

以 2-(4'-氯苯甲酰基)苯甲酸及联吡啶为配体的锌、钴两个链状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 $[\text{Zn}(\text{cbba})_2(\text{bipy})_{0.5}]_n$ (**1**) 和 $[\text{Co}(\text{cbba})_2(\text{bipy})(\text{H}_2\text{O})_2]_n$ (**2**) (Hcbba=2-(4'-氯-苯甲酰基)苯甲酸, bipy=4,4'-联吡啶)。并对其进行了元素分析、红外光谱、热重和 X-射线单晶衍射测定。它们都呈现一维链状结构。

关键词: 水热合成; 晶体结构; 配合物

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Synthesis and Crystal Structure of Two Chain-Like Complexes of Zinc, Cobalt with 2-(4'-Chlorine-benzoyl)benzoic Acid and Bipyridine Ligands

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Abstract: Two new complexes $[\text{Zn}(\text{cbba})_2(\text{bipy})_{0.5}]_n$ (**1**) and $[\text{Co}(\text{cbba})_2(\text{bipy})(\text{H}_2\text{O})_2]_n$ (**2**) (Hcbba=2-(4'-chlorine-benzoyl)benzoic acid, bipy=4,4'-bipyridine) have been hydrothermally synthesized and structurally characterized by elemental analysis, IR, TG and single-crystal X-ray diffraction. They all exhibit one-dimensional chain-like structure. CCDC: 824487, **1**; 824486, **2**.

Key words: hydrothermal synthesis; crystal structure; complex

0 Introduction

Recently, the design and synthesis of coordination compounds have attracted much attention due to their diversity structures^[1] and potential applications^[2-7]. A successful strategy for preparing coordination compounds is the assembly reaction between a transition metal ion and two types of organic ligands, one acting as a terminal ligand and the other as a bridging ligand.

In this aspect, the bridging ligand 4,4'-bipyridine has been widely used in the construction of metal-organic coordination polymers^[8]. In addition, as a rigid

and versatile ligand, 2-(4'-chlorine-benzoyl)benzoic acid (Hcbba) has been relatively less studied to construct coordination compounds containing transition metals^[9].

The hydrothermal technique is well suited to the preparation of crystals of synthetic minerals, new inorganic materials, and organometallic coordination polymers. Of particular interest to us is the construction of transition metal polymers with new structural features by utilizing hydrothermal synthesis. To extend our recent work^[9], the complex $[\text{Zn}(\text{cbba})_2(\text{bipy})_{0.5}]_n$ (**1**) and $[\text{Co}(\text{cbba})_2(\text{bipy})(\text{H}_2\text{O})_2]_n$ (**2**) were obtained by using Hcbba and bipy ligands, and they all show one-

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dimensional chain-like structure.

1 Experimental

1.1 Synthesis

[Zn(cbba)₂(bipy)_{0.5}]_n (**1**). A mixture of Zn(OAc)₂ · 2H₂O (0.088 g, 0.4 mmol), Hcbba (0.052 g, 0.2 mmol), bipy (0.030 g, 0.2 mmol) and H₂O (18 mL) was sealed in a 30 mL Teflon-lined autoclave under autogenous pressure at 150 °C for seven days. After cooling to room temperature, colorless block crystals were collected by filtration and washed with distilled water in 39% yield (based on Zn). Anal. calcd. for C₃₃H₂₀Cl₂NO₆Zn(%): C, 59.80; H, 3.04; N, 2.11. Found (%): C, 59.78; H, 3.01; N, 2.09. IR (KBr, cm⁻¹): 3 069w, 2 361w, 1 686w, 1 671w, 1 646s, 1 611w, 1 589m, 1 572w, 1 484m, 1 445w, 1 402s, 1 273w, 1 250w, 1 220w, 1 176w, 1 151w, 1 088s, 1 049w, 1 015m, 932s, 896w, 840m, 822w, 814w, 751s, 723w, 715w, 696w, 675m, 652w, 647m, 528m, 487w, 458w.

[Co(cbba)₂(bipy)(H₂O)₂]_n (**2**). A mixture of CoCl₂ · 6H₂O (0.048 g, 0.2 mmol), Hcbba (0.052 g, 0.2 mmol), bipy (0.030 g, 0.2 mmol) and H₂O (18 mL) was sealed in a 30 mL Teflon-lined autoclave under autogenous pressure at 140 °C for seven days. After cooling to room temperature, pink block crystals were collected by

filtration and washed with distilled water in 37% yield (based on Co). Anal. calcd. for C₃₈H₂₈Cl₂CoN₂O₈(%): C, 59.24; H, 3.66; N, 3.64. Found (%): C, 59.22; H, 3.62; N, 3.59. IR (KBr, cm⁻¹): 3 422m, 2 926w, 1 678s, 1 605m, 1 588m, 1 567w, 1 543w, 1 483m, 1 445w, 1 409s, 1 300w, 1 286w, 1 274w, 1 261w, 1 220w, 1 149w, 1 089s, 1 069w, 1 045w, 1 013w, 932s, 888w, 844w, 815m, 770w, 745m, 718m, 684w, 672w, 652w, 631w, 531w, 482w, 441w.

