

## 含 2-苯氧基丙酸根的镍、锌配位聚合物的合成与晶体结构

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**摘要:** 用溶液法和水热法分别合成了 2 个含 2-苯氧基丙酸配体(HL)的聚合物  $[\text{NiL}_2(\text{H}_2\text{O})_2(\text{bipy})] \cdot 2\text{H}_2\text{O}$  (**1**)、 $[\text{ZnL}_2(\text{bipy})] \cdot 2\text{H}_2\text{O}$  (**2**)(bipy=4,4'-联吡啶), 用元素分析、红外光谱、热重和单晶 X-射线衍射对产物进行了表征。在化合物 **1** 中, 镍原子与 2 个羧基氧原子、2 个配位水氧原子及 2 个 4,4'-联吡啶的 2 个氮原子配位, 配位数为 6, 镍原子的配位构型为畸变的八面体; 而在化合物 **2** 中, 锌原子与 2 个羧基氧原子及 2 个 4,4'-联吡啶中的 2 个氮原子配位, 锌原子的配位构型为畸变的四面体。在这 2 个化合物里, 4,4'-联吡啶通过氮原子连接金属原子形成一维链状。链间氢键与  $\pi$ - $\pi$  堆积作用又将一维链链接成二维层状结构。

**关键词:** 2-苯氧基丙酸; 配位聚合物; 合成; 晶体结构

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## Synthesis and Crystal Structures of Nickel(II) and Zinc(II) Coordination Polymers with 2-Phenoxypropionic Acid

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**Abstract:** Two coordination polymers based on 2-phenoxypropionic acid (HL,  $\text{C}_9\text{H}_{10}\text{O}_3$ ),  $[\text{NiL}_2(\text{H}_2\text{O})_2(\text{bipy})] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{ZnL}_2(\text{bipy})] \cdot 2\text{H}_2\text{O}$  (**2**) (bipy=4,4'-bipyridine) were synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric analyses and single crystal X-ray diffraction. In the complex **1**, the metal atoms are coordinated to two carboxylic oxygen atoms, two oxygen atoms from two water molecules and two nitrogen atoms from two 4,4'-bipyridine ligand. The nickel atoms are six coordinated in a distorted octahedron geometry. The zinc atoms are four coordinated to two carboxylic oxygen atoms and two nitrogen atoms from two 4,4'-bipyridine ligand in a distorted tetrahedron environment for complex **2**. The 4,4'-bipyridine ligands in both compounds connect the metal atoms into single dimensional chains by nitrogen atoms. Interchain hydrogen bonds and  $\pi$ - $\pi$  stacking interactions link the 1D chains into 2D layers and strengthen the stability of molecular structure. CCDC: 820470, **1**; 820471, **2**.

**Key words:** 2-phenoxypropionic acid; coordination polymer; synthesis; crystal structure

There has been great interest put in the field of coordination polymeric complexes owing to their fascinating molecular topologies<sup>[1-3]</sup> along with potential applications as functional materials<sup>[4-6]</sup>. In particular,

complexes with helical structures and 1D chain attract much attention of scientists<sup>[7-8]</sup> mainly due to their similarity to the structure of DNA molecule. To obtain new complexes, solv- and hydrothermal routes are

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currently used. In this way, the organic ligand acts as a template whereas the metal ions read stereo and interactive information stored in the ligand through the algorithm defined by their coordination geometry, the structure of the product being closely related to the geometry and the number of coordination sites provided by the ligand. As is well known, aromatic carboxylic ligands are good building units in the synthesis of coordination polymeric complexes owing to their versatile coordination modes. Aromatic carboxylic acid may form many interesting structures by hydrogen bonds and  $\pi$ - $\pi$  stacking interactions including rich coordination modes. In particular,  $\pi$ - $\pi$  stacking interactions between aromatic rings are important for structural stabilization and various regulatory processes<sup>[9-11]</sup>. Herein, we report the synthesis and crystal structures of two novel coordination polymers from nickel(II) and zinc(II) with 2-phenoxypropionic acid (HL) and 4,4'-bipyridine (bipy).

## 1 Experimental

All reagents were of analytical grade and used without further purification. Elemental analysis was performed on C,H,N elemental analyzer, Elementar Vario EL III. FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4 000~400  $\text{cm}^{-1}$ . A Mettler Toledo thermal analyzer TGA/SDTA 851<sup>e</sup> was used to carry out the thermoanalytical analysis with a heating rate of 10  $^{\circ}\text{C} \cdot \text{min}^{-1}$  from 30 to 800  $^{\circ}\text{C}$  in air atmosphere. Diffraction data were collected at 293(2) K on a Bruker APEXII CCD diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ).

