

两个由 5-硝基间苯二甲酸和双咪唑基配体构筑 的锰、钴配合物的合成及晶体结构

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摘要: 通过水热法合成了 2 个新的配合物 $[\text{Mn}(\text{NIPH})(\text{mbix})]_n$ (**1**) 和 $[\text{Co}(\text{NIPH})(\text{mbix})(\text{H}_2\text{O})_3]_{2n} \cdot 2n\text{H}_2\text{O}$ (**2**) (H_2NIPH =5-硝基间苯二甲酸, mbix =1,3-双(咪唑基-1-基)苯)。并对其进行了元素分析、红外光谱、紫外光谱、热重和 X-射线单晶衍射测定。这两个配合物通过氢键和 π - π 相互作用形成了三维超分子网状结构。

关键词: 水热合成; 晶体结构; 锰配合物; 钴配合物

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Syntheses and Crystal Structures of Two Complexes of Manganese, Cobalt Assembled by 5-Nitroisophthalic Acid and Bis(imidazol) Ligands

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Abstract: Two new complex $[\text{Mn}(\text{NIPH})(\text{mbix})]_n$ (**1**) and $[\text{Co}(\text{NIPH})(\text{mbix})(\text{H}_2\text{O})_3]_{2n} \cdot 2n\text{H}_2\text{O}$ (**2**) (H_2NIPH =5-nitroisophthalic acid, mbix =1,3-bis (imidazol-1-ylmethyl)benzene) have been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV spectrum, TG and single-crystal X-ray diffraction. They are further extended into a three-dimensional supramolecular network structure through hydrogen bonds and π - π interactions. CCDC: 979616, **1**; 1011701, **2**.

Key words: hydrothermal synthesis; crystal structure; manganese complex; cobalt complex

0 Introduction

Recently, studies on the synthesis of coordination polymers (CPs) have received much attention in coordination chemistry because of their interesting

molecular topologies and tremendous potential applications in catalysis, molecular selection, non-linear optics, ion exchange and microelectronics^[1-5]. Generally speaking, the structural diversity of such crystalline materials dependent on many factors, such

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as metal ion, templating agents, metal-ligand ratio, pH value, counteranion, and number of coordination sites provided by organic ligands^[6-7]. Among the strategies, the rational selection of organic ligands or coligands according to their length, rigidity, and functional groups is important for the assembly of structural controllable CPs, and a great deal of significant works have been done by using the strategy^[8]. Usually, the organic ligands with bent backbones, such as V-shaped, triangular, quadrangular, and so on, are excellent candidates for building highly high-connected, interpenetrating, or helical coordination frameworks due to their bent backbones and versatile bridging fashions^[9-10]. Besides, the carboxylate groups are good hydrogen-bond acceptor as well as donor, depending upon the degree of deprotonation. Among which, quadrangular polycarboxylic acids, such as 5-nitroisophthalic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 4,4'-oxydibenzoic acid, are paid much attention due to their rich coordination modes^[11]. Apart from the carboxylate linkers, bis(imidazole) bridging ligands with different length and flexibly, such as 1,3-bis(imidazol-1-ylmethyl)benzene, 1,4-bis(imidazol-1-ylmethyl)benzene, 1,4-bis(imidazol-1-yl)-butane are frequently used in the assembly process of CPs as bridging linkers^[12].

Thus, these considerations inspired us to explore new coordination architectures with 5-nitroisophthalic acid (H_2NIPH) and (bis)imidazole bridging linkers (mbix). In this paper, we reported the synthesis and characterizations of two new CPs, namely, $[\text{Mn}(\text{NIPH})(\text{mbix})]_n$ (**1**) and $[\text{Co}(\text{NIPH})(\text{mbix})(\text{H}_2\text{O})_3]_{2n} \cdot 2n\text{H}_2\text{O}$ (**2**), **1** is two-dimensional (2D) network structure and **2** exhibits a zero-dimensional structure with $\text{NIPH-Co-mbix-H}_2\text{O}$ - as building units.

1 Experimental

1.1 General procedures

All materials were commercially purchased and used without further purification. Infrared spectra (KBr pellets) were taken on a Nicolet 6700 spectrometer and elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer.

The TG studies were performed on a Perkin-Elmer TGA7 analyzer. The UV spectrum was obtained on a Shimzu UV-250 spectrometer.

