

1,4-苯二硫乙酸配体构筑的锌(II)及镉(II)配合物的合成、晶体结构及荧光性质

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摘要: 基于 1,4-苯二硫乙酸(H_2L)及中性含氮配体, 水热法合成了两个新的 d^{10} 金属配合物 $[ZnCl_{0.5}(bpp)]$ (**1**)和 $[Cd_2L(phen)_4(H_2O)_2] \cdot L \cdot 2.78H_2O$ (**2**)($bpp=1,3$ -di(4-pyridyl)propane, $phen=1,10$ -phenanthroline), 并通过单晶 X-射线衍射、元素分析、红外光谱和热重对其结构进行了表征。结构分析表明, 在配合物 **1** 中, $Zn(II)$ 呈现四配位的扭曲四面体构型, 进一步连接形成一维双链状结构。在配合物 **2** 中, $Cd(II)$ 呈现六配位的扭曲八面体构型, 并通过可能存在的氢键及 $\pi-\pi$ 堆积作用, 形成最终的三维超分子结构。同时, 讨论了两种配合物的固体荧光性质。

关键词: 锌配合物; 镉配合物; 1,4-苯二硫乙酸; 晶体结构; 荧光性质

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Synthesis, Structure, and Luminescent Property of Zinc(II) and Cadmium(II) Complex Assembled by 1,4-Benzenebis(thioacetic acid)

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Abstract: Two d^{10} complexes assembled by 1,4-benzenebis(thioacetic acid) (H_2L) and neutral N-based ligands, $[ZnCl_{0.5}(bpp)]$ (**1**) and $[Cd_2L(phen)_4(H_2O)_2] \cdot L \cdot 2.78H_2O$ (**2**) ($bpp=1,3$ -di(4-pyridyl)propane, $phen=1,10$ -phenanthroline), have been hydrothermally synthesized and characterized by single crystal X-ray diffraction, elemental analysis, IR spectroscopy, and TG analysis. In complex **1**, $Zn(II)$ ion is four-coordinated in a distorted tetrahedron coordination environment and is further linked to a one-dimensional (1D) double chain structure. In complex **2**, $Cd(II)$ ion is six-coordinated in a distorted octahedral coordination environment, and is linked by possible hydrogen bonds and $\pi-\pi$ interactions to form a 3D supramolecular structure. The luminescent property in solid state of the two complexes was also studied and discussed. CCDC: 734944, **1**; 819445, **2**.

Key words: zinc complex; cadmium complex; 1,4-benzenebis(thioacetic acid); crystal structure; luminescent property

0 Introduction

Recently, design and synthesis metal-organic hybrid complexes through coordination or noncovalent

bonds have attracted much attention due to their particular topologies^[1-2] and some potential applications such as catalysis, adsorption, magnetism, photochemistry and NLO materials^[3-5]. The selection or design of a

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suitable ligand with certain features, such as flexibility, versatile binding modes, and the ability to form hydrogen bonds^[6] is crucial to the construction of polymeric complexes. It is reported that carboxylic ligands, especially multibenzenecarboxylate ligands with various coordination modes have been successfully used to construct various extended structures with metal ions^[7-8]. 1,4-Benzenebis(thioacetic acid) (H_2L) is a multi-carboxylate ligand, which possesses flexibility owing to the presence of $-S-CH_2-$ group between the phenyl ring and carboxyl moiety. We have synthesized some complexes that contain transition metal cations bridged by H_2L and bipyridine analogues ligands^[9-12] to construct more interesting structure. Herein, we report the syntheses, structural characterizations and luminescent properties of two new d^{10} metal complexes, $[ZnClL_{0.5}(bpp)]$ (**1**) and $[Cd_2L(phen)_4(H_2O)_2] \cdot L \cdot 2.78H_2O$ (**2**) ($bpp=1,3$ -di(4-pyridyl)propane, $phen=1,10$ -phenanthroline).

1 Experimental

1.1 Materials and characterization

H_2L was obtained according to a procedure by Su et al. using 1,4-benzenebisthiol^[13]. Other reagents were purchased commercially and used without further purification. Data collection was performed on a Bruker SMART APEX II CCD diffractometer with Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Elementary analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. IR spectra were recorded in KBr pellet on a Nicolet 5DX FTIR spectrometer. Thermogravimetric analyses (TGA) were performed at a rate of $10\ ^\circ C \cdot min^{-1}$ under oxygen stream using a Netzsch STA449C apparatus. Fluorescence spectra were obtained on a HITACHI F-2500 fluorescence Spectrometer in solid state at room temperature.