### 1.1 Synthesis of $\{[\text{NiL}_2(\text{H}_2\text{O})_2(\text{bipy})]\cdot 2\text{H}_2\text{O}\}_n$ (1)

2-Phenoxypropionic acid (1 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol) and 4,4'-bipyridine (1 mmol) were dissolved in 20 mL ethanol, then 10 mL water was added to the above solution and the mixed was stirred for 12 h. After

filtration, the filter solution was allowed to stand at room temperature, and single crystals suitable for X-ray work were obtained after a week. Yield 30% (based on  $\text{NiCl}_2$ ). Elemental anal. calcd. for  $\text{C}_{28}\text{H}_{34}\text{NiN}_2\text{O}_{10}$  (%): C, 54.43; H, 5.51; N, 4.54; found(%): C, 54.24; H, 5.73; N, 4.21.

### 1.2 Synthesis of $\{[\text{ZnL}_2(\text{bipy})]\cdot 2\text{H}_2\text{O}\}_n$ (2)

A mixture of 2-phenoxypropionic acid (1 mmol), new-made  $\text{Zn}(\text{OH})_2$  (0.5 mmol), 4,4'-bipyridine (1 mmol) and 30 mL water was sealed in a 50 mL stainless steel reactor and kept five days at temperature of 433 K. Then the reactor was cooled to room temperature at a speed of 3  $^{\circ}\text{C}$  per hour. Filtrate the solution, washing deposition with ethanol, and colorless blocky crystals can be attained. Yield 35% (based on  $\text{Zn}(\text{OH})_2$ ). Elemental anal. calcd. for  $\text{C}_{28}\text{H}_{30}\text{ZnN}_2\text{O}_8$  (%): C, 57.15; H, 5.10; N, 4.76; found(%): C, 57.09; H, 5.25; N, 4.58.

### 1.3 Crystal structure determination

Intensity data of the complexes were measured at 293 K on a Bruker APEXII CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ). Structures were solved by direct methods using SHELXS-97<sup>[12]</sup> and refined on the  $F^2$  by full-matrix least-square method with SHELXL-97<sup>[13]</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and fined as riding atoms with a common fixed isotropic thermal parameter. Aromatic hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent C atom at distances of 0.093 nm with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ . H atoms of water molecule were located in a difference Fourier map and included in the subsequent refinement using restraints (O-H 0.085 nm and  $\text{H}\cdots\text{H}$  0.135 nm) with  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$ . Experimental details for X-ray data collection are presented in Table 1, and the selected bond lengths and angles are listed in Table 2.

CCDC: 820470, 1; 820471, 2.

Table 1 Crystllographic data for complexe 1 and 2

	1	2
Empirical formula	$\text{C}_{28}\text{H}_{30}\text{N}_2\text{NiO}_8 \cdot 2\text{H}_2\text{O}$	$\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_6\text{Zn} \cdot 2\text{H}_2\text{O}$
Formula weight	617.26	587.93
Crystal size / mm	0.394×0.222×0.097	0.446×0.283×0.110

Continued Table 1

Color	Green	Colorless
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
$a / \text{nm}$	1.124 40(19)	0.891 230(10)
$b / \text{nm}$	1.062 92(16)	1.765 44(2)
$c / \text{nm}$	1.357 99(16)	1.912 34(2)
$\beta / (^\circ)$	117.703(10)	108.8240(10)
$V / \text{nm}^3$	1.4370(4)	2.8479(5)
$Z$	2	4
Calculated density / ( $\text{g} \cdot \text{cm}^{-3}$ )	1.427	1.371
$F(000)$	648.0	1224.0
$\mu / \text{mm}^{-1}$	0.735	0.913
$\theta$ range / ( $^\circ$ )	2.05~24.99	2.41~25.00
Reflns collected	9 773	19 941
Reflns independent	2 527	5 012
Reflns observed	2 149	4 000
Final $R$ indices ( $I > 2\sigma(I)$ )	0.028 4	0.032 1
$R$ indices (all data)	0.076 1	0.078 7
Goodness-of-fit on $F^2$	1.044	1.074
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	494, -289	323, -239