1.2 Synthesis

$[\text{Mn}(\text{NIPH})(\text{mbix})]_n$ (**1**): A mixture of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.12 g), H_2NIPH (0.5 mmol, 0.11 g), mbix (0.5 mmol, 0.12 g) and H_2O (18 mL) was sealed in a 30 mL Teflon-lined autoclave under autogenous pressure at 120 °C for 5 d. After cooling to room temperature, yellow block crystals were collected by filtration and washed with distilled water in 32% yield (based on Mn). Anal. Calcd.(%) for $\text{C}_{22}\text{H}_{17}\text{MnN}_5\text{O}_6$: C, 52.60; H, 3.41; N, 13.94. Found (%): C, 52.12; H, 3.05; N, 13.21. IR (KBr, cm^{-1}): 3 119w, 1 610s, 1 578w, 1 561m, 1 522m, 1 447w, 1 432m, 1 370w, 1 346w, 1 290w, 1 236m, 1 196w, 1 160w, 1 107w, 1 088m, 1 031m, 932m, 851w, 840w, 791m, 774w, 730m, 716w, 656m, 634w, 547w, 524w, 461w.

$[\text{Co}(\text{NIPH})(\text{mbix})(\text{H}_2\text{O})_3]_{2n} \cdot 2n\text{H}_2\text{O}$ (**2**): A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.12 g), H_2NIPH (0.5 mmol, 0.11 g), mbix (0.5 mmol, 0.12 g) and H_2O (18 mL) was sealed in a 30 mL Teflon-lined autoclave under autogenous pressure at 140 °C for 5 d. After cooling to room temperature, purple block crystals were collected by filtration and washed with distilled water in 46% yield (based on Co). Anal. Calcd.(%) for $\text{C}_{44}\text{H}_{50}\text{Co}_2\text{N}_{10}\text{O}_{20}$: C, 45.68; H, 4.36; N, 12.11. Found (%): C, 45.07; H, 3.98; N, 11.76. IR (KBr, cm^{-1}): 3 119w, 1 629s, 1 561m, 1 523m, 1 456w, 1 433w, 1 346m, 1 237m, 1 199w, 1 157w, 1 107w, 1 087s, 1 033m, 941w, 866w, 839w, 791m, 710w, 729w, 659m, 634w, 557w, 527w, 456w, 437w.

1.3 Structure determination

Single crystal diffraction data of **1** and **2** were respectively collected on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromatic $\text{Mo K}\alpha$ ($\lambda=0.071\ 073\ \text{nm}$) radiation at room temperature. The structure was solved by direct methods with SHELXS-97 program^[13] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97^[14]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Hydrogen atoms of water

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

1					
Mn(1)-N(1)	0.218 4(3)	Mn(1)-O(1)	0.211 5(2)	Mn(1)-O(2)#2	0.219 8(2)
Mn(1)-O(3)#1	0.227 8(2)	Mn(1)-O(4)#1	0.229 8(2)	Mn(1)-N(4)#3	0.224 9(3)
O(1)-Mn(1)-N(1)	109.16(10)	O(1)-Mn(1)-N(4)#3	86.32(10)	N(1)-Mn(1)-N(4)#3	88.74(10)
O(1)-Mn(1)-O(2)#2	92.22(9)	O(1)-Mn(1)-O(3)#1	160.37(9)	O(1)-Mn(1)-O(4)#1	102.76(9)
N(1)-Mn(1)-O(2)#2	91.19(9)	N(1)-Mn(1)-O(3)#1	89.87(10)	N(1)-Mn(1)-O(4)#1	146.79(10)
2					
Co(1)-N(1)	0.209 0(3)	Co(1)-O(1)	0.222 8(2)	Co(1)-O(7)	0.210 4(2)
Co(1)-N(4)#1	0.209 8(3)	Co(1)-O(8)	0.234 0(2)	Co(1)-O(9)	0.236 8(3)
N(1)-Co(1)-O(7)	87.55(11)	N(4)#1-Co(1)-O(7)	91.61(11)	N(1)-Co(1)-O(8)	90.51(11)
N(4)#1-Co(1)-O(8)	90.34(11)	O(7)-Co(1)-O(8)	177.86(10)	N(1)-Co(1)-O(9)	89.54(11)
N(4)#1-Co(1)-O(9)	91.79(11)	O(7)-Co(1)-O(9)	89.26(10)	O(8)-Co(1)-O(9)	89.83(9)
N(1)-Co(1)-O(1)	89.94(11)	N(4)#1-Co(1)-O(1)	88.77(11)	O(7)-Co(1)-O(1)	92.69(9)
O(8)-Co(1)-O(1)	88.21(9)	O(9)-Co(1)-O(1)	177.96(9)		

