

Cd(II)/Zn(II)与三(2-巯吡啶基)甲烷配合物的合成、 表征及配合物中 C-S 键的断裂机理

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摘要: 以三(2-巯吡啶基)甲烷(L)为配体合成了 2 个 Cd(II)和 Zn(II)的配合物: Cd(L)₄(NO₃)₂ 和 Zn(L)₄(ClO₄)₂, 发现在配合物中配体的 C-S 键发生了断裂, 通过紫外、质谱手段研究并预测了其反应机理。单晶 X-射线衍射的结果显示, 配合物 **1** 和 **2** 中金属原子均处于扭曲的四面体配位环境中, 分子间 π - π 堆积作用将配合物 **1** 的分子结构延伸为二维网状结构。

关键词: 三(2-巯吡啶基)甲烷; C-S 键断裂; π - π 堆积作用

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Syntheses, Crystal Structures and Cleavage Mechanism of C-S Bond in Cd(II) and Zn(II) Complexes with Tris(2-mercaptopyridyl)methane

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Abstract: Two complexes of Cd(II) or Zn(II) with L (L=tris(2-mercaptopyridyl)methane), Cd(L)₄(NO₃)₂ (**1**) and Zn(L)₄(ClO₄)₂ (**2**), have been synthesized and characterized. The cleavage of the C-S bonds of the ligand has been discovered and the cleavage mechanism has been studied by UV-Vis titration and GC-MS. The possible reaction mechanism has been proposed. Single crystal X-ray analyses show that the Cd and Zn atoms are all in a four-coordinated distorted tetrahedron environment. The intermolecular π - π stacking action extends the complex **1** to a 2D net work. CCDC: 627210, **1**; 644051, **2**.

Key words: tris(2-mercaptopyridyl)methane; cleavage of the C-S bonds; π - π stacking action

0 Introduction

Sulfur-containing heterocyclic complexes have attracted enormous attentions, not only because of their versatile structure topologies, but also because of their potential applications in farm drugs and medicines^[1], semiconducting materials, fluorescent, biomi-

metic and so on^[2-4]. In this paper, we choose tris(2-mercaptopyridyl)methane(L) as ligand to coordinate to metal ions. It has been found that when it coordinates, the C-S bonds of the ligand in complexes are all cleaving. So we obtained the complexes of 2-thiopyridone coordinating to metal ions. The cleavage of C-S bonds in the tripodal ligand does not depend on the

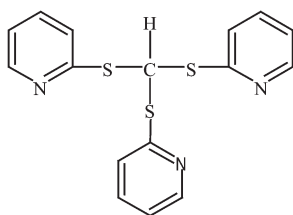
kinds of metal ions, because when various metal salts are employed to prepare the metal complexes, the same result has been obtained.

The desulfurization reactions caused by cleavage of C-S bonds have been found under hydrothermal or solvothermal conditions, even under room temperature^[5-8]. But few reports on the cleavage of C-S bonds for metal complexes with tripodal ligand have been found so far. Herein we report the crystal structures of Cd and Zn complexes with 2-thiopyridone which comes from the tripodal ligand L, and studies of the cleavage mechanism by UV-Vis titration and GC-MS.

1 Experimental

1.1 Materials and general methods

The ligand L was prepared via a previously reported method^[9]. The molecular structure of L is shown in Scheme 1. All the other starting materials were of reagent grade and obtained from commercial sources without further purification. Elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with KBr pellets. The UV-Vis titration were carried out on a Shimadzu UV-2450 spectrophotometer. The GC-MS were carried out with a TRACE DSQ instrument.



Scheme 1 Molecular structure of L

1.2 Synthesis of the complex 1

The solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30.8 mg, 0.1 mmol) in methanol (3 mL) was added dropwise to the solution of L (34.3 mg, 0.1 mmol) in chloroform (3

mL), and the resulting mixture was stirred for 0.5h at room temperature. The final mixture was transferred to a test tube which was left to stand for about two weeks, and the yellow single crystals of **1** were obtained. Yield: 47.1mg, 61% (based on Cd). Anal. Calcd.(%) for $\text{C}_{20}\text{H}_{16}\text{CdN}_6\text{O}_6\text{S}_4$: C,35.48; H,2.38; N,12.42. Found (%): C,35.39; H,2.45; N,12.38. IR (KBr, cm^{-1}): 3 178s, 3 079vs, 2 901br, 1 863m, 1 743m, 1 611s, 1 577s, 1 522 m, 1 379br, 1 245m, 980m, 903m, 761vs, 616m, 494s.