Table 2 Selected bond distances (nm) and bond angles ( $^\circ$ ) for complex 1 and 2

Ni1-O1	0.204 6(13)	Ni-O1A	0.204 6(13)	Ni1-O1W	0.208 1(14)
Ni1-O1WA	0.208 1(14)	Ni1-N1	0.208 8(15)	Ni1-N1A	0.208 8(15)
Zn1-O4	0.199 1(16)	Zn1-O1	0.200 6(15)	Zn1-N1	0.204 2(16)
Zn1-N2A	0.209 0(16)				
O1A-Ni1-O1	180.00(4)	O1A-Ni1-O1WA	90.33(5)	O1-Ni1-O1WA	89.67(5)
O1A-Ni1-O1W	89.67(5)	O1-Ni1-O1W	90.33(5)	O1WA-Ni1-O1W	180.00(10)
O1A-Ni1-N1	88.66(6)	O1-Ni1-N1	91.34(6)	O1WA-Ni1-N1	87.10(6)
O1W-Ni1-N1	92.90(6)	O1A-Ni1-N1A	91.34(6)	O1-Ni1-N1A	88.66(6)
O1W-Ni1-N1A	87.10(6)	O1WA-Ni1-N1A	92.90(6)	N1-Ni1-N1A	180.00(12)
O4-Zn1-O1	109.50(7)	O4-Zn1-N1	135.68(7)	O1-Zn1-N1	104.99(7)
O4-Zn1-N2A	98.73(7)	O1-Zn1-N2A	97.01(6)	N1-Zn1-N2A	103.84(7)

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

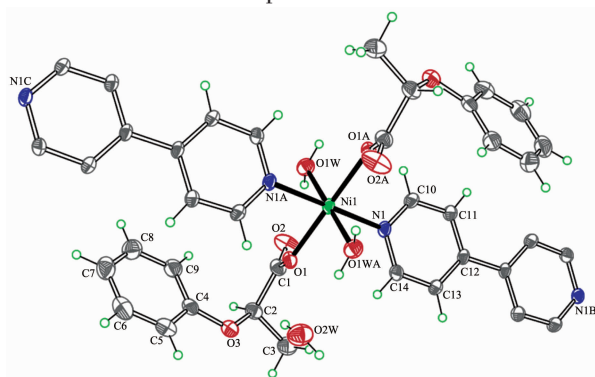
## 2 Results and discussion

### 2.1 Structure of complex 1

The crystal structure of polymer  $\{[\text{NiL}_2(\text{H}_2\text{O})_2(\text{bipy})] \cdot 2\text{H}_2\text{O}\}_n$  consist of countless 1D linear chains, in which every linear chain is composed of a number of  $[\text{Ni}(\text{C}_9\text{H}_9\text{O}_3)_2(\text{H}_2\text{O})_2(\text{bipy})] \cdot 2\text{H}_2\text{O}$  unit. The Ni atoms are surrounded by two carboxylate oxygen atoms from two different L ligands, two N atoms from two 4,4'-bipyridine molecules and two oxygen atoms from two

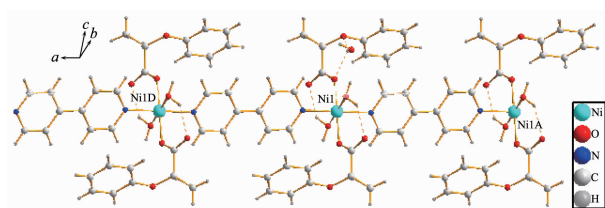
coordinated water molecules to shape a octahedral coordination environment (Fig.1). The distances between the Ni-O (carboxylate group) bond are 0.204 9(13) nm, which is slightly shorter than the Ni-O (water) distance of 0.208 3(16) nm. The Ni-N distances are 0.208 7(18) nm. These values are similar to those analogous complexes in the reported literature<sup>[14-16]</sup>. The L ligand coordinated to the Ni atoms by monodentate mode. The 4,4'-bipyridine ligands which extend the supramolecular into 1D linear chain are parallel each other and

coplanar, with the distance of neighbouring 4,4'-bipyridine ligands is 0.417 3(27) nm. The lattice water link to the carboxyl O atoms and the coordinated water molecules by interchain hydrogen bonds strengthen the stabilization of the polymer. The coordinated water as well as lattice water is not only the hydrogen-bond acceptor but also proton donor to form intramolecular and intermolecular hydrogen bonds. Furthermore, three-dimensional supermolecule were generated by these hydrogen bonds (Fig.2), which contribute to the stability of the crystal structure. In the linear single chain, the distance between the neighbouring Ni(II) is 1.124 4(19) nm, and all carboxylic aromatic ring on one side or on both sides are parallel each other.