Symmetry transformations used to generate the equivalent atoms: **1**: #1: $x, 1+y, z$; #2: $1-x, -y, -z$; #3: $-1+x, y, 1+z$; **2**: #1: $1-x, 1-y,$

$2-z$.

molecule were located from the different Fourier maps. The selected bond parameters are given in Table 1.

Crystal data for **1**: $C_{22}H_{17}MnN_5O_6$, triclinic, space group $P\bar{1}$, $M_r=502.35$, $a=0.841\ 59(7)$ nm, $b=1.040\ 95(9)$ nm, $c=1.348\ 07(12)$ nm, $\alpha=76.082\ 0(10)^\circ$, $\beta=72.112\ 0(10)^\circ$, $\gamma=74.667(2)^\circ$, $V=1.067\ 43(16)$ nm³, $Z=2$, $F(000)=514$, $\mu(Mo\ K\alpha)=0.670$ mm⁻¹, $D_c=1.563$ g·cm⁻³, 5 752 reflections measured, 4 110 unique ($R_{int}=0.021\ 5$), 3 370 observed reflections with $I>2\sigma(I)$, $R=0.048\ 0$, $wR=0.107\ 8$, $S=1.074$.

Crystal data for **2**: $C_{44}H_{50}Co_2N_{10}O_{20}$, triclinic, space group $P\bar{1}$, $M_r=1\ 156.80$, $a=0.865\ 73(8)$ nm, $b=1.195\ 78(11)$ nm, $c=1.258\ 22(12)$ nm, $\alpha=69.494(2)^\circ$, $\beta=81.480(2)^\circ$, $\gamma=85.311(2)^\circ$, $V=1.205\ 91(19)$ nm³, $Z=1$, $F(000)=598$, $\mu(Mo\ K\alpha)=0.780$ mm⁻¹, $D_c=1.593$ g·cm⁻³, 5 990 reflections measured, 4 151 unique ($R_{int}=0.025\ 3$), 3 281 observed reflections with $I>2\sigma(I)$, $R=0.050\ 9$, $wR=0.120\ 3$, $S=1.083$.

CCDC: 979616, **1**; 1011701, **2**.

2 Results and discussion

2.1 IR spectrum

Complex **1**: The COO⁻ is coordinated with its asymmetric and symmetric stretching appearing at

1 610 cm⁻¹ ($\nu(OCO)_{asym}$) and 1 432 cm⁻¹ ($\nu(OCO)_{sym}$)^[15], respectively. The $\Delta\nu(\nu(OCO)_{asym}-\nu(OCO)_{sym})$ is 178 cm⁻¹ (<200), showing the presence of bidentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as bidentate ligands via the carboxylate groups^[16].

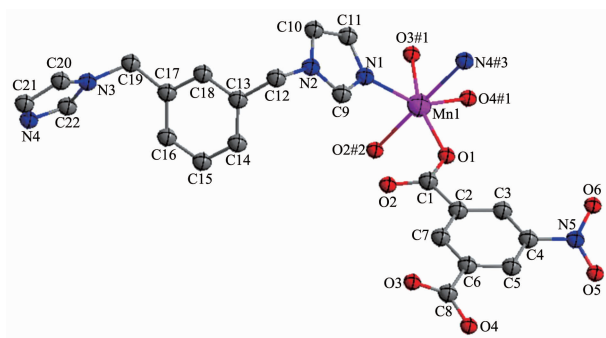
Complex **2**: The COO⁻ is coordinated with its asymmetric and symmetric stretching appearing at 1 629 cm⁻¹ ($\nu(OCO)_{asym}$) and 1 346 cm⁻¹ ($\nu(OCO)_{sym}$)^[15], respectively. The $\Delta\nu(\nu(OCO)_{asym}-\nu(OCO)_{sym})$ are 283 cm⁻¹ (>200), showing the presence of monodentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as monodentate ligands via the carboxylate groups^[16].

