0.161\ 5$	$R_1=0.054\ 6$ , $wR_2=0.142\ 9$

## 2 Results and discussion

### 2.1 Quantum chemical calculation for 3,3'-Hbpt

DFT method was carried out to get an insight of the electronic structures and bonding properties of 3,3'-Hbpt. The following calculation and discussion are resulted from the optimized structure. The full geometry optimization is performed without constraints on symmetry. The optimized geometries of different conformations have been obtained at the B3LYP/6-31G (d, p) level and shown in Fig.1. Selected bond lengths and angles of *cis*-I and *cis*-II conformations are summarized in Table 2. For *cis*-I conformation, the bond lengths of N1-C5, N2-C6, N3-N4 and N5-C12 are calculated to be 0.133 527, 0.136 689, 0.134 913 and 0.135 133 nm, respectively, while the corresponding bond lengths of *cis*-II are 0.133 896, 0.1326 55, 0.135 322 and 0.133 389 nm.

The molecular total energies, zero-point energies and frontier orbital energies and the energy gaps of four different conformations had been calculated and listed

in Table 3. The total energies of four different conformations are calculated to be -736.464 0, -736.462 5, -736.463 9, -736.462 8 a.u., respectively. Obviously, the *cis*-I conformation provides relatively lower energy, representing more stable geometry. The surfaces of HOMO-1, HOMO, LUMO and LUMO +1 for four conformations are shown in Fig.2. The frontier molecular orbitals of four kinds of conformations are mainly composed of  $p$  atomic orbitals, and the electronic transitions are mainly assigned to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transitions. The same electron distribution of the frontier orbitals indicates similar electronic transition model. As listed in Table 3, the energy gap of *cis*-II conformation ( $\Delta E_{(\text{LUMO}-\text{HOMO})}=4.71\text{ eV}$ ) is lower than that of other three conformations, suggesting the greater ability of electron transition under external stimuli. To estimate the possible coordinated condition of the *cis*-II conformation, the natural charges and electron configurations of the atoms have been calculated by using natural bond orbital (NBO) analysis. As shown in Table 4, mulliken charges and