Displacement ellipsoids are drawn at the 30% probability level; Symmetry operate: A:  $-x+1, -y, -z$ ; B:  $-x+2, -y, -z$ ; C:  $x-1, y, z$

Fig.1 Coordination environment of Ni(II) in complex **1**, showing the atom-labelling scheme



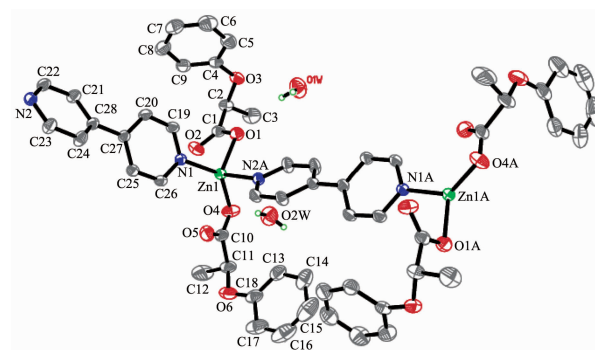
Symmetry transformations used to generate equivalent atoms: a:  $-x+1, -y, -z$ ; b:  $-x+3/2, y+1/2, -z+1/2$ ; Hydrogen bonds are depicted as dashed lines

Fig.2 Packing drawing of complex **1** along *a* axis

## 2.2 Structure of complex 2

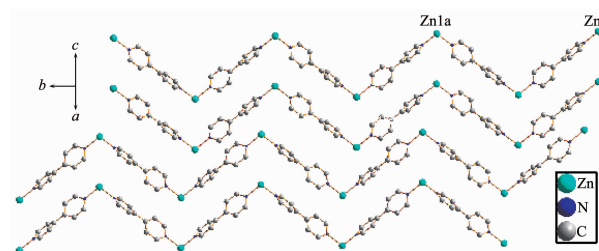
The polymer  $\{[ZnL_2(bipy)] \cdot 2H_2O\}_n$  consist of large number of  $[Zn(C_9H_9O_3)_2(bipy)] \cdot 2H_2O$  unit, in which the zinc atoms are four coordinated to two carboxylate oxygen atoms from two different L ligands and two N atoms from two 4,4'-bipyridine ligands in a tetrahedron geometry, the water molecules are not coordinated(Fig.

3). The Zn-N1, Zn-N2 bond lengths are 0.204 1(17) and 0.208 8(18) nm, respectively, the distances between the Zn-O bond are 0.198 9(18) and 0.200 6(18) nm. The bond lengths and bond angles are proximity to some similar complexes<sup>[17-18]</sup>. The dihedral angle between the neighbouring 4,4'-bipyridine ligands are 69.612 (28)°. The L ligands coordinate to the Zn atoms by monodentate mode and the 4,4'-bipyridine molecules connect the Zn atoms extend the structure into 1D zigzag chains by N atoms (Fig.4). The lattice water make hydrogen bonds to the coordinated carboxyl oxygen atoms, moreover the interchain hydrogen bonds from the four lattice water molecules form numerous four-membered rings. The hydrogen bonds include the C-H...O hydrogen bonds and  $\pi$ - $\pi$  stacking interactions between the neighbouring chains develop the chains into 3D framework and have a stabilization to the structure of polymer.



Symmetry operate: A:  $-x+1, -y, -z$ ; B:  $-x+2, -y, -z$ ; C:  $x-1, y, z$

Fig.3 Molecular structure of the title complex **2**, showing the atom-labelling scheme with displacement ellipsoids are drawn at the 30%



