

基于一种三角柔性羧酸配体构筑的含镍配位聚合物的水热合成、结构和光化学性质

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摘要: 通过水热法合成了一种配位聚合物 $[\text{Ni}(\text{H}_2\text{BCPBA})_2(\text{H}_2\text{O})_4]_n$ (**1**, $\text{H}_3\text{BCPBA}=3,5\text{-二(4-羧酸-酚氧基)-苯甲酸}$), 并对其进行了元素分析、红外光谱、紫外光谱、热重和 X 射线单晶衍射表征。 $[\text{Ni}(\text{H}_2\text{BCPBA})_2(\text{H}_2\text{O})_4]_n$ 属于三斜晶系, $P\bar{1}$ 空间群。中心 Ni(II) 和来自于 2 个配体与 4 个水分子配位, 形成八面体结构。固体紫外光谱表明配合物有一个强的光谱吸收。

关键词: 水热合成; 晶体结构; 镍配合物; 紫外光谱

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Hydrothermal Synthesis, Crystal Structure and Photochemical Properties of a Nickel(II) Coordination Polymer Based on a Tripodal Flexible Carboxylate Ligand

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Abstract: A coordination polymer $[\text{Ni}(\text{H}_2\text{BCPBA})_2(\text{H}_2\text{O})_4]_n$ (**1**, $\text{H}_3\text{BCPBA}=3,5\text{-bi(4-carboxy-phenoxy)-benzoic acid}$) has been synthesized from H_3BCPBA by using hydrothermal method and structurally characterized by elemental analysis, IR spectrum, UV spectroscopy, TG and single-crystal X-ray diffraction. Single-crystal X-ray analysis reveals that the coordination polymer **1** is crystallized in the triclinic system, space group $P\bar{1}$. The Ni(II) ion is six-coordinated by two oxygen atoms from H_2BCPBA^- ligand and four oxygen atoms from water molecules, generating a octahedral coordination geometry. UV spectroscopy study reveals that the coordination polymer exhibits strong ultraviolet absorption in the solid state at room temperature. CCDC: 837882.

Key words: hydrothermal synthesis; crystal structure; Ni(II) coordination polymer; UV spectroscopy

0 Introduction

Today, organic/inorganic functional hetero-structures are one of the hot topics most of all because they might combine within a single edifice the properties of their constituents^[1-7]. Multicarboxylate ligands

are often selected as multifunctional organic linkers because of their abundant coordination modes to metal ions, allowing for various structural topologies, and also because of their ability to act as H-bond acceptors and donors to assemble supramolecular structures^[8]. Recently, nonrigid ligands are usually the

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typical building elements in the multidimensional networks. The conformational freedom nature of the flexible ligand may provide more possibility for the construction of unusual topology structures and microporous coordination polymers. Therefore, 3,5-bi(4-carboxy-phenoxy)-benzoic acid (H_3BCPBA) triangular flexible ligand can be considered to be excellent candidates for the preparation of functional coordination polymers. Herein, to expand our work, we report the synthesis, crystal structure and the photochemical property of a new coordination polymer $[\{\text{Ni}(\text{H}_2\text{BCPBA})_2(\text{H}_2\text{O})_4\}]_n$.

1 Experimental

1.1 Materials and measurements

The ligand H_3BCPBA was prepared according to literature^[9]. All the other starting reagents were of AR grade and used as purchased. IR spectra were taken on a Perkin-Elmer Spectrum One FT-IR Spectrometer in the $4\,000\sim400\text{ cm}^{-1}$ region with KBr pellets. Elemental analyses for C, H and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=0.154\,18\text{ nm}$), in which the X-ray tube was operated at 40 kV and 40 mA. Solid-state UV-Vis diffuse reflectance spectra was obtained at room temperature using a Shimadzu UV-3600 double monochromator spectrophotometer, and BaSO_4 was used as a 100% reflectance standard for all materials. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on

a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 Kmin^{-1} under N_2 atmosphere.