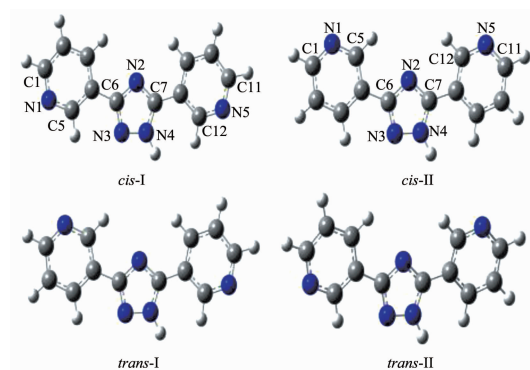


Fig.1 Optimized structures of four conformations for 3,3'-Hbpt

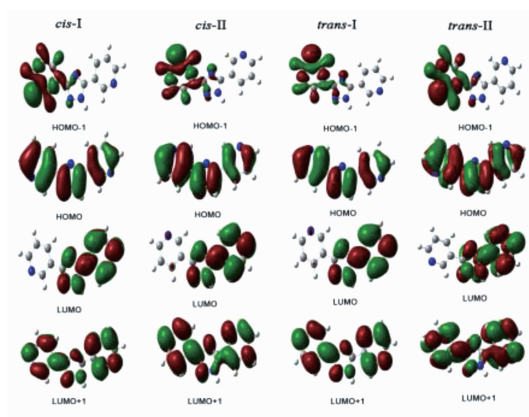


Fig.2 Isodensity surfaces of HOMO-1, HOMO, LUMO and LUMO+1 for 3,3'-Hbpt

**Table 2** Experimental and theoretical bond lengths(nm) and angles(°) for 3,3'-Hbpt in two compounds

Compound 1			Compound 2		
<i>cis</i> - I	Caled.	Exp.	<i>cis</i> - II	Caled.	Exp.
N1-C1	0.134 037	0.132 5(3)	N1-C1	0.1338 96	0.133 9(3)
N1-C5	0.133 527	0.133 2(3)	N1-C5	0.1336 71	0.133 9(3)
N2-C6	0.136 689	0.136 5(3)	N2-C6	0.1366 22	0.136 1(3)
N2-C7	0.132 692	0.133 6(3)	N2-C7	0.1326 55	0.133 5(3)
N3-N4	0.134 913	0.135 6(3)	N3-N4	0.1353 22	0.135 3(3)
N3-C6	0.135 879	0.133 9(3)	N3-C6	0.1333 67	0.132 6(3)
N4-C7	0.134 727	0.132 6(3)	N4-C7	0.1359 55	0.134 0(3)
N5-C11	0.134 557	0.133 3(3)	N5-C11	0.1339 74	0.132 9(4)
N5-C12	0.135 133	0.133 6(3)	N5-C12	0.1333 89	0.134 0(3)
C1-N1-C5	117.396 02	116.2(2)	C1-N1-C5	117.382 29	117.9(2)
C6-N2-C7	103.900 31	102.8(4)	C6-N2-C7	103.950 37	103.6(2)
C6-N3-N4	110.830 42	110.2(2)	C6-N3-N4	102.202 35	102.8(2)
C7-N4-N3	102.594 32	102.7(3)	C7-N4-N3	110.943 86	110.6(2)
C11-N5-C12	118.236 48	117.0(2)	C11-N5-C12	117.586 20	117.6(2)

**Table 3** Calculated total energies, zero-point energies(ZPE) and frontier orbit energies of 3,3'-Hbpt

	<i>cis</i> - I	<i>cis</i> - II	<i>trans</i> - I	<i>trans</i> - II
$E$ / a.u.	-736.464 0	-736.462 5	-736.463 9	-736.462 8
$(E+ZPE)$ / a.u.	-736.265 7	-736.264 3	-736.265 7	-736.264 5
$E_{(HOMO-1)}$ / a.u.	-0.250 50	-0.248 96	-0.250 14	-0.249 76
$E_{HOMO}$ / a.u.	-0.234 68	-0.234 67	-0.234 35	-0.235 10
$E_{LUMO}$ / a.u.	-0.060 31	-0.060 92	-0.061 21	-0.059 57
$E_{(LUMO+1)}$ / a.u.	-0.041 07	-0.038 43	-0.041 20	-0.038 66
$\Delta E_{(HOMO-LUMO)}$ / eV	4.74	4.71	4.73	4.78

natural charges of N1, N2, N3, N4 and N5 atoms are calculated as negative values. The charge of N2 atom shows more negative than that of N3 and N4 atoms in

the triazole ring. The natural charge of N1 and N5 atoms in pyridine rings are indentified to be -0.440 60 and -0.449 06. The results above demonstrate N1, N2

**Table 4** Natural configurations and natural charges for the selected atoms of *cis*-II

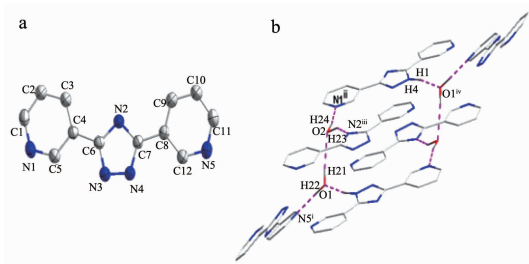
Atom	Configuration	Natural charge	Mulliken charge
N1	[core]2s(1.38)2p(4.05)3p(0.01)3d(0.01)	-0.449 06	-0.441 517
N2	[core]2s(1.40)2p(4.09)3p(0.01)3d(0.01)	-0.503 97	-0.565 965
N3	[core]2s(1.44)2p(3.84)3p(0.01)3d(0.01)	-0.296 01	-0.342 132
N4	[core]2s(1.24)2p(4.12)3p(0.01)	-0.369 59	-0.407 651
N5	[core]2s(1.38)2p(4.04)3p(0.01)3d(0.01)	-0.440 60	-0.434 512
C5	[core]2s(0.93)2p(3.00)3p(0.02)	0.051 31	0.072 385

and N5 atoms are prone to coordinate with metal ions.

