

4,4'-联吡啶-2,2',6,6'-四羧酸与含氮配体构筑的 金属配合物的结构和荧光性质

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摘要: 用水热法合成了 2 个化合物 $[M_2(L)(phen)_2(H_2O)_2] \cdot 6H_2O$ [$M=Ni$ (1), Zn (2), $H_4L=4,4'$ -联吡啶-2,2',6,6'-四羧酸, $phen=1,10$ -邻菲咯啉], 并进行了元素分析、IR 及 X-射线单晶结构测定等表征。晶体结构解析结果表明: 配合物 **1** 和 **2** 的晶体都属于三斜晶系, $P\bar{1}$ 空间群。配合物的中心金属离子都是六配位变形的八面体配位构型, 配体 4,4'-联吡啶-2,2',6,6'-四羧酸的羧基均以单齿形式配位。室温固体荧光测试结果显示配合物 **2** 具有较强的荧光。

关键词: 4,4'-联吡啶-2,2',6,6'-四羧酸; 晶体结构; 水热合成; 荧光性质

中图分类号: O614.81+3; O614.24+1 文献标识码: A 文章编号: 1001-4861(2009)03-0402-05

Hydrothermal Syntheses, Crystal Structures and Photoluminescence of Two Complexes with 4,4'-Bipyridine-2,2',6,6'-Tetracarboxylate and N-Donor Ligand

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Abstract: Two coordination complexes, $[M_2(L)(phen)_2(H_2O)_2] \cdot 6H_2O$ [$M=Ni$ (**1**), Zn (**2**), $H_4L=4,4'$ -bipyridine-2,2',6,6'-tetracarboxylic acid, $Phen=1,10$ -phenanthroline], were synthesized by hydrothermal method, and their structures were determined by X-ray crystal structure analysis. Both compounds crystallize in triclinic, space group $P\bar{1}$ with $a=0.827\ 87(15)$ nm, $b=1.057\ 1(18)$ nm, $c=1.226\ 6(2)$ nm, $\alpha=79.150(3)^\circ$, $\beta=84.760(3)^\circ$, $\gamma=67.866(3)^\circ$, $V=0.976\ 4(3)$ nm³, $Z=1$, $R=0.031\ 2$, $wR=0.078\ 8$ for **1**, and $a=0.874\ 8(15)$ nm, $b=1.057\ 46(19)$ nm, $c=1.131\ 5(2)$ nm, $\alpha=91.849(4)^\circ$, $\beta=97.599(3)^\circ$, $\gamma=108.034(4)^\circ$, $V=0.979\ 8(3)$ nm³, $Z=1$, $R=0.063\ 0$, $wR=0.137\ 8$ for **2**. The central metal atoms with octahedral coordination geometry in the two complexes are six-coordinated by three oxygen and three nitrogen atoms. Photoluminescence studies revealed that complex **2** exhibits strong fluorescent emission in the solid state at room temperature. CCDC: 710494, **1**; 710495, **2**.

Key words: 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid; crystal structure; hydrothermal synthesis; luminescence property

0 Introduction

In recent years, there are great interests in the crystal engineering of metal-organic frameworks (MOFs) with different dimensionality due to their intriguing

network topologies as well as their potential application as functional materials in areas such as separations, catalysis, gas storage and magnetism^[1~6]. Among the reported organic ligands, carboxylate-containing ones are particularly interested because the carboxylate

收稿日期: 2008-11-22。收修改稿日期: 2009-01-13。

国家自然科学基金资助项目(No.20731004)。

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groups can have a variety of binding modes, for example monodentate terminal, chelating, bidentate bridging, and monodentate bridging^[7]. A number of MOFs with carboxylate ligands, e.g. 1,4-benzenedicarboxylic acid (H₂BDC), 1,3,5-benzenetricarboxylic acid (H₃BTC) and pyridine-2,6-dicarboxylic acid, have been obtained and well characterized^[8–10]. We focus our attention on the construction of MOFs with polytopic organic acids due to their abundant coordination modes in connecting metal atoms into clusters and/or multi-dimensional frameworks^[11–13]. In this study we carry out our study using an interesting multifunctional organic ligand 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid (H₄L) and 1,10-phenanthroline (phen) to construct new MOFs. Herein we report the syntheses, crystal structures and luminescent property of the two binuclear complexes, [M₂(L)(phen)₂(H₂O)₂]·6H₂O [M=Ni (**1**), Zn (**2**)].

1 Experimental

1.1 Materials and instruments

Ligand 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid was prepared according to the literature method^[14]. The other reagents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on Bruker Vector22 FTIR spectrophotometer using KBr discs. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm. All the measurements were carried out under the same experiment conditions.