1.2 Synthesis of 1

A mixture of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (29.1 mg, 0.1 mmol), H_3BCPBA (39.4 mg, 0.1 mmol) was added to in 8 mL of DMF/ H_2O (1:3, V/V). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at $95\text{ }^\circ\text{C}$ for 3 d, colorless crystals were obtained. (Yield: 40% based on Cd). Anal. Calcd. for $\text{C}_{42}\text{H}_{34}\text{NiO}_{20}$ (%): C, 54.98, H, 3.73; Found(%): C, 54.62, H, 3.84. IR (KBr, cm^{-1}): 3 410 (w), 1 683(w), 1 606(m), 1 547(s), 1 490, 1 401(m), 1 215 (m), 1 150(m), 996(m), 850(m), 761(m).

1.3 X-ray crystallography

Suitable crystal of **1** (dark green, dimensions of $0.23\text{ mm}\times 0.12\text{ mm}\times 0.09\text{ mm}$) was used for the structure determination. Data collection at 291 (2) K was carried out with a Bruker SMART APEX CCD instrument using a $\text{Mo K}\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$). The data were integrated by using the SAINT program, which also did the intensity corrections for Lorentz and polarization effect. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97^[10]. All non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least squares technique using the SHELXL-97 crystallographic software package. For **1**, convergence was reached at the final $R=0.064\,6$ ($I>2\sigma(I)$) and $wR=0.171\,0$ (for all data), with allowance for the thermal anisotropy for all non-hydrogen atoms. A summary of the crystallographic

Table 1 Crystallographic data and structure refinement details for **1**

Compound	1	$\gamma / (^\circ)$	98.252(2)
Empirical formula	$\text{C}_{42}\text{H}_{34}\text{NiO}_{20}$	Z	1
Formula weight	917.38	V / nm^3	0.991 9(2)
Crystal system	Triclinic	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.536
Space group	$P\bar{1}$	$\mu(\text{Mo K}\alpha) / \text{mm}^{-1}$	0.577
a / nm	0.578 70(7)	$F(000)$	474
b / nm	1.353 23(16)	R_{int}	0.018 9
c / nm	1.390 90(17)	Measured reflection / observed data ($I>2\sigma(I)$)	3 470 / 3 120
$\alpha / (^\circ)$	109.566(1)	R_1, wR_2 ($I>2\sigma(I)$)	0.036 5 / 0.109 9
$\beta / (^\circ)$	98.792(1)	S	1.095

Table 2 Selected bond lengths (nm) and angles (°) for **1**

Ni(1)-O(7)	0.204 36(15)	Ni(1)-O(10W)	0.205 48(15)	Ni(1)-O(9W)	0.206 19(16)
O(7)A-Ni(1)-O(7)	179.998(1)	O(7)A-Ni(1)-O(10W)	87.49(6)	O(7)-Ni(1)-O(10W)	92.51(6)
O(7)A-Ni(1)-O(9W)	90.22(7)	O(10W)-Ni(1)-O(9W)	90.58(6)		

Symmetry transformations used to generate equivalent atoms: A: $-x, -y+1, -z+2$.

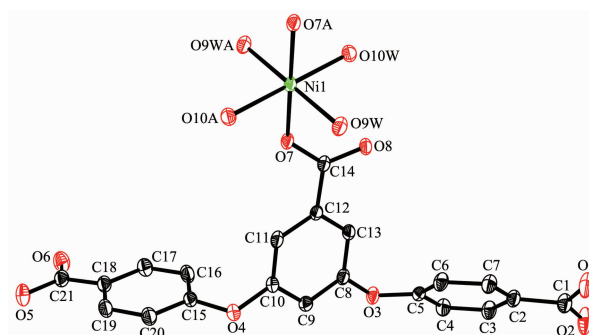
data and structural determination for **1** is provided in Table 1. The selected bond lengths and bond angles are given in Table 2.

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2 Results and discussion

2.1 Crystal structure

The selected bond lengths and bond angles are listed in Table 2. Single crystal X-ray analysis reveals the compound crystallized in triclinic crystal system of $P\bar{1}$. As showed in Fig.1, the asymmetric unit consists of one Ni(II) cation, one H_2BCPBA^- ligand, four coordinated water molecules. Each Ni(II) ion is six-coordinated by two oxygen atoms from H_2BCPBA^- ligand and four oxygen atoms from water molecules, generating a octahedral coordination geometry. In the octahedral, O(10W) and O(9W) locate at the equatorial plane, O(7) occupy the axial position. Bond angles O(9WA)-Ni(1)-O(10W), O(9W)-Ni(1)-O(10W), are $92.50(2)^\circ$ and $87.49(8)^\circ$, respectively. The sum of these angles is 360.00° , suggesting a planar nature of O(10W) and O(9W). The Ni(1)-O distances range from 0.20438(16) to 0.206 18(17) nm. The Ni-O and Ni-N bond lengths for **1** are comparable to that found in