1.2 Synthesis of complex 1

A mixture of H_2L (0.103 g, 0.4 mmol), $ZnCl_2 \cdot 2H_2O$ (0.054 g, 0.4 mmol), bpp (0.040 g, 0.2 mmol), and NaOH (0.032 g, 0.8 mmol) in H_2O (18 mL) was placed in a Teflon-lined stainless steel vessel and heated at $160^\circ C$ for 72 h, then cooled to room temperature over 3 d. The reaction mixture was filtered and well-shaped

colourless crystals of **1** were obtained from the mother liquor by slow evaporation at room temperature for several days (yield 42%). Anal. Calcd. for $C_{18}H_{18}ClN_2O_2SZn$ (%): C, 50.45; H, 3.98; N, 6.78; S, 7.45. Found (%): C, 50.60; H, 4.2; N, 6.56; S, 7.50. IR (KBr, cm^{-1}): 3 421, 2 925, 1 612, 1 400, 1 222, 1 124, 1 165, 806, 698.

1.3 Synthesis of complex 2

A mixture of H_2L (0.103 g, 0.4 mmol), $Cd(Ac)_2 \cdot 3H_2O$ (0.104 g, 0.4 mmol), $phen$ (0.040 g, 0.2 mmol), and NaOH (0.032 g, 0.8 mmol) in C_2H_5OH (2 mL)/ H_2O (16 mL) was placed in a Teflon-lined stainless steel vessel and heated at $160\ ^\circ C$ for 72 h, then cooled to room temperature over 3 d. The reaction mixture was filtered and well-shaped colourless crystals of **2** were obtained from the mother liquor by slow evaporation at room temperature for several days (yield 42%). Anal. Calcd. for $C_{68}H_{56}N_8O_{12}S_4Cd_2$ (%): C, 53.65; H, 3.56; N, 7.35; S, 8.49. Found (%): C, 53.37; H, 3.76; N, 7.32; S, 8.38. IR (KBr, cm^{-1}): 3 421, 1 596, 1 522, 1 513, 1 211, 1 104, 847, 728.

1.4 X-ray crystallography

Two crystals of **1** (0.30 mm \times 0.17 mm \times 0.15 mm) and **2** (0.22 mm \times 0.10 mm \times 0.07 mm) were selected for structure analyses. The diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 296(2) K. Intensity data were corrected by Lorentz-polarization factors and empirical absorption. The structures were solved with direct methods and expanded with difference Fourier techniques. Except the location of the hydrogen atoms on oxygen atoms from the difference Fourier maps, the other hydrogen atoms were generated geometrically. All calculations were performed using SHELXS-97^[14] and SHELXL-97^[15] program package. In **1**, the C1, C2, C3, C4, S1 of L^{2-} ligands are disordered over two positions in 0.86:0.14 ratio. In **2**, the lattice water molecules are disordered over two positions in 0.59:0.27 and 0.30:0.23 ratios, respectively. The crystallographic data and structural determination parameters are summarized in Table 1, and selected bond lengths and bond angles are listed in Tables 2.

CCDC: 734944, **1**; 819445, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	C ₁₈ H ₁₈ ClN ₂ O ₂ SZn	C ₆₈ H _{57.56} N ₈ O _{12.78} S ₄ Cd ₂
Formula weight	427.22	1 544.30
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	0.564 80(3)	1.015 000(10)
<i>b</i> / nm	1.285 47(7)	1.255 48(2)
<i>c</i> / nm	1.291 10(7)	1.381 10(2)
α / (°)	76.940(2)	97.013 0(10)
β / (°)	86.836(3)	90.354 0(10)
γ / (°)	88.742(3)	110.977 0(10)
<i>V</i> / nm ³	0.911 7(1)	1.628 6(5)
<i>Z</i>	2	1
<i>D_c</i> / (g·cm ⁻³)	1.556	1.575
μ / mm ⁻¹	1.622	0.852
<i>F</i> (000)	438	784
θ_{\min} , θ_{\max} / (°)	1.62, 27.54	1.49, 27.54
Reflections collected	15 763	26 040
Unique reflections (<i>R_{int}</i>)	4 189 (0.026 6)	7 425 (0.036 5)
Data with <i>I</i> > 2σ(<i>I</i>)	3 613	6 002
Parameters refined	262	451
<i>R</i> , <i>wR</i> (observed reflections)	0.032 8, 0.079 9	0.036 8, 0.096 2
<i>R</i> , <i>wR</i> (all reflections)	0.041 8, 0.086 6	0.049 2, 0.103 1
Goodness-of-fit (on <i>F</i> ²)	1.069	1.038
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / (e·nm ⁻³)	361, -236	628, -379