## 2.2 Structure of 3,3'-Hbpt·2H<sub>2</sub>O (1)

Single crystal X-ray analysis reveals that the elementary unit of compound **1** consists of one discrete 3,3'-Hbpt molecule and two lattice water (Fig. 3a). The 3,3'-Hbpt ligand performs *cis*-I conformation in the crystal structure, which is in agreement with calculated molecular total energies of four kinds of conformations. The dihedral angles between the two

pyridine planes and triazole are 2.012° and 8.640°, respectively. The supramolecular architecture is formed by hydrogen-bonding interactions including O1-H21···O2 (0.276 1(3) nm), O1-H22···N5<sup>i</sup> (2.804 nm), O2-H24···N1<sup>ii</sup> (0.291 0(3) nm), O2-H23···N2<sup>iii</sup> (0.309 6(3) nm) and N4-H1···O1<sup>iv</sup> (0.270 7(3) nm) (Fig. 3b). The comparisons of observed and calculated geometric parameters for compound **1** are listed in Table 3.



Only H atoms involved in Hydrogen are shown; Symmetry code: <sup>i</sup>  $x-1/2, -y+3/2, z-1/2$ ; <sup>ii</sup>  $-x, -y+1, -z$ ; <sup>iii</sup>  $-x+1, -y+1, -z+1$ ; <sup>iv</sup>  $x, y+1, z$

Fig.3 (a) Structure of **1** with 50% thermal ellipsoids; (b) Supramolecular structure assembled by hydrogen bonds through the free water molecules

## 2.3 Structure of [Co(3,3'-Hbpt)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](ad)·6H<sub>2</sub>O (2)

Compound **2** is a 0D motif with one Co(II) cation, two 3,3'-Hbpt molecules, four coordinated water molecules, one free adipate anion and six lattice water molecules. As illustrated in Fig.4a, the Co(II) center presents a slightly distorted octahedron by two axial nitrogen atoms from two different 3,3'-Hbpt groups (Co-N 0.211 8(2) nm) and four oxygen atoms of four water molecules (Co-O 0.2055 2~0.2108 5(19) nm). Adjacent mononuclear molecules are integrated by diverse hydrogen-bonding interactions derived from the free water molecules and 3,3'-Hbpt ligands (O1-H1A···O5<sup>iv</sup> 0.270 7(3) nm; O5-H5B···N2<sup>v</sup> 0.294 9(3) nm; O5-H5A···O6 0.273 2(4) nm; O6-H6B···N3 0.284 1(4) nm; O7-H7B···N5<sup>vi</sup> 0.292 9(7) nm; N4-H4N···O7<sup>vii</sup>

0.279 2(3) nm). Subsequently, the 3D supramolecular network is constructed by the non-covalent interactions between the oxygen atoms in coordinated water and adipate anions (O2-H2A···O3<sup>iii</sup> 0.266 8(3) nm; O2-H2B···O3<sup>ii</sup> 0.265 1(3) nm; O1-H1B···O4<sup>ii</sup> 0.267 4(3) nm) (Fig.4c), in which the rectangular channels are filled by free adipate anions.