1.2 Structure determination

Single crystal diffraction data of **1** and **2** were respectively collected on a Bruker SMART APEX-CCD diffractometer equipped with a graphite-monochromatic Mo K α (λ =0.071 073 nm) radiation at room temperature. The structure was solved by direct methods with SHELXS-97 program^[10] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97^[11]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. The selected bond parameters are given in Table 1.

Crystal data for **1**: C₃₃H₂₀Cl₂NO₆Zn, monoclinic, space group $C2/c$, M_r =662.77, a =1.823 8(3), b =1.411 8(2), c =2.460 9(4) nm, β =111.299(2)°, V =

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

1					
Zn(1)-O(2)	0.203 3(2)	Zn(1)-O(4)	0.203 9(2)	Zn(1)-N(1)	0.202 7(3)
Zn(1)-O(2A)	0.203 3(2)	Zn(1)-O(4A)	0.203 9(2)		
N(1)-Zn(1)-O(2)	105.90(6)	O(2)-Zn(1)-O(4)	87.75(10)	O(2)-Zn(1)-O(4A)	87.72(10)
N(1)-Zn(1)-O(2A)	105.90(6)	O(2A)-Zn(1)-O(4)	87.72(10)	O(2A)-Zn(1)-O(4A)	87.75(10)
O(2)-Zn(1)-O(2A)	148.21(13)	N(1)-Zn(1)-O(4A)	98.29(6)	O(4)-Zn(1)-O(4A)	163.41(12)
N(1)-Zn(1)-O(4)	98.29(6)				
2					
Co(1)-O(1)	0.209 4(2)	Co(1)-O(4)	0.206 1(2)	Co(1)-N(1)	0.219 7(3)
Co(1)-O(1A)	0.209 4(2)	Co(1)-O(4A)	0.206 1(2)	Co(1)-N(1A)	0.219 7(3)
O(4)-Co(1)-O(4A)	180.00(10)	O(1)-Co(1)-O(1A)	180.0	O(4A)-Co(1)-N(1)	93.25(10)
O(4)-Co(1)-O(1)	88.73(10)	O(4)-Co(1)-N(1A)	93.25(10)	O(1)-Co(1)-N(1)	89.09(9)
O(4A)-Co(1)-O(1)	91.27(10)	O(4A)-Co(1)-N(1A)	86.75(10)	O(1A)-Co(1)-N(1)	90.91(9)
O(4)-Co(1)-O(1A)	91.27(10)	O(1)-Co(1)-N(1A)	90.91(9)	N(1A)-Co(1)-N(1)	180.00(14)
O(4A)-Co(1)-O(1A)	88.73(10)	O(1A)-Co(1)-N(1A)	89.09(9)		
O(4A)-Co(1)-O(1)	91.25(10)	O(4)-Co(1)-N(1)	86.75(10)		

Symmetry transformations used to generate the equivalent atoms: **1**: A: 1-x, y, -z+1/2; **2**: A: -x+1, -y, -z+1.

5.903 4(15) nm³, $Z=8$, $F(000)=2\ 696$, $\mu(\text{Mo } K\alpha)=1.060$ mm⁻¹, $D_c=1.491$ g·cm⁻³, 21 966 reflections measured, 7 209 unique ($R_{\text{int}}=0.065\ 9$), 4 164 observed reflections with $I>2\sigma(I)$, $R=0.051\ 0$, $wR=0.101\ 6$, $S=1.036$.

Crystal data for **2**: C₃₈H₂₈Cl₂CoN₂O₈, triclinic, space group $P\bar{1}$, $M_r=770.45$, $a=0.543\ 0(4)$, $b=1.147\ 5(8)$, $c=1.533\ 2(10)$ nm, $\alpha=68.864(6)^\circ$, $\beta=81.264(6)^\circ$, $\gamma=79.084(6)^\circ$, $V=0.871\ 2(10)$ nm³, $Z=1$, $F(000)=395$, $\mu(\text{Mo } K\alpha)=0.702$ mm⁻¹, $D_c=1.468$ g·cm⁻³, 6 501 reflections measured, 3 283 unique ($R_{\text{int}}=0.038\ 9$), 2 064 observed reflections with $I>2\sigma(I)$, $R=0.055\ 2$, $wR=0.123\ 9$, $S=1.061$.

