

## 新型三维超分子化合物 $\{[\text{Co}(\text{H}_2\text{bptc})(\text{ptcp})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ 的水热合成和晶体结构

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## Hydrothermal Synthesis and Crystal Structure of a Novel 3D Supramolecular Complex $\{[\text{Co}(\text{H}_2\text{bptc})(\text{ptcp})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$

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**Abstract:** A novel cobalt(II) complex with biphenyl-3,3',4,4'-tetracarboxylic acid ( $\text{H}_4\text{bptc}$ ) and 2-phenyl-1,3,7,8-tetraazacyclopenta[1]-phenanthrene ( $\text{ptcp}$ ),  $\{[\text{Co}(\text{H}_2\text{bptc})(\text{ptcp})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**1**), has been synthesized by hydrothermal method and was characterized by elemental analysis, single crystal X-ray diffraction and thermal gravimetry (TG). It crystallizes in monoclinic, space group  $Pn$  with  $a=0.719\ 44(14)$  nm,  $b=1.259\ 4(3)$  nm,  $c=1.681\ 9(3)$  nm,  $\beta=93.30(3)^\circ$ ,  $V=1.521\ 5(5)$  nm<sup>3</sup>,  $Z=2$ ,  $\text{C}_{38}\text{H}_{26}\text{CoN}_4\text{O}_{11}$ ,  $M_r=737.53$ ,  $D_c=1.610\ \text{g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha)=0.639\ \text{mm}^{-1}$ ,  $F(000)=758$ ,  $S=1.024$ ,  $R_1=0.076\ 7$  and  $wR_2=0.120\ 6$ . The structural analyses reveal that the title complex is a 1D zigzag chain structure along the  $c$  axis, which is stacked to furnish a three-dimensional supramolecular net structure via hydrogen bonding interactions. CCDC: 793796.

**Key words:** cobalt complex; biphenyl-3,3',4,4'-tetracarboxylic acid; supramolecular structure

## 0 Introduction

Metal-organic polymeric frameworks have been rapidly expanding in recent years not only because of their potential applications in gas adsorption, ion exchange, magnetism, catalysis, luminescence and

nonlinear optics<sup>[1-6]</sup>, but also because of their intriguing variety of architectures<sup>[7]</sup>. In these complexes, weak intermolecular forces, such as hydrogen bonding,  $\pi$ - $\pi$  stacking, dipole-dipole attractions and van der Waals interactions, have been studied in depth and can be used in the design of molecular solids with specific

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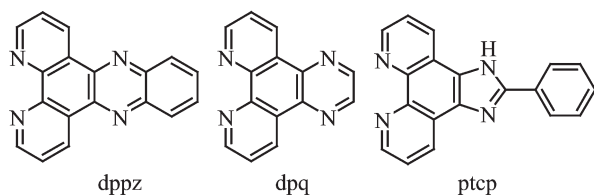
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supramolecular structures and functions<sup>[8-10]</sup>. The self-assemblies of supramolecular complexes can be achieved by controlling the noncovalent interactions among the ligands, which are, in most casts, organic groups<sup>[11-12]</sup>.

Therefore, an enormous amount of research is being focused on constructing novel coordination polymers by choosing versatile organic ligands. Aromatic polycarboxylic acids as versatile ligands have been used widely in constructing the metal-organic polymeric frameworks for the reasons as follows<sup>[13]</sup>: (i) the mutiple coordiantion sites; (ii) the mutiple  $\pi$ -bonds of the aromatic rings; (iii) the excellent hydrogen-bonding abilities; (iv) the long aromatic ligands can form large channel with metal ions. Based on the above causes, the biphenyl-3,3',4,4'-tetracarboxylic acid ( $\text{H}_4\text{bptc}$ ) ligands are choosed to design and synthesize the novel MOFs<sup>[14]</sup>.

On the other hand, phenanthroline (phen) are used mostly as secondary ligands in the metal containing supramolecular for the good coordination abilities which can enhance the stability of the polymers, as well as large  $\pi$ -conjugated planes which can generate various cooperative  $\text{CH}\cdots\pi/\text{NH}\cdots\pi$  and  $\pi\cdots\pi$  stacking interactions<sup>[15]</sup>. To enlarge the phen  $\pi$ -conjugated planes, one of the effective methods is connecting another plane in the positions 5 and 6<sup>[16]</sup>. So some ligands such as dppz<sup>[17]</sup>, dpq<sup>[18]</sup> are used in constructing new structures and application. In these ligands, the N atoms in the distended plane are just H-acceptor which is the defects to form metal-organic supramolecule. Herein, 2-phenyl-1,3,7,8-tetraazacyclopenta[1]-phenanthrene (ptcp) ligand was synthesized to design MOFs in which the imidazole rings both are the H-donor and H-acceptor.