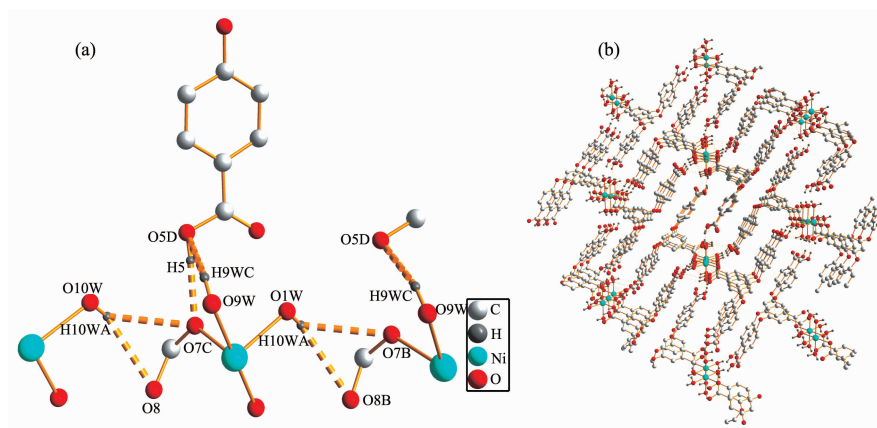


H atoms are omitted for the sake of clarity; Symmetry transformations used to generate equivalent atoms: A $-x, -y+1, -z+2$

Fig.1 Asymmetric unit and coordination environment of Ni(II) in **1**

similar types of Ni(II) octahedral polymers^[11-12]. Interestingly, the three carboxylate groups of H_3BCPBA ligand were all deprotonated and do not take part in coordination.

It is noteworthy that there are a lot of intermolecular hydrogen bonds between carboxyl groups and coordinated water molecules in **1** (Fig.2a). The structure of the title complex from 0D to 3D depends upon intermolecular hydrogen interaction between the coordinated water molecules and carboxylate oxygen atoms, such as $\text{O}(1)-\text{H}(1)\cdots\text{O}(8)^{\text{B}}$



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

Fig.2 (a) Hydrogen bonds in **1**, (b) Views 3D structure by H-bond net

Table 3 Hydrogen bonds of the complex **1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O1-H1...O8B	0.082 0	0.182 2	0.261 9	163.57
O5-H5...O7C	0.082 0	0.188 4	0.270 2	176.20
O9W-H9WB...O2B	0.085 0	0.230 5	0.276 4	114.22
O9W-H9WB...O8	0.085 0	0.245 2	0.309 2	132.64
O9W-H9WC...O5D	0.085 0	0.251 7	0.331 0	155.57
O10W-H10A...O8B	0.085 0	0.253 3	0.321 2	137.48
O10W-H10A...O7B	0.085 0	0.265 8	0.316 5	119.59
O10W-H10B...O6D	0.085 0	0.193 6	0.277 9	171.47

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

and O(5)-H(5)···O(7)^C, with D···A separations and the D-H-A angles. In addition, lattice water molecules attached to coordinated water molecules and carboxyl groups through intermolecular hydrogen bonds: O9W-H9WB···O2^B, O9W-H9WB···O8, O9W-H9WC···O5^D, O10W-H10A···O8^B, O10W-H10A···O7^B, and O10W-H10B···O6^D (Fig.2a and b). Obviously, **1** is stabilized by intramolecular hydrogen bond interactions. The detailed data of hydrogen bonds for **1** are shown in Table 3.