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

1					
Zn(1)-O(1)	0.194 40(2)	Zn(1)-N(2) ⁱ	0.203 44(2)	Zn(1)-N(1)	0.204 24(2)
Zn(1)-Cl(1)	0.225 24(6)				
O(1)-Zn(1)-N(2) ⁱ	118.35(8)	O(1)-Zn(1)-Cl(1)	109.78(6)	O(1)-Zn(1)-N(1)	106.03(8)
N(2) ⁱ -Zn(1)-Cl(1)	106.28(6)	N(2) ⁱ -Zn(1)-N(1)	110.50(7)	N(1)-Zn(1)-Cl(1)	105.19(5)
2					
Cd(1)-O(1)	0.221 2(2)	Cd(1)-O(1W)	0.227 9(2)	Cd(1)-N(1)	0.238 9(2)
Cd(1)-N(3)	0.236 4(2)	Cd(1)-N(2)	0.235 3(2)	Cd(1)-N(4)	0.247 2(2)
O(1)-Cd(1)-O(1W)	103.22(9)	O(1)-Cd(1)-N(2)	94.55(9)	O(1W)-Cd(1)-N(2)	114.01(9)
O(1)-Cd(1)-N(3)	98.83(8)	O(1W)-Cd(1)-N(3)	88.74(8)	N(2)-Cd(1)-N(3)	150.07(9)
O(1)-Cd(1)-N(1)	164.12(9)	O(1W)-Cd(1)-N(1)	87.11(8)	N(2)-Cd(1)-N(1)	70.12(9)
N(3)-Cd(1)-N(1)	93.12(9)	O(1)-Cd(1)-N(4)	89.66(8)	O(1W)-Cd(1)-N(4)	156.02(8)
N(2)-Cd(1)-N(4)	84.27(8)	N(3)-Cd(1)-N(4)	69.24(8)	N(1)-Cd(1)-N(4)	84.81(8)

Symmetry transformation used to generate equivalent atoms: **1**: ⁱ *x*, *y*, *z*+1.

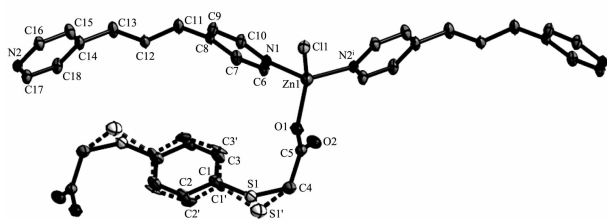
2 Results and discussion

2.1 Crystal structure of complex **1**

Single-crystal X-ray diffraction analysis reveals

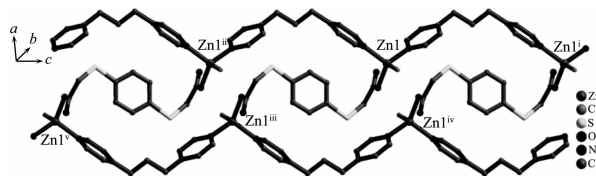
that **1** is a 1D double chain structure. The asymmetric unit consists of one Zn(II) ion, half a L²⁻ ligand, one bpp molecule, and one Cl⁻ ion. As shown in Fig.1, the Zn(II) ion is four-coordinated by one carboxylate O atom from

one L^{2-} ligand (Zn-O 0.194 40(2) nm), two N atoms from two bpp molecules (Zn-N 0.204 24 (2) and 0.203 44(2) nm), and one Cl^- ion (Zn-Cl 0.225 24 (6) nm) to form a distorted tetrahedron geometry. L^{2-} ligand possesses better flexibility owing to the presence of $-S-CH_2-$ group, and the torsion angle of C1-S1-C5-C4 is 71.33° . As illustrated in Fig.2, the Zn(II) atoms are linked by bpp molecules to generate a single-strand zigzag chain with the $Zn \cdots Zn$ distance of 1.291 10(9) nm along c direction. Then each L^{2-} ligand serves as a bridging ligand to link two adjacent single-strand zigzag chain, leading to a double chain structure along c direction.