In addition, X-ray diffraction analysis further indicates the bidentate coordination manners of carboxylate groups in **1** and monodentate coordination manners of carboxylate groups in **2**.

2.2 Description of the structure

Complex **1** crystallizes in the triclinic space group $P\bar{1}$ and features a two-dimensional (2D) network structure. The coordination environment of Mn(II) in **1** is shown in Fig.1. There are one Mn(II) ion, one NIPH ligand and one mbix ligand in the asymmetric unit. Each Mn(II) ion is six-coordinated by four carboxylate

oxygen atoms (O (1), O (2)#2, O (3)#1, O (4)#1) from three different NIPH ligands and two nitrogen donors (N(1) and N(4)#3) from two flexible mbix molecules to furnish a distorted octahedral coordination architecture. The bond distances of Mn-O in compound **1** fall in range of the 0.211 5 (2)~0.229 8 (2) nm, and Mn-N bond length fall in the range of 0.218 4(3)~0.224 9(3) nm, which are in the normal range and the coordination angles around Mn atom are in the range 57.71(8)°~178.42(9)°. In the coordination environment, the three carboxylate oxygen atoms (O(1), O(3)#1, O(4)#1) and one imidazole nitrogen atom (N(1)) are located in the basal plane, whereas one carboxylate oxygen atom (O(2)#2) and one imidazole nitrogen atom (N(4)#3) occupy the axial positions from the opposite direction.



Symmetry codes: #1: $x, y+1, z$; #2: $1-x, -y, -z$; #3: $x-1, y, z+1$

Fig.1 Coordination environment of the Mn(II) center

In **1**, each NIPH ligand adopts $\mu_3\text{-}\eta^1:\eta^1:\eta^1:\eta^1$ coordination mode to bridge Mn^{II} atoms into an infinite 1D chain, which alternately contains 8-membered rings and 16-membered rings with Mn...Mn distances of 0.462 3 and 0.766 7 nm, respectively (Fig.2a), and is similar to the reported complex [Cd(nip)(bix)_{0.5}H₂O]_n [12g]. Moreover, the mbix ligands adopt *cis*-conformation bridging mode with a dihedral angle between the two imidazole rings of 79.02°, and pillar these 1D chains into 2D coordination network (Fig.2b). Further investigation of the crystal packing of compound **1** suggests that there are one kinds of C-H...O hydrogen bonding interactions between carboxylate oxygen atom and carbon atoms of mbix ligands in complex **1** (Table 2). Moreover, there are π - π interactions in complex **1** between benzene rings of mbix ligands. The centroid-to-centroid distance between adjacent ring is 0.361 7(2) nm for C13C14 C15C16C17C18 and C13' C14' C15' C16' C17' C18' (Symmetry codes: $1-x, -y, -1+z$) benzene rings. The perpendicular distance is 0.342 0(5) nm for C13C14 C15C16C17C18 and C13' C14' C15' C16' C17' C18' (Symmetry codes: $1-x, -y, -1+z$) benzene rings. Therefore, through hydrogen bonds and π - π interactions, the two-dimensional networks are further extended into a three-dimensional supramolecular

Table 2 Hydrogen bonds for **1** and **2**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
1				
C(7)-H(7A)...O(3)	0.093	0.259	0.322 7(4)	126
C(14)-H(14A)...O(4)	0.093	0.258	0.314 80	144
C(14)-H(14A)...O(1)	0.093	0.248	0.339 72	147
C(18)-H(18A)...O(5)	0.093	0.252	0.340 56	159
C(20)-H(20A)...O(4)	0.093	0.247	0.335 99	161
C(22)-H(22A)...O(4)	0.093	0.254	0.307 88	117
2				
O(7)-H(7B)...O(4)	0.082 0	0.185 1	0.267 1	178
O(7)-H(7C)...O(10)	0.083 4	0.189 5	0.270 0	162
O(8)-H(8A)...O(2)	0.082 0	0.185 6	0.262 7	156
O(8)-H(8B)...O(2)	0.074 6	0.214 9	0.283 4	153
O(9)-H(9B)...O(3)	0.077 7	0.210 7	0.286 7	166
O(9)-H(9C)...O(3)	0.080 7	0.200 0	0.280 5	175
O(10)-H(10B)...O(1)	0.087 1	0.197 2	0.278 1	154
O(10)-H(10C)...O(4)	0.080 7	0.197 7	0.276 2	164

framework (Fig.3).