1.3 Synthesis of the complex 2

The same procedure was run as that of **1**, except $\text{Zn}(\text{ClO}_4)_2$ was used instead of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Colorless crystals of **2** suitable for X-ray analysis were obtained after two weeks. Yield: 39.5 mg, 56% (based on Zn). Anal. Calcd. (%) for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{N}_4\text{O}_8\text{S}_4\text{Zn}$: C, 34.07; H,2.29; N,7.95. Found(%): C,33.84; H,2.46; N, 7.81. IR (KBr, cm^{-1}): 3 414w, 3 232m, 3 056br, 1 596 s, 1 550vs, 1 419s, 1 308m, 1 208m, 1 137s, 1 070 br, 920m, 757w, 707m, 681s, 626s, 522m, 483m, 438m.

1.4 Crystal structure determination

The crystals with dimensions of 0.24 mm×0.20 mm×0.16 mm for complex **1**, and 0.20 mm×0.18 mm×0.14 mm for complex **2** were carefully selected for structure determination. All the data were collected on a Bruker Smart CCD diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at room temperature using the φ - ω scan technique. The structure was solved by the direct method and subsequent difference Fourier syntheses and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the structure factor calculation but not refined. All the calculations were carried out with SHELXS-97 and SHELXL-97 programs^[10-11]. The crystal data and data collection details for complexes **1** and **2** are summarized in Table 1.

CCDC: 627210, **1**; 644051, **2**.

Table 1 Crystallographic data and structure refinements for complexes **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{20}\text{H}_{16}\text{CdN}_6\text{O}_6\text{S}_4$	$\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{N}_4\text{O}_8\text{S}_4\text{Zn}$
Formula weight	677.03	704.88
Crystal system	Monoclinic	Monoclinic
Temperature / K	294(2)	294(2)

Continued Table 1

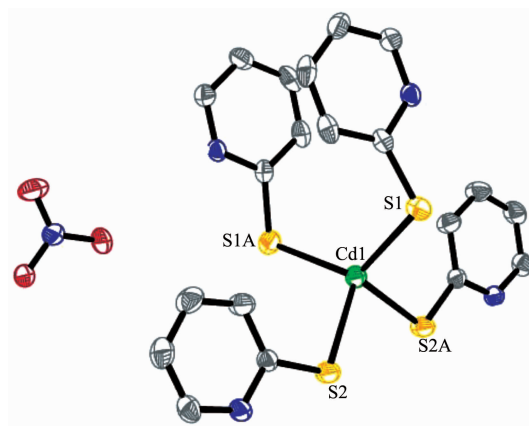
Space group	<i>P2₁/c</i>	<i>C2/c</i>
<i>a</i> / nm	0.946 56(16)	1.585 0(3)
<i>b</i> / nm	1.036 34(16)	2.054 7(4)
<i>c</i> / nm	1.431 6(2)	1.876 6(3)
β / (°)	106.567(2)	109.120(3)
<i>V</i> / nm ³	1.346 1(4)	5.774 3(17)
<i>Z</i>	2	8
<i>D_c</i> / (g·cm ⁻³)	1.670	1.622
μ / mm ⁻¹	1.168	1.375
<i>F</i> (000)	676	2848
θ range for data collection / (°)	1.79~26.38	1.68~25.02
Limiting indices	$-11 \leq h \leq 11, -6 \leq k \leq 12, -17 \leq l \leq 17$	$-18 \leq h \leq 16, -23 \leq k \leq 24, -22 \leq l \leq 22$
Reflections collected	7 196	14 842
Independent reflections (<i>R_{int}</i>)	2 643(0.021 8)	5 113(0.033 7)
Final GOF	1.026	1.042
<i>R₁</i> , <i>wR₂</i> (<i>I</i> > 2 σ (<i>I</i>))	0.022 4, 0.057 1	0.035 7, 0.084 6
<i>R₁</i> , <i>wR₂</i> (all data)	0.026 8, 0.060 8	0.060 2, 0.102 4
Largest peak and hole/(e·nm ⁻³)	355, -363	351, -416