In addition, all of the 3,3'-Hbpt ligand keeps uniform *cis*-II conformation in compound **2**, corresponding to the lower energy gap value from frontier orbitals obtained by theoretical calculation. In the structure of **2**, the ligands display identical coordination mode where the pyridine N1 atom connects to Co(II) ions, which is in good agreement with the calculated results of atomic charge density. As shown in Table 3, the experimental bond lengths of N1-C1,



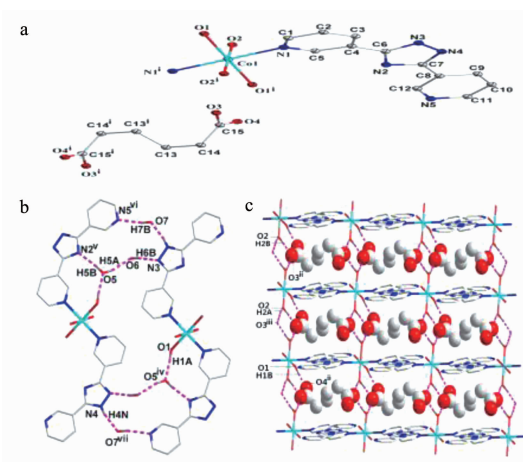


Fig.4 (a) Coordination environment of cobalt ion with 50% thermal ellipsoids; (b) Hydrogen-bonding between two mono-molecules; (c) Supramolecular network with rectangle channels encapsulated by adipate anions

N2-C7, N3-N4 and N5-C12 and the bond angles of C6-N2-C7, C6-N3-N4, C7-N4-N3 and C11-N5-C12 are well in accordance with the calculated values. In this case, the satisfying result is that the calculated geometry slightly differs from the observed parameters only by an average of 0.000 5 nm, emphasizing that the calculation method and basis set are habituated to the present system.

## 2.4 Thermal decomposition process of compound 2

Before to study the thermal stability, the phase purity of the bulk materials of compound **2** was confirmed by comparison of powder X-ray diffraction (PXRD) with that calculated from the single-crystal study (Fig.S1). Then, the thermal behavior of **2** was determined using TG measurement with the linear heating rate of 10 °C ·min<sup>-1</sup> under nitrogen atmosphere. As shown in Fig.5, the first stage occurs with weight loss of 22.09% between 71 and 137 °C, coinciding with the loss of coordinated water and lattice water molecules (Calcd. 21.80%). The second process of weight loss appears from 290 °C to 424 °C, and the weight loss of 16.78% is attributed to the release of adipate anions (Calcd. 17.44%). After that, the consecutive third step is considered as the decomposition of the 3,3'-Hbpt ligands. The remainder might be CoO since the weight (10.22%) is in agreement with the calculated value of 9.08%.

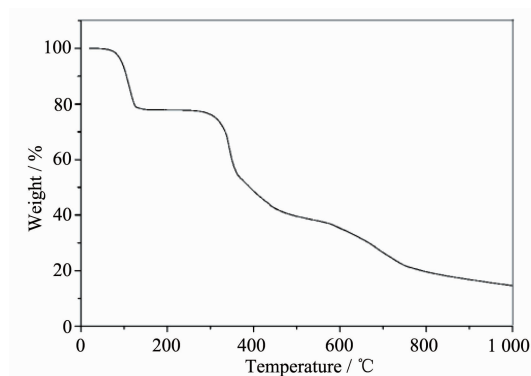


Fig.5 TG curve for compound **2**

### 3 Conclusions

In summary, 3,3'-Hbpt  $\cdot$  2H<sub>2</sub>O (**1**) and its coordination compound, [Co(3,3'-Hbpt)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]  $\cdot$  (ad)  $\cdot$  6H<sub>2</sub>O (**2**), have been successfully synthesized and structurally investigated. Single-crystal structure analysis reveals that compound **2** possesses a 0D mononuclear structure which can be extended to the 3D supra-molecular network with rectangular channels packed by free adipate anions. The optimized structure, preferred conformation, charge distribution and frontier molecular orbitals of 3,3'-Hbpt ligand are obtained by theoretical calculation, which is in good agreement with the experimental results. The crystalline 3,3'-Hbpt maintains the *cis*-I conformation which displays the lowest molecular total energy, while the *cis*-II

conformation with minimum energy gaps of frontier molecular orbital appears in the coordination compound when the ligand combines with the metal ion. The present work shows a practical case for the combination of theory and experiment, leading to the sophisticated concepts for the design and synthesis of desired coordination polymers.

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