1.2 Synthesis of the compounds **1** and **2**

Complex **1** was synthesized by hydrothermal method in a 23 mL Teflon-lined autoclave by heating a mixture of 0.1 mmol H₄L, 0.2 mmol Ni(NO₃)₂·6H₂O, 0.4 mmol NaOH, 0.1 mmol Phen and 10 mL water at 160 °C

for three days. Large green single crystals were collected by filtration and washed by water and ethanol for several times with a yield of 54%. Anal. Calcd. for C₃₈H₃₆N₆O₁₆Ni₂ (%): C, 48.04; H, 3.82; N, 8.85. Found (%): C, 48.12; H, 3.73; N, 8.80. IR (KBr pellet, cm⁻¹): 3 433(s), 3 171(br), 3 107(m), 1 646(s), 1 611(s), 1 426(m, br), 1 376(s), 1 352(s), 850(m), 727(w), 690(w), 633(w).

Complex **2** was obtained by the same synthetic procedure as that for **1** except using Zn(NO₃)₂·6H₂O instead of Ni(NO₃)₂·6H₂O. Colorless block crystals of **2** were collected by filtration and washed by water and ethanol for several times with a yield of 58%. Anal. Calcd. for C₃₈H₃₆N₆O₁₆Zn₂ (%): C, 47.37; H, 3.77; N, 8.72. Found (%): C, 47.44; H, 3.83; N, 8.76. IR (KBr pellet, cm⁻¹): 3 434(s, br), 1 646(vs), 1 600(s), 1 426(m, br), 1 376(s), 1 352(s), 850(m), 727(w), 665(m).

1.3 X-ray crystal structure determination

The X-ray diffraction measurements for **1** and **2** were performed on Bruker Smart Apex CCD diffractometer with graphite-monochromatized Mo K α radiation ($\lambda=0.071\,075\text{ nm}$) at room temperature. Empirical absorption corrections were applied to the data using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-square on F^2 using the SHELXTL program^[15]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms except for those of water molecules were generated geometrically and refined isotropically using the riding model. The hydrogen atoms of the water molecules except for O3W and O4W in **2** were located in a difference Fourier map, while the ones of O3W and O4W in **2** could not be found from the Fourier map. Details of the crystal parameters, data collection and refinements for **1** and **2** are summarized in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2.

CCDC: 710494, **1**; 710495, **2**.

Table 1 Crystallographic data of complexes **1** and **2**

Complex	1	2
Empirical formula	C ₃₈ H ₃₆ N ₆ O ₁₆ Ni ₂	C ₃₈ H ₃₆ N ₆ O ₁₆ Zn ₂
Formula weight	950.11	963
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$

Continued Table 1

a / nm	0.827 8(15)	0.871 48(15)
b / nm	1.057 12(18)	1.057 46(19)
c / nm	1.226 6(2)	1.131 5(2)
$\alpha / (^{\circ})$	79.150(3)	91.849(4)
$\beta / (^{\circ})$	84.760(3)	97.599(3)
$\gamma / (^{\circ})$	67.866(3)	108.034(4)
V / nm^3	0.976 4(3)	0.979 8(3)
Z	1	1
$\theta / (^{\circ})$	1.69~25.00	1.82~25.00
Absorption coefficient / mm^{-1}	1.048	1.308
$F(000)$	490	486
Reflections collected / unique	4 874 / 3 385	4 945 / 3 412
R_{int}	0.052 7	0.031 9
Observed reflections [$I > 2\sigma(I)$]	3 034	2 812
Data / restraints / parameters	3 385 / 0 / 312	3 412 / 0 / 280
Final R indices [$I > 2\sigma(I)$]	$R=0.031\ 2$, $wR=0.078\ 8$	$R=0.063\ 0$, $wR=0.137\ 8$
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	307, -323	552, -498

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) of complexes **1** and **2**