CCDC: 824487, **1**; 824486, **2**.

2 Results and discussion

2.1 IR spectrum

Complex **1**: The COO⁻ is coordinated with its asymmetric and symmetric stretching appearing at 1 589 cm⁻¹ ($\nu(\text{OCO})_{\text{asym}}$) and 1 402 cm⁻¹ ($\nu(\text{OCO})_{\text{sym}}$)^[12], respectively. The $\Delta\nu(\nu(\text{OCO})_{\text{asym}}-\nu(\text{OCO})_{\text{sym}})$ are 187 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 carboxylic carboxylate groups^[13].

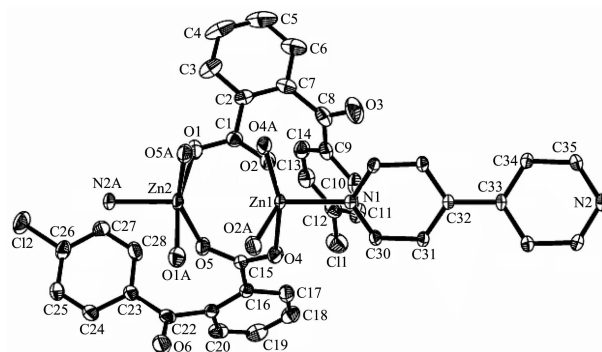
Complex **2**: The COO⁻ is coordinated with its asymmetric and symmetric stretching appearing at 1 678 cm⁻¹ ($\nu(\text{OCO})_{\text{asym}}$) and 1 409 cm⁻¹ ($\nu(\text{OCO})_{\text{sym}}$)^[12], respectively. The $\Delta\nu(\nu(\text{OCO})_{\text{asym}}-\nu(\text{OCO})_{\text{sym}})$ are 269 cm⁻¹ (>200), showing the presence of monodentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as monodentate ligands via the carboxylic carboxylate groups^[13].

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

2.2 Description of the structure

Complex **1** crystallizes in $C2/c$ space group and consists of a one-dimensional chain-like structure. The molecular structure of **1** is shown in Fig.1. There are one Zn(II) ion, half bipy ligand and two cbba ligands in the asymmetric unit. The Zn(1) ion is five-coordinated by four carboxylate oxygen atoms (O(2), O(2A), O(4), O

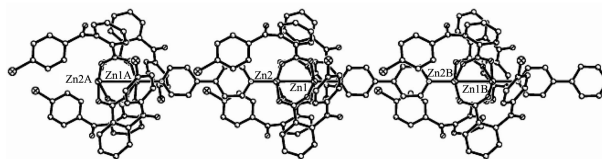
(4A)) from four different cbba ligands and one nitrogen atoms N(1) from bipy ligand, showing a slightly distorted square-pyramidal geometry. The N(1) atom locates at the apex site, four carboxylate oxygen atoms (O(2), O(2A), O(4), O(4A)) define an equatorial plane. The bond distance of Zn-O in compound **1** fall in the range of 0.203 3(2)~0.239 2(2) nm, and that of Zn-N is 0.202 7(3) nm. The N(O)-Zn-O(N) angles range from 87.72(10)° to 163.41(12)°.



Symmetry code: A: 1-x, y, -z+1/2

Fig.1 Molecular structure of complex **1**

One coordination mode of the cbba ligand is present in the structure of compound **1**, namely bidentate bridging mode. The bipy ligand also exhibits classic bridging mode, based on this, two Zn(II) ions are linked by cbba ligands to yield dinuclear subunits, each pair of the dinuclear are bridged by bipy ligands to yield a one-dimensional chain-like structure, as depicted in Fig.2. The Zn...Zn distance linked by bipy ligand along the chain direction is 1.112 3 nm. In addition, there are C-H...O hydrogen bonding interactions in compound **1** (Table 2). By virtue of C-H...O interactions, compound **1** forms a three-dimensional supramolecular network.