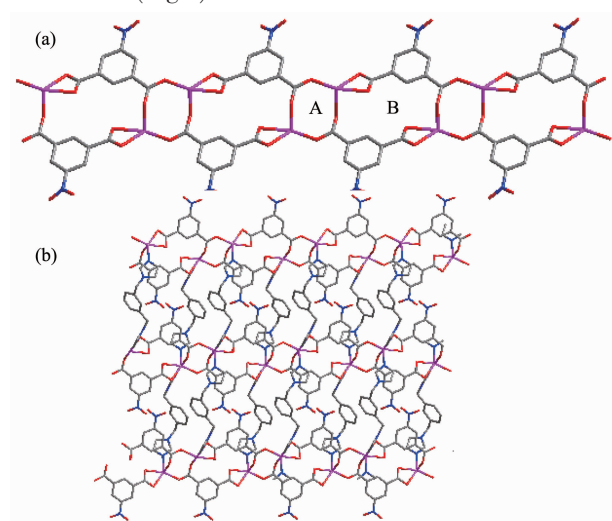


Fig.2 (a) 1D chain structure of complex **1** with alternately contain 8-member (A) ring and 16-member (B) ring; (b) 2D network structure of complex **1**

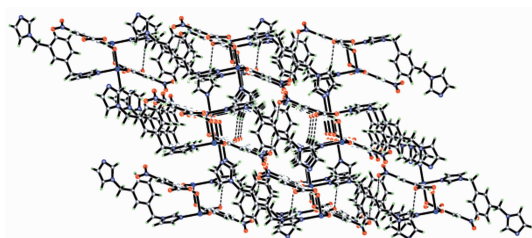
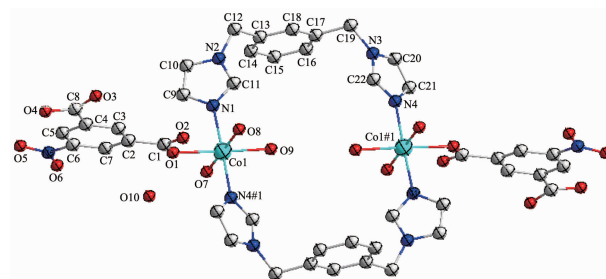


Fig.3 View of the 3D supramolecular architecture of **1** formed by hydrogen-bonding and π - π interactions

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ and exhibits a zero-dimensional structure. The molecular structure of compound **2** is shown in Fig.4. There are two coordination centers, Co(1) and Co(1)#1, in the crystal with the same coordination modes. The Co(1) ion is six-coordinated by one carboxylate oxygen atoms (O(1)) from NIPH ligand, two nitrogen atoms (N(1), N(4)#1) from two different mbix ligands and three coordinated water molecular (O(7), O(8), O(9)), showing a slightly distorted octahedral geometry. The Co-O bond distances are in the range of 0.209 0~0.222 8(2) nm, and those of Co-N are from 0.209 0(3) to 0.209 8(3) nm. The N(O)-Co-O(N) angles fall in the range of 87.55(11)°~178.43(11)°.

One coordination mode of the NIPH ligand is present in the structure of compound **2**, namely monodentate bridging mode. The mbix ligand exhibits



Symmetric code: #1: 1-x, 1-y, 2-z

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

cis-conformation bridging mode with a dihedral angle between the two imidazole rings of 51.32°, based on this, two Co (II) ions are linked by mbix ligands to yield a binuclear unit with 24-number ring. The Co...Co distance linked by mbix ligand is 0.799 4 nm.

There are persistent O-H...O hydrogen bonding interactions in the complex (Table 2), which play an important role in stabilizing the network structure. Moreover, there are π - π interactions in complex **2** between benzene rings of NIPH and mbix ligands (Table 3). Therefore, through hydrogen bonds and π - π interactions, the network structures are further extended into a three-dimensional supramolecular framework (Fig.5).

