

甲酸及联吡啶配体构筑的三维网状镍(II)/钴(II)配位聚合物的合成及晶体结构

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摘要: 通过水热法合成两个混配的配位聚合物 $[M(\text{bipy})(\text{Metha})_2]_n \cdot n\text{H}_2\text{O}$ ($M=\text{Ni}$, **1**; Co , **2**; $\text{bipy}=4,4'$ -联吡啶; Metha =甲酸), 并对配合物进行了元素分析、红外光谱和 X-射线单晶衍射测定。结果表明, 2 个配合物为单斜晶系, $C2/c$ 空间群。配合物 **1** 和 **2** 具有相似的三维网状结构。配体 Metha 以 2 种不同的类型与 M^{2+} 离子配位, 一种是 Metha 中的 2 个氧原子作为桥联配位原子, 连接着由 bipy 作为双基配体连接 2 个不同的金属离子构成的链, 另一个 Metha 中的羧基氧只有 1 个氧原子与金属离子配位, 使配合物构成三维结构。

关键词: 晶体结构; 配位化学; 网状结构

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Synthesis and Crystal Structure of Two 3D Networks Ni(II)/Co(II) Coordination Complexes Based on Bipyridine and Methanoic acid

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Abstract: Two transition metal complexes, $[M(\text{bipy})(\text{Metha})_2]_n \cdot n\text{H}_2\text{O}$ ($M=\text{Ni}$, **1**; Co , **2**; $\text{bipy}=4,4'$ -bipyridine, Metha =methanoic acid), have been synthesized by hydrothermal synthesis and characterized by elemental analyses, IR spectroscopy, and X-ray single-crystal diffraction etc. The single crystal structures show the two complexes belong to monoclinic system, $C2/c$ space group. Complexes **1** and **2** have similar 3D network structures. Metha have two kinds of different types with M^{2+} ion, one kind is the two oxygen atoms of the Metha as bridging ligand atoms, connected by chain with bipy , another is the carboxyl oxygen of the Metha with only one oxygen atom with another M^{2+} ion. CCDC: 942546, **1**; 942547, **2**.

Key words: crystal structure; coordination complex; network structure

0 Introduction

Metal-organic coordination complexes have drawn great research interest in recent years because of their

potential applications in molecular adsorption and separation processes^[1-3], magnetic properties^[4-5], ion exchange^[6], catalysis^[7-8], sensor technology^[9-10]. However, it is found that many factors, such as the different

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organic ligands^[11-13], solvent system^[14-15], metal ions^[16-17], counterions^[18-20], greatly influence the structures, which render the difficulty of predicting the construction of molecular architecture. Therefore, the systematic study of diversified conditions is still an important and interesting issue in the formation of coordination complexes.

Recently, a large number of mixed-ligands MOFs have been reported^[21-26]. The combination of different ligands can result in greater tunability of structural frameworks than single ligand. It is undoubted that a mixed ligand is a good choice for the construction of new frameworks, especially the mixed polycarboxylate and N-containing ones^[27-28]. On the other hand, as we know bipy is a good kind of ligand, which can coordinated with many transition metals^[29-31]. Following such a mixed-ligand strategy, we selected Metha and biby (bipy=4,4'-bipyridine, Metha=methanoic acid) as the primary ligands for coordination to the Ni salt and Co salt to synthesize two complexes $[\text{Ni}(\text{bipy})(\text{Metha})_2]_n \cdot n\text{H}_2\text{O}$ (**1**) and $[\text{Co}(\text{bipy})(\text{Metha})_2]_n \cdot n\text{H}_2\text{O}$ (**2**). Herein, we report the syntheses, crystal structures of the new coordination complexes. The new complexes are characterized by elemental analysis, IR spectra, X-ray crystallography, and thermal analysis.

1 Experimental

1.1 Materials and Instruments

Reagents and solvents employed were commercially available and used as received. IR absorption spectra of the complexes were recorded in the range of 400~4 000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using $\text{Cu-K}\alpha$ radiation (0.154 18 nm), in which the X-ray tube was operated at 40 kV and 40 mA. TGA analysis was performed on a NETZSCH-STA 409 PC thermal analysis instrument at a heating rate of 20 $^\circ\text{C}\cdot\text{min}^{-1}$.