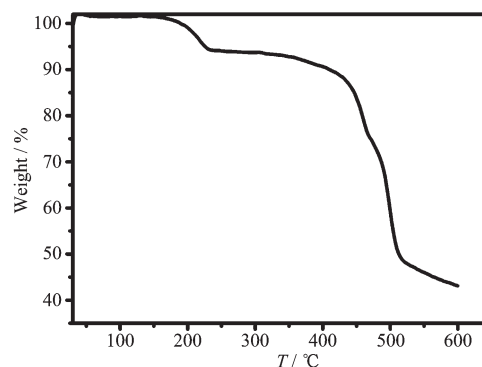
2.2 IR spectra

IR spectra of **1** show a wide band of strong intensity at 3 433 cm⁻¹ from ν_{OH} of water molecules, and the asymmetric $\nu_{\text{as}}(\text{COO})$ and symmetric $\nu_{\text{s}}(\text{COO})$ stretching bands fall in the 1 690~1 350 cm⁻¹ region. The presence of the characteristic bands around 1 686 cm⁻¹ in **1** attributed to the protonated carboxylic group indicates that the present protonation of H₂BCPBA⁻ ligand. The separation ($\Delta\nu$) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ is 289 cm⁻¹ for **1**, which is more than 200 cm⁻¹, indicating monodentate coordinating modes^[13]. The band at 3 419 cm⁻¹ due to the $\nu(\text{O-H})$ absorptions of water molecules. In addition, X-ray diffraction analysis further indicates the existence of the protonation of H₂BCPBA⁻ ligand. So, these IR results are coincident with the crystallographic structural analyses.

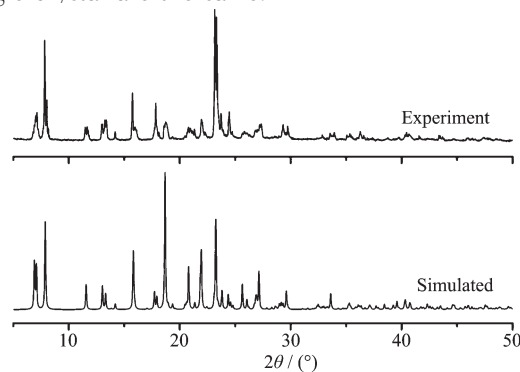
2.3 Thermal analysis and PXRD result

To estimate the stability of **1**, its thermal behavior was carried out by TGA in flow of N₂, in the temperature range from 20 to 700 °C (Fig.3), with a heating rate of 10 °C·min⁻¹. The TGA curve indicates that **1** starts to lose four coordination waters and ends

at about 220 °C (the lost weight is 7.84%, calculated value is 7.72%). After the loss of all the water molecules, the supramolecular framework is stable up to 410 °C, followed by another weight loss at high temperature. The thermal decomposition feature of **1** is in good agreement with the crystal structure.

Fig.3 TG curve of **1**

To confirm whether the crystal structure is truly representative of the bulk materials, XRD experiment was carried out for **1**. The experimental and simulated XRD patterns of **1** are shown in Fig.4, and it shows that the bulk synthesized materials and the measured single crystal are the same.

Fig.4 Experimental and simulated XRD spectra of **1**

2.4 UV-Vis spectrum

As can be seen in Fig.5, the H₃BCPBA, and the Ni (II) coordination polymer show intense absorption peaks at 302, and 313 nm respectively, which can be ascribed to $\pi-\pi^*$ transitions of the ligands. The second small peak centers at 656 nm in [$^3T_{1g}(F) \rightarrow ^3A_{2g}$], which are typical for octahedrally coordinated Ni (II) polymers [14]. UV-Vis spectrum of **1** is in complete agreement with the coordination environment revealed by X-ray single-crystal structure analysis.

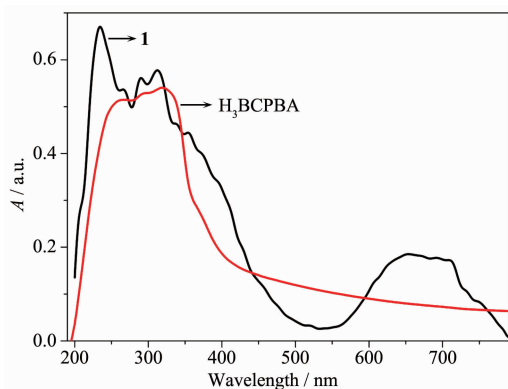


Fig.5 Solid-state ultraviolet absorption spectra of H₃BCPBA and **1** at room temperature

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