In this work, we report a novel complex  $[\text{Co}(\text{H}_2\text{bptc})(\text{ptcp})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ , which is a one dimensional zigzag chainlike motif, and then form a 3D supramolecular structure via hydrogen-bonding interactions. And the thermal stability has been investigated too.

## 1 Experimental

### 1.1 Physical measurements

The ptcp ligands were prepared by the literature method<sup>[19]</sup>. All other chemicals purchased were of reagent grade or better and were used without further purification. Elemental analyses were performed with an Perkin-Elmer 240C element analyzer. Thermogravimetric analysis (TGA) was performed on a NETZCH STA 449C with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$  under an air atmospher.

### 1.2 Preparation of complex 1

Complex **1** was synthesized by hydrothermal reaction of  $\text{Co}(\text{NO}_3)_2$  (0.058 2 g, 0.2 mmol),  $\text{H}_4\text{bptc}$  (0.066 0 g, 0.2 mmol), ptcp (0.059 2 g, 0.2 mmol) and NaOH (0.016 0 g, 0.40 mmol) in an aqua solution (18 mL). The mixture was sealed in a 25 mL Teflon reactor, which was heated to  $160\text{ }^\circ\text{C}$  for 3 d and then cooled to room temperature. Pale yellow single crystals of complex **1** suitable for X-ray single-crystal diffraction analysis were obtained (yield 58%). Anal. calc. for  $\text{C}_{35}\text{H}_{26}\text{CoN}_4\text{O}_{11}$ (%): C 56.98; H 3.53; N 7.60; found(%): C 56.90; H 3.55; N 7.64.

### 1.3 Structure determination

Suitable single crystal with dimensions of  $0.235\text{ mm} \times 0.037\text{ mm} \times 0.013\text{ mm}$  was mounted on glass fiber and reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\text{ 073 nm}$ ) at  $292(2)\text{ K}$  by using an  $\varphi$ - $\omega$  scan mode. A total of 14 391 reflections were collected in the range of  $3.02^\circ \leq \theta \leq 27.45^\circ$ , of which 6 349 were unique with  $R_{\text{int}}=0.136$ . A semi-empirical absorption correction based on SADABS was applied<sup>[20]</sup>. The structure was solved by direct methods and refined by full-matrix least-squares based on  $F^2$  using SHELXTL-97 program<sup>[21]</sup>. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and details of the data collection and the structure refinement are given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 793796.

**Table 1** Crystal data and structure refinement for complex **1**

Formula	C <sub>35</sub> H <sub>26</sub> N <sub>4</sub> O <sub>11</sub> Co	$D_c$ / (g·cm <sup>-3</sup> )	1.610
Formula weight	737.53	$F(000)$	758
Temperature / K	292(2)	Crystal size / mm	0.235×0.037×0.013
Crystal system	Monoclinic	$\theta$ / (°)	3.02 to 27.45
Space group	$Pn$	Limiting indices	$-9 \leq h \leq 7, -16 \leq k \leq 16, -21 \leq l \leq 21$
$a$ / nm	0.719 44(14)	Reflections collected / unique ( $R_{int}$ )	14 391 / 6 349 (0.136 1)
$b$ / nm	1.259 4(3)	Goodness of fit on $F^2$	1.024
$c$ / nm	1.681 9(3)	Data / restraints / parameters	6 349 / 8 / 454
$\beta$ / (°)	93.30(3)	Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.076$ 7, $wR_2=0.120$ 6
$V$ / nm <sup>3</sup>	1.521 5(5)	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	434 and -400
$Z$	2		

**Table 2** Selected bond lengths (nm) and angles (°)

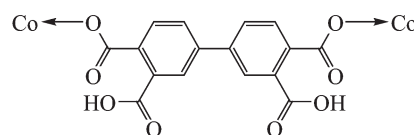
Co-O(1W)	0.206 6(4)	Co-O(7)	0.209 3(4)	Co-O(2W)	0.209 8(4)
Co-O(1)	0.213 3(4)	Co-N(2)	0.215 9(5)	Co-N(1)	0.216 5(5)
O(1W)-Co-O(7)	89.68(16)	O(1W)-Co-O(2W)	171.11(15)	O(7)-Co-O(2W)	89.05(17)
O(1W)-Co-O(1)	82.82(18)	O(7)-Co-O(1)	86.15(18)	O(2W)-Co-O(1)	88.32(17)
O(1W)-Co-N(2)	97.75(19)	O(7)-Co-N(2)	165.76(18)	O(2W)-Co-N(2)	85.43(19)
O(1)-Co-N(2)	106.75(18)	O(1W)-Co-N(1)	88.06(18)	O(7)-Co-N(1)	92.18(17)
O(2W)-Co-N(1)	100.78(17)	O(1)-Co-N(1)	170.7(2)	N(2)-Co-N(1)	76.03(18)