1.2 Preparation

Complex **1**: A mixture of $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.2

mmol, 0.398 g), 4,4'-dipyridyl (0.10 mmol, 0.156 g), methanoic acid (0.3 mmol, 0.014 g) was added slowly to H_2O (15 mL). The resultant solution was continuously stirred for 30 min and then filtered. The mixture was transferred to a Parr Teflonlined reaction vessel (ca. 25 mL) and placed inside a preheated oven at 403 K for 3 d. After the reaction, the vessel was allowed to cool slowly to room temperature, the green block single crystals suitable for X-ray diffraction study were obtained (Yield 82%). Elemental analysis (%): calculated for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{NiO}_5$: C, 44.63; H, 3.75; N, 8.67. Found (%): C, 44.52; H, 3.83; N, 8.72. IR data (cm^{-1}): 3 260(s), 1 608(s), 1 588(m), 1 392(s), 1 365(m), 1 340(w), 1 223(ms), 1 072(w), 827(m), 813(m), 732(m), 635(m).

Complex **2**: The preparation of **2** is similar to **1**, except $\text{Co}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ instead of $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, the purple block single crystals suitable for X-ray diffraction study were obtained (Yield 76%). Elemental analysis (%): calculated for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{CoO}_5$: C, 44.60; H, 3.74; N, 8.67. Found (%): C, 44.62; H, 3.81; N, 8.70. IR data (cm^{-1}): 3 261 (s), 1 610(s), 1 592(m), 1 395(s), 1 375(m), 1 342(w), 1 233(ms), 1 082(w), 830(m), 735(m), 645(m).

1.3 X-ray single-crystal structure determination

Crystallographic measurements were carried out using a Bruker SMART APEX-CCD (Version 5.0) diffractometer, φ - ω scans, graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 291 (2) K. SMART for data collection, SAINT (Version 6.02) for data integration, SADABS for absorption correction, and the structures were solved by direct methods with SHELXS-97^[32] and refined by full-matrix least squares on F^2 values using the SHELXL-97^[33] package of crystallographic software. The hydrogen atoms of bipy and Metha ligands, water molecules were placed at the calculated positions, allowed to ride on their respective parent atoms, and assigned by fixed isotropic thermal parameters. Crystal and structure refinement data for complexes are presented in Table 1, while the selected bond lengths and angles are given in Table 2.

CCDC: 942546, **1**; 942547, **2**.

Table 1 Crystallographic data for complexes

complex	1	2
Empirical formula	C ₁₂ H ₁₂ N ₂ NiO ₅	C ₁₂ H ₁₂ N ₂ CoO ₅
Formula weight	322.95	323.17
Temperature / K	291(2)	291(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / nm	1.045 6(3)	1.047 6(3)
<i>b</i> / nm	2.001 7(6)	2.020 5(6)
<i>c</i> / nm	0.810 77(19)	0.810 9(2)
β / (°)	102.602(4)	102.265(4)
Volume / nm ³	1.656 0(7)	1.677 3(8)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ⁻³)	1.295	1.280
Absorption coefficient / (mm ⁻¹)	1.188	1.039
<i>F</i> (000)	664	660
Reflections collected	4 365	4 420
Independent reflections (<i>R</i> _{int})	1 609 (0.046)	1 634 (0.049)
Observed reflections (<i>I</i> >2σ(<i>I</i>))	1 042	1 039
Refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
Number of parameters	111	111
Goodness-of-fit on <i>F</i> ²	1.039	1.063
Final <i>R</i> indices (<i>I</i> >2σ(<i>I</i>))	<i>R</i> ₁ =0.046 6, <i>wR</i> ₂ =0.102 8	<i>R</i> ₁ =0.048 9, <i>wR</i> ₂ =0.101 5
Final weighting scheme	Calcd. $w=1/[\sigma^2(F_o^2)+(0.05P)^2+0.55P]$, where $P=(F_o^2+F_c^2)/3$	Calcd. $w=1/[\sigma^2(F_o^2)+(0.04P)^2+1.22P]$, where $P=(F_o^2+2F_c^2)/3$
(Δρ) _{max} / (e·nm ⁻³)	598	522
(Δρ) _{min} / (e·nm ⁻³)	-327	-369