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

Fig.4 2D layer of complex **2** make of 1D zigzag bipy chains

## 2.3 Spectroscopic and thermal analysis

The IR spectrum of the complex  $\{[NiL_2(H_2O)_2]$

Table 3 Hydrogen bond parameters for complex 1 and 2

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠DHA / (°)
<b>1</b>				
O1W-H1WA...O2WA	0.083 5(17)	0.200(2)	0.273 5(2)	144(8)
O1W-H1WB...O2	0.084 1(17)	0.201(2)	0.279 5(2)	156(5)
O2W-H2WA...O1	0.084 6(17)	0.231(3)	0.296 4(2)	134(8)
O2W-H2WA...O3	0.083 6(17)	0.235(2)	0.313 4(2)	154(8)
<b>2</b>				
O1W-H1WA...O2WA	0.084 5(17)	0.230(2)	0.279 8(3)	118(5)
O1W-H1WB...O3A	0.082 1(17)	0.244(2)	0.309 3(3)	133(6)
O1W-H1WB...O1A	0.086 8(16)	0.246(2)	0.320 6(2)	145(5)
O2W-H2WA...O1WB	0.082 6(17)	0.199(3)	0.279 3(2)	156(4)
O2W-H2WB...O3C	0.082 6(17)	0.201(2)	0.285 9(3)	172(2)

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

C:  $x+1, y, z$ .

(bipy)]·2H<sub>2</sub>O)<sub>n</sub> displays characteristic strong bands at 1 603 and 1 408 cm<sup>-1</sup>, indication of the presence of  $\nu_{as}(-COO^-)$  and  $\nu_s(-COO^-)$  for the carboxylic group, respectively, which are finally confirmed by X-ray diffraction analysis. The broad band of 3 426 cm<sup>-1</sup> indicated the existence of water molecules. The peaks at 753 and 692 cm<sup>-1</sup> typically for benzene ring. The absorption at 1 454, 805, 635 cm<sup>-1</sup> are the characteristic absorption peak of 4,4'-bipyridine. The stretching bands in the ligand spectrum at 2 940 cm<sup>-1</sup> was assigned to the methyl. The IR spectrum of {[ZnL<sub>2</sub>(bipy)]·2H<sub>2</sub>O)<sub>n</sub> is very similar to that of {[NiL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(bipy)]·2H<sub>2</sub>O)<sub>n</sub>. The characteristic bands of the carboxylate groups for {[ZnL<sub>2</sub>(bipy)]·2H<sub>2</sub>O)<sub>n</sub> are observed at 3 416, 1 609, 1 409, 820 and 635 cm<sup>-1</sup>.

As shown in Fig.5, the TG-DTG curves of complex **1** indicate a weight loss of 12.20% (calcd. 11.66%) occurs from 30 to 160 °C, which is attributed to the loss of four water molecules. A continuous weight loss of 76.63% can be detected from 240 to 390 °C attributed to the decomposition of L ligands and 4,4'-bipyridine. The remaining weight of 10.97% corresponds to the percentage (calcd. 11.26%) of the nal product NiO. Thermogravimetric analysis of complex **2** (Fig.6) shows that the first step weight loss of 5.89% occurred between 30 and 135 °C, corresponding to the loss of two water molecules (calcd. 6.12%). The following weight loss of 80.52% corresponding to the loss of L ligands (reserve an oxygen atom) and 4,4'-bipyridine (calcd.

80.16%). The nal weight is 14.02%, which can be rene as ZnO (calcd. 13.78%).

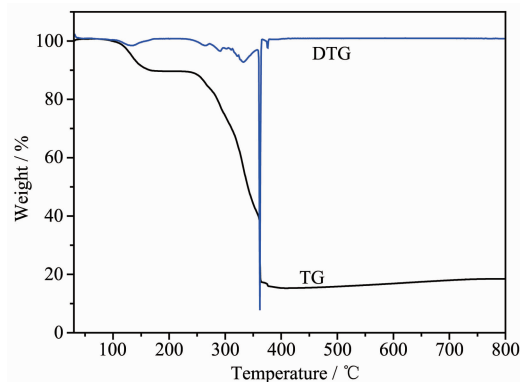


Fig.5 TG and DTG curves of complex 1

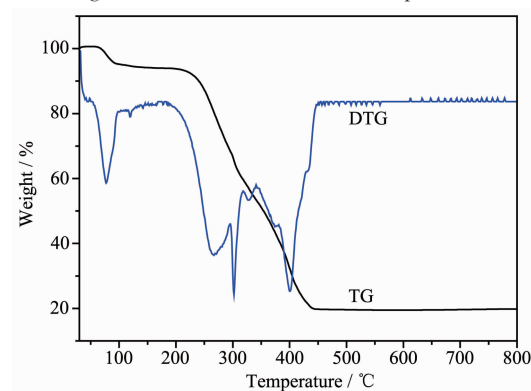


Fig.6 TG and DTG curves of complex 2

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