Symmetry transformations used to generate equivalent atoms: $^i x, y, z+1$; H atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level

Fig.1 Coordination environment of Zn(II) atom



Symmetry transformations used to generate equivalent atoms: $^i x, y, z+1$; $^{ii} x, y, z-1$; $^{iii} -x+1, -y, -z$; $^{iv} -x+1, -y, -z+1$; $^v -x+1, -y, -z-1$

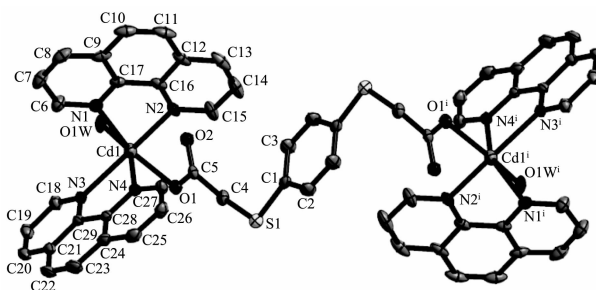
Fig.2 View of the 1D chain of the complex 1

2.2 Crystal structure of complex 2

Single-crystal X-ray diffraction analysis reveals that **2** is a discrete Cd(II) complex, and further linked into a 3D supramolecular structure by hydrogen bonds π - π stacking interaction. The asymmetric unit consists of one Cd(II) ion, half a coordinated L^{2-} ligand, two phen molecules, one coordinated water molecules, and half a free L^{2-} , one point three nine lattice water molecules. As shown in Fig.3, the Cd(II) is six-coordinated in a distorted octahedral coordination environment: one carboxylate O atom from one L^{2-} ligand [Cd-O 0.221 2(2) nm], four N atoms from two phen molecules [Cd-N 0.235 3(2)~0.247 2(2) nm], and one water molecule. L^{2-}

ligand also possesses better flexibility, and the torsion angle of C1-S1-C4-C5 is $70.9(3)^\circ$.

It is worth noting that hydrogen bond and π - π stacking interaction play an important role in the formation and stability of high-dimensional structures, especially those structure containing phen and water molecules^[16]. In **2**, the possible O-H \cdots O and O-H \cdots S hydrogen bonds link the neighboring molecules to form a 3D supramolecular structure. Meanwhile, the adjacent phen molecules are parallel to each other with the centroid-centroid distance of 0.3513 nm, which would be expected for π - π interactions (Fig.4). All hydrogen bond parameters of this complex are listed in Table 3.



Symmetry transformation used to generate equivalent atoms: $^i -x, -y-1, -z$; Lattice waters molecules, free L^{2-} and H atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level

Fig.3 Coordination environment of Cd(II) atom

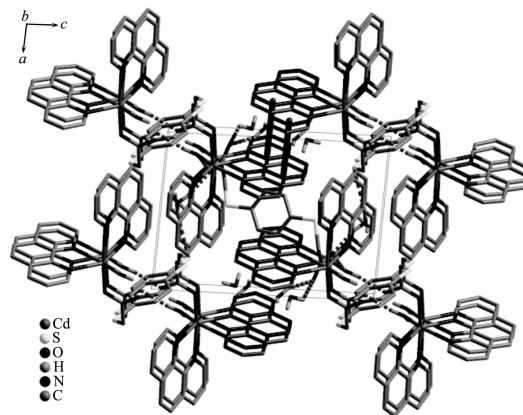


Fig.4 3D supramolecular structure by hydrogen bond interactions and π - π interactions in **2**

2.3 Photoluminescent properties

The d^{10} metal complexes exhibit some interesting photoluminescent properties^[17-20]. The solid-state luminescent properties of the complexes **1** and **2** were investigated at room temperature and the emission