Table 2 Select bond lengths (nm) and bond angles (°) for complexes

1					
Ni(1)-O(1)	0.209 5(3)	Ni(1)-O(2)	0.209 8(4)	Ni(1)-N(1)	0.211 7(3)
Ni(1)-O(1) ^a	0.209 5(3)	Ni(1)-O(2) ^a	0.209 8(4)	Ni(1)-N(1) ^a	0.211 7(3)
O(1)-Ni(1)-O(2)	91.78(15)	O(1)-Ni(1)-N(1)	86.87(11)	O(1)-Ni(1)-O(1) ^a	180.00(12)
O(1)-Ni(1)-O(2) ^a	88.22(15)	O(1)-Ni(1)-N(1) ^a	93.13(11)	O(2)-Ni(1)-N(1)	90.72(15)
O(1) ^a -Ni(1)-O(2)	88.22(15)	O(2)-Ni(1)-O(2) ^a	180	O(2)-Ni(1)-N(1) ^a	89.28(15)
O(1) ^a -Ni(1)-N(1)	93.13(11)	O(2) ^a -Ni(1)-N(1)	89.28(15)	N(1)-Ni(1)-N(1) ^a	180.00(8)
O(1) ^a -Ni(1)-O(2) ^a	91.78(15)	O(1) ^a -Ni(1)-N(1) ^a	86.87(11)	O(2) ^a -Ni(1)-N(1) ^a	90.72(15)
2					
Co(1)-O(1)	0.204 2(5)	Co(1)-O(3)	0.210 4(2)	Co(1)-N(1)	0.217 8(3)
Co(1)-O(1) ^a	0.204 2(5)	Co(1)-O(3) ^a	0.210 4(2)	Co(1)-N(1) ^a	0.217 8(3)
O(1)-Co(1)-O(3)	89.57(14)	O(1)-Co(1)-N(1)	92.11(16)	O(1)-Co(1)-O(1) ^a	180.0(3)
O(1)-Co(1)-O(3) ^a	90.43(14)	O(1)-Co(1)-N(1) ^a	87.89(16)	O(3)-Co(1)-N(1)	93.87(11)
O(1) ^a -Co(1)-O(3)	90.43(14)	O(3)-Co(1)-O(3) ^a	180.00(14)	O(3)-Co(1)-N(1) ^a	86.13(11)
O(1) ^a -Co(1)-N(1)	87.89(16)	O(3) ^a -Co(1)-N(1)	86.13(11)	N(1)-Co(1)-N(1) ^a	180
O(1) ^a -Co(1)-O(3) ^a	89.57(14)	O(1) ^a -Co(1)-N(1) ^a	92.11(16)	O(3) ^a -Co(1)-N(1) ^a	93.87(11)

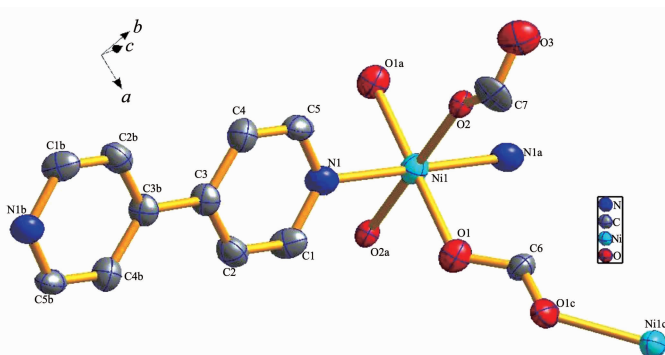
Symmetry codes: ^a 1.5-*x*, 0.5-*y*, -*z*