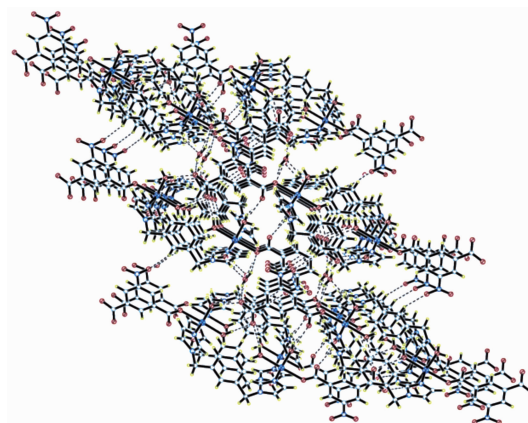


Fig.5 View of the 3D supramolecular architecture of **2** formed by hydrogen-bonding and π - π interactions

To investigate whether the analyzed crystal structures are truly representative of the bulk materials, powder X-ray diffraction (PXRD) technologies have been performed for the complex **1** and **2** at room temperature (Fig.6). The main peak positions observed are in good agreement with the simulated ones.

Table 3 Parameters between the planes in **2**

Plane	Distance between ring centroids / nm	Dihedral angle / (°)	Perpendicular distance of plane (I) on ring J / nm	Perpendicular distance of plane (J) on ring I / nm	Symmetry codes
C2C3C4C5C6C7->C2'C3'C4'C5'C6'C7'	0.402 8(2)	0	-0.376 35(15)	-0.376 34(15)	1-x, -y, 1-z
C2C3C4C5C6C7->C13C14C15C16C17C18	0.403 2(2)	10.74(18)	0.353 94(15)	0.348 48(16)	2-x, 1-y, 1-z
C13C14C15C16C17C18->C13'C14'C15'C16'C17'C18'	0.404 7(2)	0	-0.330 30(16)	-0.330 31(16)	2-x, 1-y, 2-z