## 2 Results and discussion

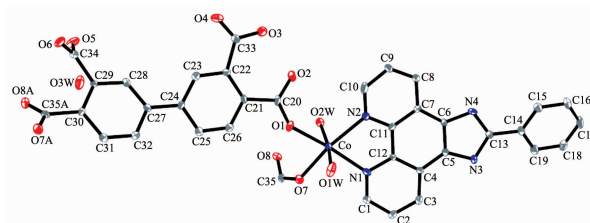
### 2.1 Description of crystal structure

A single-crystal X-ray analysis reveals that complex **1** is a 1D zigzag polymeric coordination chain. An asymmetric unit  $[\text{Co}(\text{H}_2\text{bptc})(\text{ptcp})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  contains one six-coordinated cobalt ion, one  $\text{H}_2\text{bptc}^{2-}$ , one ptcp ligands, two coordination water and one free water molecule. In **1**, the cobalt center adopts a distorted octahedral geometry by linking to two nitrogen atoms of one chelating ptcp ligands, four oxygen atoms in which two oxygen atoms (O(1), O(7)) of two monodentate carboxylate groups from two  $\text{H}_2\text{bptc}^{2-}$  ligands and the other two oxygen atoms (O(1W), O(2W)) are from two coordinated water as shown in Fig.1. Co-O bond lengths fall in the range 0.206 6(4)~0.213 3(4) nm, and Co-N bond lengths are 0.215 9(5) (Co-N(2)) and 0.216 5(5) nm (Co-N(1)). These values are within the normal experimental limitation. It is well-known that  $\text{H}_4\text{bptc}$  ligands have possibly many types of coordination modes<sup>[14]</sup>, but to our knowledge, the coordination modes (Scheme 1) of  $\text{H}_4\text{bptc}$  ligand in complex **1** have

not reported as yet.



Scheme 1 Coordination modes of  $\text{H}_4\text{bptc}$  in the title complex



Symmetry codes: A:  $x+1/2, -y+1, z+1/2$ ; Thermal ellipsoids are drawn at the 30% probability level, the hydrogen atoms are omitted for clarity

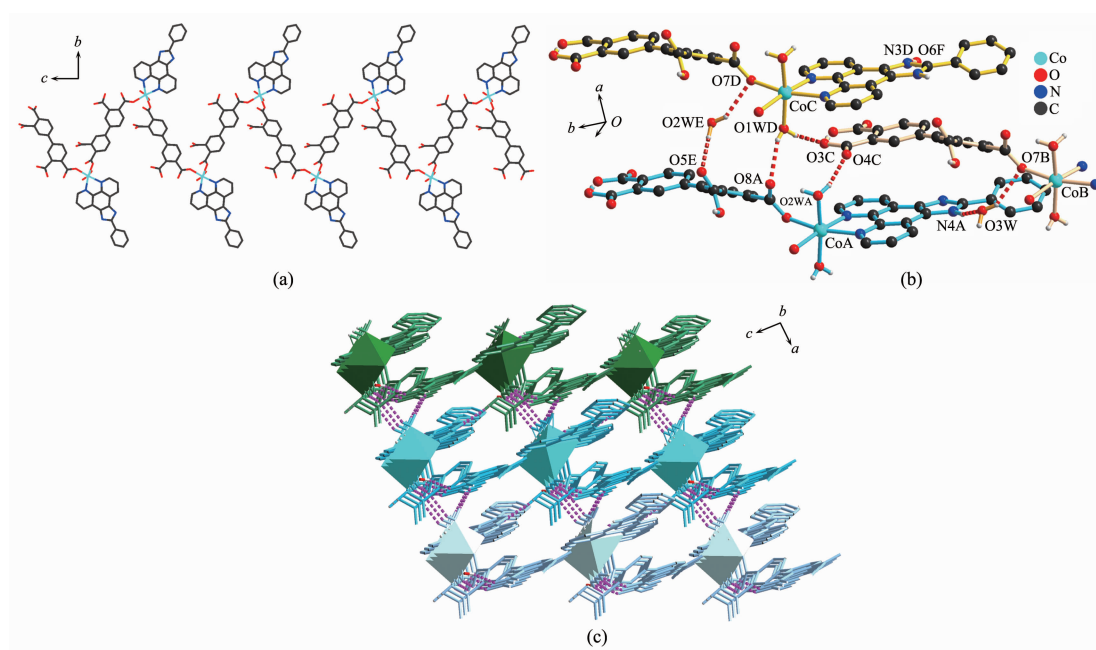
Fig.1 View of the coordination environment of Co(II) in complex **1**