2 Results and discussion

2.1 Crystal structure

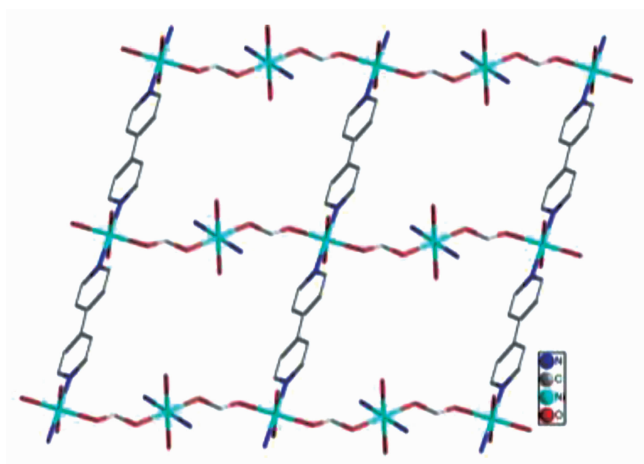
X-ray single-crystal diffraction study reveals that complex **1** crystallizes in the space group $C2/c$. The asymmetric unit of complex **1** contains half a Ni(II) cation, half a biby ligand, one Metha anion and one water molecule. As shown in Fig.1, the central Ni(II) atom is six-coordinate with distorted octahedral coordination geometry, composed of four carboxylic O (O(1), O(1a), O(2), O(2a)) atoms derived from four different Metha anions and two N(N(1), N(1a)) atoms from two different biby ligands. The bond lengths of Ni(1)-N(1), Ni(1)-O(1) and Ni(1)-O(2) are 0.211 7(3), 0.209 5(3) and 0.209 8(4) nm, respectively (Table 2). The biby ligand and Metha link two Ni ions, respectively, giving rise to the two-dimensional rhombic grid planar layers (Fig.2), then the planar layers are further

connected by Metha ligand leading to the formation of a 3D framework. There is a channel with a rhombic cross section in net of the title complex (see Fig.3a), and for the rhombic grid channel, the side lengths are $\sim 1.175\ 04(25)$ and $\sim 1.129\ 17(27)$ nm, respectively, the angles between the two adjacent sides are $\sim 110.017(1)^\circ$ and $\sim 69.893(1)^\circ$, respectively, and the biby from adjacent layers are intercrossing, as shown in Fig.3b. In addition, the distance between two benzene rings from different biby ligand in adjacent layers is 0.400 76 nm, there is weak π - π interactions between the biby ligands, to a certain extent, which can enhance the stability of complex (Fig.3c). As we known, Metha as bridging ligand to construct metal-organic frameworks have seldom been reported. On the other hand, few crystal structure of complexes, in which two biby ligands from adjacent layers are intercrossing have been report to date.



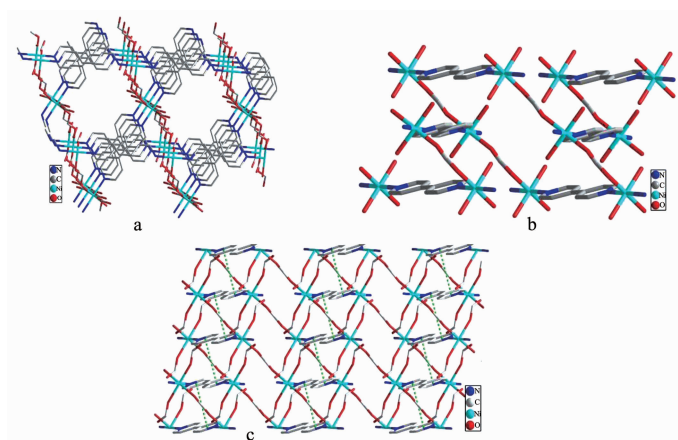
Hydrogen atoms are omitted for clarity; Symmetry codes: a: $1.5-x, 0.5-y, -z$; b: $1-x, -y, -z$; c: $2-x, y, 0.5-z$

Fig.1 Coordination environment of the Ni(II) ion in complex **1**



Hydrogen atoms are omitted for clarity

Fig.2 2D molecular array of complex **1**

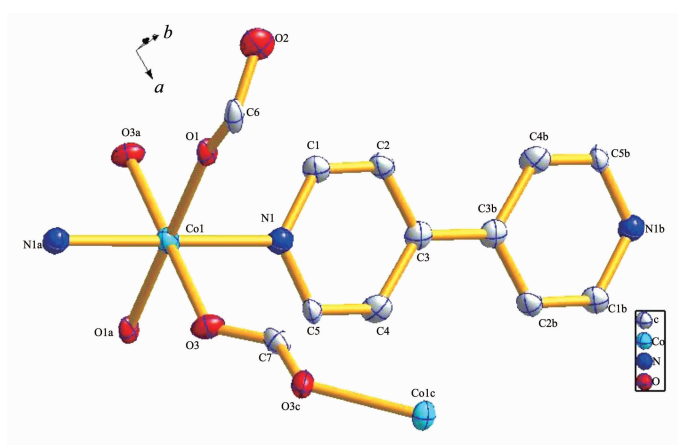


Hydrogen atoms are omitted for clarity

Fig.3 (a) View of the Ni(II) and biby formed 3D networks structure; (b) Intercrossing structure of biby from adjacent layers; (c) π - π interactions between the adjacent 2D layers