Symmetry code: A: x, y-1, z; B: x, y+1, z

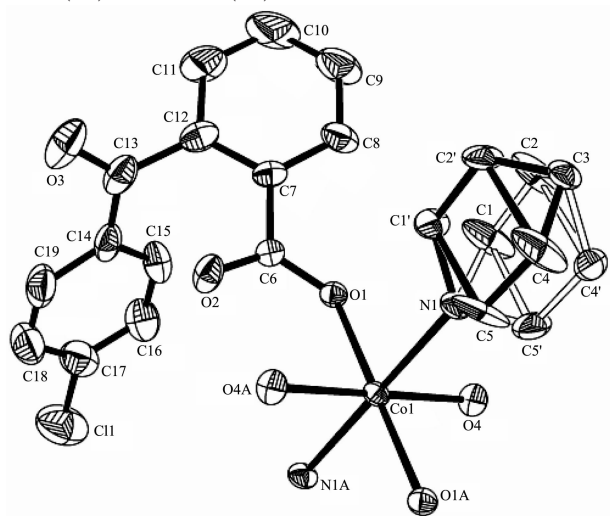
Fig.2 A view of the one-dimensional architecture for **1**

Complex **2** crystallizes in $P\bar{1}$ space group and consists of a one-dimensional chain-like structure. The molecular structure of **2** is shown in Fig.3. There are half Co(II) ion, half bipy ligand, one coordinated water

Table 2 Hydrogen bonds for complex 1

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠(DHA) / (°)
C(20)-H(20A)···O(3)	0.093	0.226	0.318 2(5)	173
C(20)-H(20A)···O(4)	0.093	0.259	0.316 1(4)	120

molecules and one cbba ligands in the asymmetric unit. The Co(1) ion is six-coordinated by two carboxylate oxygen atoms (O(1), O(1A)) from two different cbba ligands, two coordinated water molecules (O(4), O(4A)) and two nitrogen atoms (N(1), N(1A)) from two different bipy ligands, showing a slightly distorted octahedral geometry. Two carboxylate oxygen atoms and two coordinated water molecules (O(1), O(1A), O(4), O(4A)) define an equatorial plane, while the axial coordination sites are occupied by two nitrogen atoms (N(1), N(1A)). The bond distances of Co-O in compound 1 fall in the range of 0.206 0(2)~0.209 4(2) nm, and those of Co-N are 0.219 7(3) nm. The N(O)-Co-O(N) angles range from 86.69(10)° to 180.00(13)°.

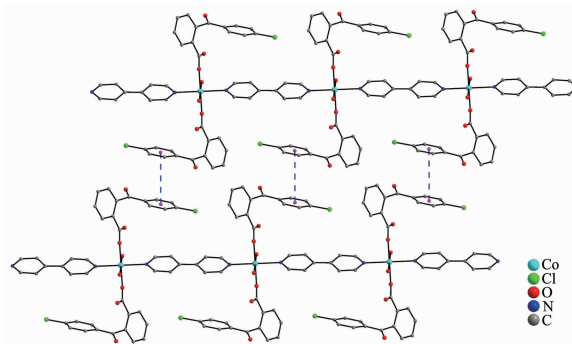


Symmetric code: A: $-x+1, -y, -z+1$

Fig.3 Molecular structure of complex 2

One coordination mode of the cbba ligand is present in the structure of complex 2, namely monodentate bridging mode. The bipy ligand also exhibits classic bridging mode, based on this, two Co(II) ions are linked by bipy ligands to form a one-dimensional chain-like structure. The Co···Co distance along the chain direction is 1.147 5 nm. In addition, there are aromatic π - π stacking interactions between neighboring chains in complex 2. The centroid-to-centroid distance between two adjacent phenyl rings

(C14C15C16C17C18C19 and C14'C15'C16'C17'C18'C19'; symmetry code: $x, -y, 2-z$) arising from cbba ligands is 0.444 7 nm. The perpendicular distance between such two rings is 0.416 9 nm, which is reasonable^[14]. By virtue of π - π interactions, complex 2 forms a three-dimensional supramolecular network (Fig.4).

Fig.4 Perspective view of the 3D supramolecular network along the *a* axis

2.3 Thermal analysis

TG curve of 1 shows that the first weight loss of 12.9% from 78 to 283 °C corresponds to the removal of bipy ligands (calcd. 13.6%). Upon further heating, an obvious weight loss (75.9%) occurs in the temperature range of 283~628 °C, corresponding to the release of cbba ligands (calcd. 76.5%). After 628 °C no weight loss is observed, which means the complete decomposition of 1. The residual weight should be ZnO.

TG curve of 2 shows that the first weight loss of 25.2% from 23 to 149 °C corresponds to the removal of coordinated water molecules and bipy ligand (calcd. 24.9%). Upon further heating, an obvious weight loss (63.8%) occurs in the temperature range of 149~782 °C, corresponding to the release of cbba ligands (calcd. 67.4%). After 782 °C no weight loss is observed, which means the complete decomposition of 2. The residual weight should be CoO.

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