1					
Ni(1)-N(1)	0.196 52(16)	Ni(1)-N(3)	0.208 81(18)	Ni(1)-O(2)	0.213 42(15)
Ni(1)-N(2)	0.204 22(17)	Ni(1)-O(1W)	0.209 60(16)	Ni(1)-O(4)	0.214 33(14)
N(1)-Ni(1)-N(2)	172.04(7)	N(3)-Ni(1)-O(1W)	174.42(6)	N(1)-Ni(1)-O(4)	77.72(6)
N(1)-Ni(1)-N(3)	93.88(7)	N(1)-Ni(1)-O(2)	78.02(6)	N(2)-Ni(1)-O(4)	96.97(6)
N(2)-Ni(1)-N(3)	80.33(7)	N(2)-Ni(1)-O(2)	107.42(6)	O(1W)-Ni(1)-O4	89.49(6)
N(1)-Ni(1)-O(1W)	91.61(7)	N(3)-Ni(1)-O(2)	91.52(6)	O(2)-Ni(1)-O(4)	155.61(5)
N(2)-Ni(1)-O(1W)	94.29(7)	O(1W)-Ni(1)-O(2)	88.67(6)	N(3)-Ni(1)-O(4)	92.61(6)
2					
Zn(1)-N(1)	0.206 2(4)	Zn(1)-N(3)	0.212 1(4)	Zn(1)-O(2)	0.223 2(3)
Zn(1)-N(2)	0.211 6(4)	Zn(1)-O(1W)	0.207 3(3)	Zn(1)-O(4)	0.223 2(3)
N(1)-Zn(1)-O(1W)	95.48(14)	N(2)-Zn(1)-N(3)	77.98(16)	N(3)-Zn(1)-O(2)	92.02(15)
N(1)-Zn(1)-N(2)	161.75(16)	N(1)-Zn(1)-O(2)	74.37(13)	N(1)-Zn(1)-O(4)	74.72(13)
O(1W)-Zn(1)-N(2)	90.58(15)	O(2)-Zn(1)-O(4)	149.09(12)	O(1W)-Zn(1)-O(4)	86.47(13)
N(1)-Zn(1)-N(3)	98.13(16)	O(1W)-Zn(1)-O(2)	96.50(13)	N(2)-Zn(1)-O(4)	122.95(14)
O(1W)-Zn(1)-N(3)	165.48(15)	N(2)-Zn(1)-O(2)	87.87(14)	N(3)-Zn(1)-O(4)	92.25(15)

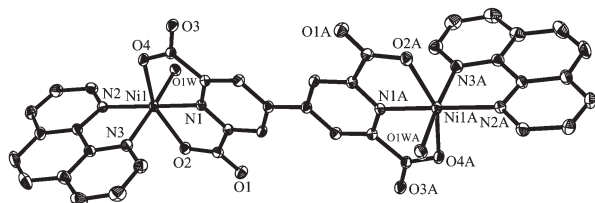
2 Results and discussion

2.1 Structure description

Complexes **1** and **2** crystallize in the same triclinic space group $P\bar{1}$ with similar cell parameters as listed in Table 1, and the results of IR and X-ray crystal structure analysis confirmed that they are isomorphous and isostructural. Thus, as a typical example, only the

structure of **1** is described here in detail. The structure of complex **1** is shown in Fig.1. All the carboxylate groups of the H_4L ligand are deprotonated, which is in good agreement with the IR spectral data of the complex since no strong band around $1\ 710\ \text{cm}^{-1}$ was observed for the $-\text{COOH}$ [16]. The metal central Ni (II) atom with distorted octahedral coordination geometry is six-coordinated by two oxygen atoms and one nitrogen

atom from one L^{4-} ligand, two other nitrogen atoms from phen ligand and one oxygen of water molecule. The bond angles around the Ni(II) are in the range of $77.72(6)^\circ$ and $174.42(6)^\circ$ (Table 2). For **1**, the Ni-O bond lengths are in the range of 0.209 60(16) to 0.214 33(14) nm and Ni-N bond length in the range of 0.196 52(16) to 0.208 81(18) nm. For **2**, the Zn-O distances vary from 0.207 3(3) to 0.223 2(3) nm and Zn-N bond length vary from 0.206 2(4) to 0.212 1(4) nm (Table 2). In this structure, one side of the L^{4-} ligand chelates one metal atom in which both two carboxylate groups adopt monodentate coordination mode, thus a



All the uncoordinated water molecules and hydrogen atoms are omitted for clarity

Fig.1 Crystal structure of complex **1**

complex with a binuclear structure is generated (Fig.1).

An interesting feature of the structure is the presence of inter-molecular hydrogen bonding interactions between the water O-H groups and carboxylate oxygen atoms. The hydrogen bonding data are summarized in Table 3. The $O \cdots O$ distance of 0.282 nm between O3W and O4W in complex **2** implies the presence of $O-H \cdots O$ hydrogen bond although the hydrogen atoms of O3W and O4W could not be found. A three-dimensional (3D) structure is generated and is further consolidated by the $O-H \cdots O$ and $C-H \cdots O$ hydrogen bonding interactions. In addition to the hydrogen bonds, there are three kinds of inter-molecular $\pi \cdots \pi$ interactions between the phen moieties in complex **1** with $d=0.361$ nm, $\theta=0^\circ$; $d=0.364$ nm, $\theta=1.5^\circ$ and $d=0.370$ nm, $\theta=0^\circ$, respectively in which the d is the centroid-centroid distance and θ is the dihedral angle between two phen rings (the corresponding values in complex **2** are $d=0.367$ nm, $\theta=2.9^\circ$; $d=0.390$ nm, $\theta=0.02^\circ$ and $d=0.359$ nm, $\theta=0^\circ$).