The structure of complex **2** is same as the structure of **1**. The complex **2** crystallizes also in the space group $C2/c$. The asymmetric unit of complex **2** contains half a Co(II) cation, one Metha anion, half a biby ligand, and one water molecule. The central Co(II) atom is six-coordinate with distorted octahedral

coordination geometry, composed of four carboxylic O (O(1), O(1a), O(3), O(3a)) atoms from four different Metha anions and two N(N(1), N(1a)) atoms from two different biby ligands (Fig.4). The supramolecular structures of **2** and **1** are kindred, except Co instead of Ni, as shown in Fig.2, Fig.3.



Hydrogen atoms are omitted for clarity; Symmetry codes: a: $1.5-x, 0.5-y, -z$; b: $2-x, 1-y, -z$; c: $2-x, y, 0.5-z$

Fig.4 Coordination environment of the Co(II) ion in complex **2**

2.2 XRD results and thermal analysis

The phase purity of the as-synthesized complexes were confirmed by X-ray powder diffraction (XRD) pattern, which are consistent with the simulated (see Fig.5).

To study the stability of **1** and **2**, thermogravimetric analysis (TGA) was performed on

polycrystalline sample. The TGA curve of two complexes are almost the same, they exhibit three weight loss stages (Fig.6). For complex **1**, the first weight loss of 5.57% occurred over the temperature range 60~145 °C, corresponding to removal of one guest water in the channel (Calcd. 5.58%). The second weight loss of 27.89% between 145 and 260 °C is consistent

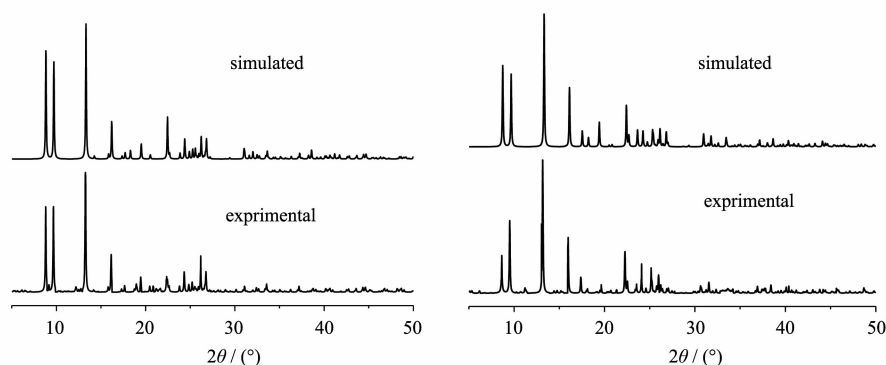


Fig.5 Experimental and simulated X-ray powder diffraction patterns of the complexes **1** (left) and **2** (right)

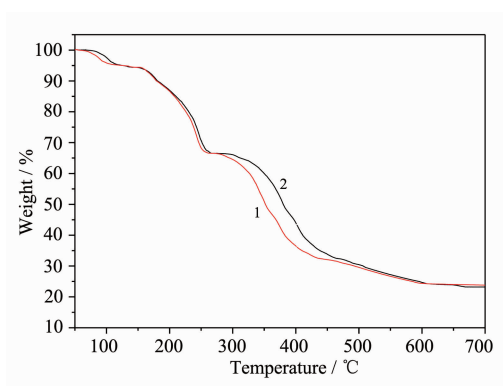


Fig.6 TGA curves of complex **1** and **2**

with removal of one coordinated metha ligand (Calcd. 27.87%). The third weight loss of occurred over the temperature range 260~710 °C. The remaining weight of 23.76% corresponds to the percentage (23.19%) of the Ni and O components, indicating the final product is NiO. For complex **2**, the first weight loss of 5.57% (Calcd. 5.57%) is observed from 70 to 140 °C, which is attributed to the loss of the lattice water, and the second weight loss of 27.87% between 140 and 265 °C is consistent with removal of one coordinated metha ligand (Calcd. 27.85%). The third weight loss of occurred over the temperature range 265~700 °C. The remaining weight of 23.21% corresponds to the percentage (23.18%) of the Co and O components, indicating the final product is CoO.

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