To distinctly investigate the structures for frameworks, it would be important to explore the connection modes of the metal centers and organic ligands. In **1**, each  $\text{H}_2\text{bptc}^{2-}$  links two Co(II) ions by means of bridging coordination mode which generates a

one-dimensional zigzag chain. The long ptcp ligands play a templet role because of their steric effect and they are decorated at both sides of the zigzag chain that look like a zipper (Fig.2a).

A fascinating and peculiar structural feature is that there are multiplicate hydrogen bond bridges involving water molecules and carboxylate anions as well as the imidazole ring of ptcp ligands. The imidazole rings of ptcp ligands can provide one hydrogen bonding donors and one N acceptor which lead to two strong hydrogen bonds. One is the  $\text{O}-\text{H} \cdots \text{N}$

which occurs between carboxylate O(6) and N(3), and the other is  $\text{N}-\text{H} \cdots \text{O}$  type hydrogen bonds between N-H of imidazole and water molecular. In addition, the coordination lattice water molecules O(1W), O(2W) and lattice water O(3W) serve as H-donor and interact with the carboxylate oxygen atoms of the  $\text{H}_2\text{bptc}^{2-}$  ligands Fig.2b. So a 3D supramolecular net structure is formed via those hydrogen bonding as shown in Fig.2c. The hydrogen bond distances and angles are selected to show in Table 3.



Symmetry codes (b): A:  $x-1, y+1, z$ ; B:  $x-1, y, z$ ; C:  $x-1/2, -y+1, z-1/2$ ; D:  $x, y+1, z$ ; E:  $x-1/2, -y+2, z-1/2$ ; F:  $x, y, z-1$

Fig.2 (a) Views of the structural motifs in **1**, 1D covalently bonded chain, all hydrogen atoms are omitted for clarity; (b) hydrogen bonding interactions in complex **1** viewed along  $c$  axis; (c) 3D supramolecular net structure constructed by hydrogen bonding

Table 3 Distances and angles of hydrogen bonds for complex **1**

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{D-H}\cdots\text{A}) / (^\circ)$
O(6)-H(6) $\cdots$ N(3)A	0.082	0.181	0.261 7	166.01
O(2W)-H(2WA) $\cdots$ O(8)	0.082	0.183	0.263 8	166.60
O(2W)-H(2WB) $\cdots$ O(4)B	0.082	0.188	0.268 2	163.72
N(4)-H(4) $\cdots$ O(3W)C	0.086	0.189	0.273 1	164.92
O(1W)-H(1WA) $\cdots$ O(3)C	0.086	0.189	0.273 4	167.02
O(3W)-H(3WA) $\cdots$ O(5)	0.082	0.193	0.275 3	178.90
O(1W)-H(1WB) $\cdots$ O(8)D	0.086	0.210	0.286 1	148.21
O(3W)-H(3WB) $\cdots$ O(7)E	0.083	0.225	0.296 9	146.12
O(3)-H(3A) $\cdots$ O(2)	0.082	0.157	0.238 7	170.13

Symmetry codes: A:  $x, y+1, z+1$ ; B:  $x+1/2, -y, z-1/2$ ; C:  $x-1/2, -y, z-1/2$ ; D:  $x-1, y, z$ ; E:  $x+1/2, -y+1, z+1/2$ .

## 2.2 TG analysis

Complex **1** is stable at ambient conditions, and thermogravimetric experiment was performed to explore its thermal stability. For **1**, the first gradual weight loss is 2.47% in the temperature range of 80 to 110 °C (calcd. 2.44%), corresponding to the release of one free water molecule. The second step (4.90%) from 190 to 220 °C is attributed to the release of two coordinated water molecules (calcd. 4.88%). The third weight loss of 40.15% in the 300~350 °C range is attributable to the removal of ptc<sup>+</sup> ligands (calcd. 40.18%). The last weight loss of 44.48% is ascribable to the loss of H<sub>2</sub>bptc<sup>2-</sup> (calcd. 44.50%) from 380 to 460 °C. The final product may be CoO.

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