Table 3 Hydrogen bond lengths and angles

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O(1W)-H(1WA) \cdots O(2) ⁱⁱⁱ	0.081	0.203	0.281 9(3)	165.0
O(1W)-H(1WB) \cdots O(3)	0.081	0.186	0.266 1(3)	171.8
O(2W)-H(2WB) \cdots O(3)	0.082	0.201	0.279(2)	160.7
O(2W)-H(2WA) \cdots S(1) ^{iv}	0.082	0.279	0.357(2)	158.7
O(4W)-H(4WA) \cdots O(4)	0.085	0.223	0.271 4(9)	116.5
O(5W)-H(5WB) \cdots O(4)	0.085	0.211	0.284 1(11)	144.1

Symmetry transformation used to generate equivalent atoms: ⁱⁱⁱ $-x, -y, -z$; ^{iv} $x+1, y+1, z$.

spectra are given in Fig.5. Complex **1** shows a blue fluorescent, and the maximum emission wavelength at 470 nm upon photo-excitation at 337 nm. The free H₂L and bpp ligands that display the fluorescent properties with the emission maxima at 338 nm^[9] and 523 nm^[21], respectively. Complex **2** shows a green fluorescent with a maximum emission wavelength at 538 nm upon photo-excitation at 390 nm. It is known that free phen·H₂O ligand displays the fluorescent property at 365 and 388 nm^[22]. The maximum emission bands of **2** are red-shifted compared to free ligands. According to the literatures^[23-24], d^{10} configuration of Zn(II) and Cd(II) ions is difficult to oxidize or to reduce. The emission bands may tentatively be assigned to the ligand-to-ligand charge transfer (LLCT).

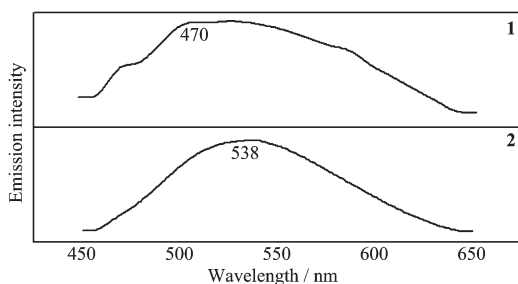


Fig.5 3D supramolecular structure by hydrogen bond interactions and π - π interactions in **2**

2.4 Thermal analyses

The TG curve of **1** exhibits two main weight losses (Fig.6). The first weight loss of 45.1% from 220 to 475 °C corresponds to the loss of one bpp molecule (calcd. 45.9%). The second weight loss of 37.4% between 475 and 600 °C corresponds to the removal of half a L²⁻ ligand and one Cl⁻ ion (calcd. 38.3%). The final residual may be ZnO (obsd. 18.3%, calcd. 18.9%). For **2**, the first weight loss of 5.5% (calcd. 5.0%) from 70 to 110 °C corresponds to the loss of the two lattice water

molecules and two coordinated water molecules. The further decomposition occurs in the range of 200~645 °C, which attributes to the elimination of the organic ligands. The final residual may be CdO (obsd. 16.6%, calcd. 16.8%).

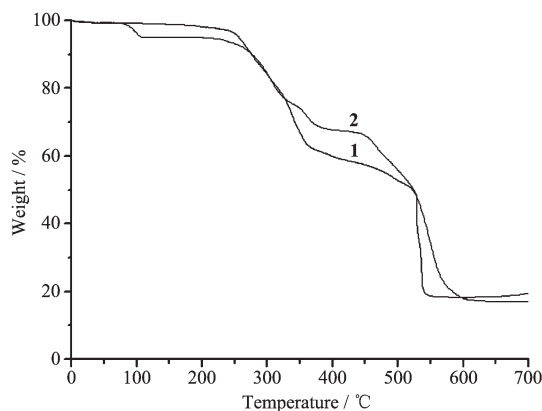


Fig.6 TGA curves of the complexes **1** and **2**

In summary, we have successfully synthesized two new Zn(II) and Cd(II) complexes based on 1,4-benzenedis(thioacetic acid) ligand under hydrothermal conditions. Single-crystal X-ray diffraction analysis reveals that **1** is a 1D double chain complex, while **2** is a discrete Cd(II) complex, and further linked into a 3D supramolecular structure by possible hydrogen bonds. These two d^{10} metal complexes exhibit the strong fluorescence in solid state at room temperature.

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