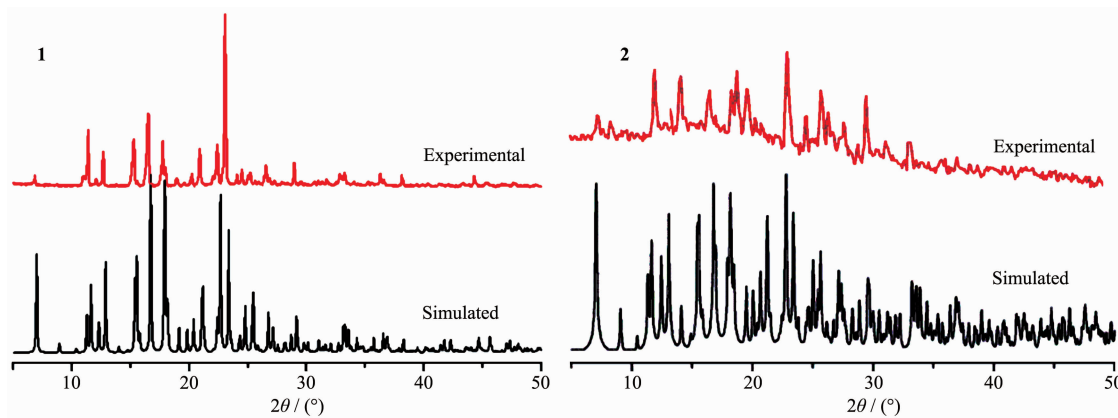


Fig.6 PXRD analysis of the complex

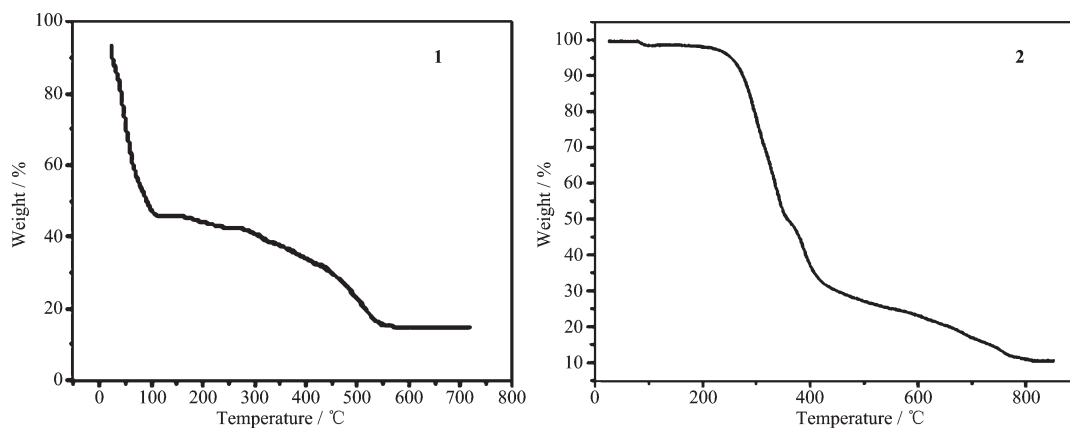
Although minor differences can be found in the positions, widths, and intensities of some peaks, it still can be considered that the bulk synthesized materials and the analyzed crystal are homogeneous. The differences may be due to the preferred orientation of the powder samples^[17-18].

2.3 Thermal analysis

TG curve of **1** (Fig.7) show that the first weight loss of 45.9% from 22 to 115 °C corresponds to the removal of mbix ligand (Calcd. 47.4%). Upon further heating, an obvious weight loss (39.6%) occurs in the temperature range of 115~550 °C, corresponding to the release of NIPH ligand (Calcd. 41.6%). After 550

°C no weight loss is observed, which means the complete decomposition of **1**. The residual weight should be MnO.

TG curve of **2** (Fig.7) shows that the first weight loss of 50.03% from 37 to 414 °C corresponds to the removal of water molecules and NIPH ligand (Calcd. 48.6%). Upon further heating, an obvious weight loss (40.1%) occurs in the temperature range of 414~809 °C, corresponding to the release of mbix ligands (Calcd. 41.2%). After 809 °C no weight loss is observed, which means the complete decomposition of **1**. The residual weight should be CoO.

Fig.7 TG curve of complex **1** and **2**

2.4 UV spectrum

The UV spectra for the compound **1**, compound **2**, H₂NIPH and mbix ligands have been investigated in the solid state. H₂NIPH has one absorption band at about 274 nm and mbix has one absorption band at

about 277 nm, while the title compound **1** and **2** have one absorption band at about 279, 344 nm, respectively (Fig.9), which should be assigned to the $n \rightarrow \pi^*$ transition of mbix and the charge transfer transition^[19].

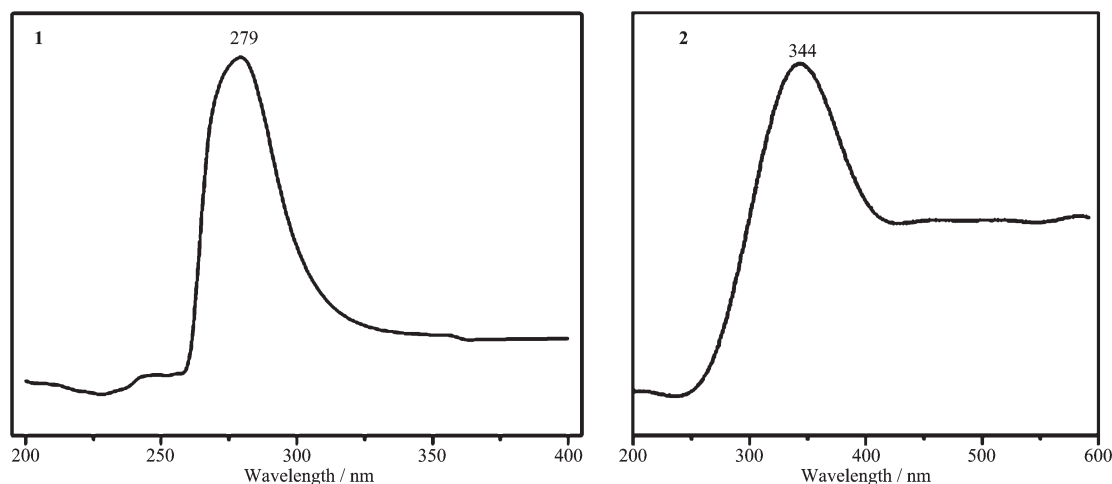


Fig.8 UV spectra of complexes **1** and **2**

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