Table 3 Distances and Angles of hydrogen bonding for complexes **1** and **2**

D-H \cdots A	Distance (D \cdots A) / nm	Angle (D-H-A) / ($^\circ$)
1		
O(1W)-H(1WA) \cdots O(2W)	0.179(3)	162(2)
O(1W)-H(1WB) \cdots O(3) ^{#1}	0.211(2)	178(2)
O(2W)-H(2WA) \cdots O(1) ^{#2}	0.216(4)	158(4)
O(2W)-H(2WB) \cdots O(3W) ^{#3}	0.209(4)	166(4)
O(3W)-H(3WA) \cdots O(1) ^{#4}	0.201(4)	178(5)
O(3W)-H(3WB) \cdots O(3) ^{#5}	0.215(3)	167(4)
O(4W)-H(4WA) \cdots O(3W)	0.243(5)	152(6)
O(4W)-H(4WB) \cdots O(4) ^{#5}	0.224(5)	157(4)
C(8)-H(8) \cdots O(1) ^{#4}	0.255	130
C(10)-H(10) \cdots O(2) ^{#6}	0.25	138
2		
O(1W)-H(1WA) \cdots O(1) ^{#2}	0.178	173
O(1W)-H(1WB) \cdots O(3) ^{#7}	0.187	169
O(2W)-H(2WA) \cdots O(3) ^{#5}	0.196	175
O(2W)-H(2WB) \cdots O(3W)	0.242	110
C(10)-H(10) \cdots O(4W) ^{#5}	0.242	144
C(19)-H(19) \cdots O(4W) ^{#3}	0.246	130

Symmetry nodes: ^{#1} 1-x, 2-y, 1-z; ^{#2} 2-x, 1-y, 1-z; ^{#3} 1+x, y, z; ^{#4} x-1, y, z; ^{#5} x, y-1, z; ^{#6} 1-x, 1-y, 2-z;

^{#7} 2-x, 2-y, 1-z.

2.2 Spectral characteristics

The infrared spectra of the title complexes have

been recorded and the IR data confirmed the deprotonation of the carboxylate groups of the ligand as discus-

ssed above. Another feature of the IR data of the complexes is the separation between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, which have often been used to discuss the coordination mode of carboxylate group in the carboxylate complexes. The separation for monodentate carboxylate groups is $>200\text{ cm}^{-1}$ ^[17]. The separations (Δ) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ for **1** and **2** are both 220 cm^{-1} , indicating monodentate coordinating mode for the coordinated carboxylate groups. The vibration bands at 1426 , 850 and 727 cm^{-1} could be assigned to the characteristic peaks of phen molecules. Compared to those of free phen (1421 , 858 and 725 cm^{-1}), these peaks shift to some extent, indicating that phen has participated in coordination. The band at 3433 cm^{-1} is assigned to the $\nu(\text{O-H})$ of the water molecules. The IR data are coincident with the crystallographic structural analysis.

Metal complexes, particularly with d^{10} metal centers, have been investigated for fluorescence properties owing to their potential applications as luminescent materials, such as light-emitting diodes (LEDs)^[18]. Therefore, in the present study, the photoluminescence property of **2** was investigated in the solid state at room temperature. As illustrated in Fig.2, intense emission band was observed around 460 nm ($\lambda_{\text{ex}}=370\text{ nm}$) for **1**. Because the free H_4L and phen do not emit luminescence in the range of $400\sim800\text{ nm}$ under the same conditions, the emission observed in **2** may be attributed to metal-to-ligand charge transfer (MLCT) or

ligand-to-metal charge transfer (LMCT) as discussed previously for the Cd(II) complex^[19].

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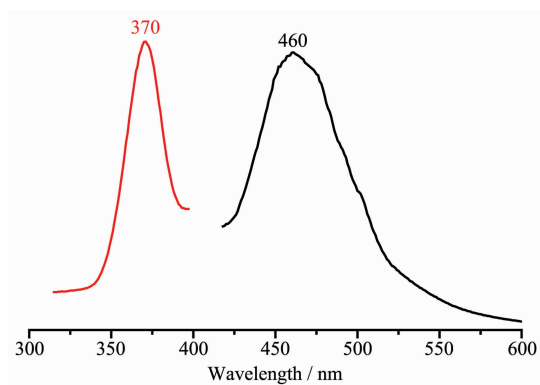


Fig.2 Excitation and emission spectra of complex **2**