2 Results and discussion

2.1 Crystal structure of complexes 1 and 2

X-ray single-crystal diffraction study reveals that complexes **1** and **2** all crystallize with the unbound 2-thiopyridone, not the tripodal ligand tris(2-mercaptopyridyl)methane. Selected bond distances and angles are given in Table 2. The structure of **1** consists of four 2-thiopyridone units and an uncoordinated NO₃⁻ anion (Fig.1). In this complex, the Cd atom coordinate with S atoms of the four 2-thiopyridone, forming a distorted tetrahedron environment. The bond distance of Cd1-S1 and Cd1-S1A (0.250 70 nm) is slight shorter than that of Cd1-S2 and Cd1-S2A (0.253 98 nm). All of them are normal bonds. In addition, the distances between two pyridine rings from different 2-thiopyridone ligands in adjacent layers are 0.360 9 and 0.364 9 nm, respectively, so there is weak π - π interactions between the ligands, which extend the structure to 2D networks (Fig.2). To a certain extent, the π - π interactions can enhance the stability of complex. It is noticed that there is a four-member ring [Cd₄] with Cd-Cd separation of 0.737, 0.946 6, 1.036 3 and 1.119 5 nm, namely a second building unit (SUB)^[12] (Fig.3), which is the basic unit of the 2D networks.

The structure of **2** is different from **1**. Complex **2** consists of two asymmetric units (Fig.4). The Zn1 and Zn2 are both tetra-coordinated with four S atoms of



H atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level

Fig.1 Perspective view of the coordination environment of Cd in **1**

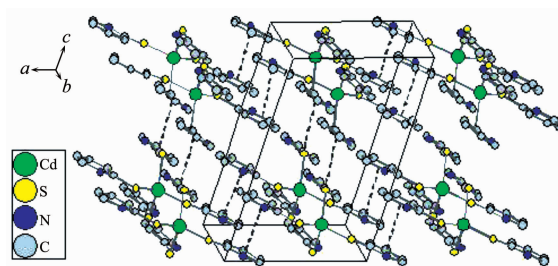


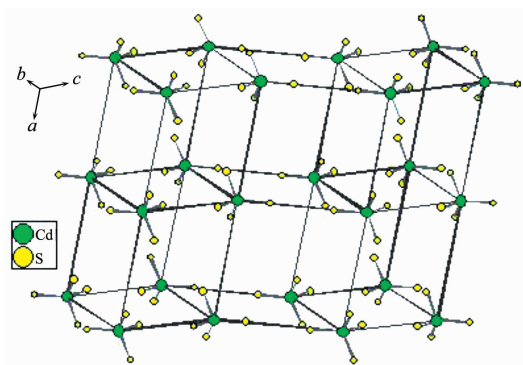
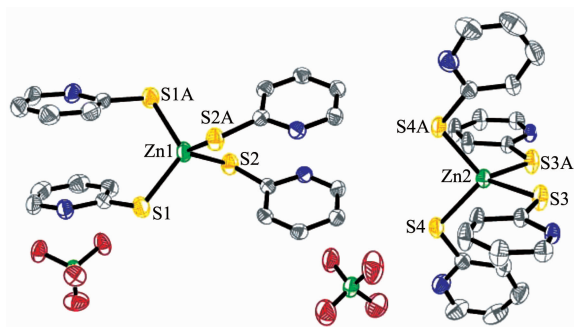
Fig.2 2D networks of complex **1**

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

1					
Cd(1)-S(1)	0.250 70(7)	Cd(1)-S(1A)#1	0.250 75(7)	Cd(1)-S(2A)#1	0.253 98(6)
Cd(1)-S(2)	0.253 98(6)	S(1)-C(2)	0.173 6(2)	S(2)-C(6)	0.171 8(2)
S(1)-Cd(1)-S(1A)#1	120.68(3)	S(1)-Cd(1)-S(2A)#1	105.57(2)	S(1A)#1-Cd(1)-S(2A)#1	115.14(2)
S(1)-Cd(1)-S(2)	115.14(2)	S(1A)#1-Cd(1)-S(2)	105.57(2)	S(2A)#1-Cd(1)-S(2)	91.08(3)
C(1)-S(1)-Cd(1)	109.09(8)	C(6)-S(2)-Cd(1)	107.85(8)		
2					
Zn(1)-S(2)	0.234 53(11)	Zn(1)-S(2A)#1	0.234 53(11)	Zn(1)-S(1A)#1	0.235 37(10)
Zn(1)-S(1)	0.235 37(10)	Zn(2)-S(4)	0.232 10(10)	Zn(2)-S(4A)#2	0.232 10(10)
Zn(2)-S(3)	0.233 57(9)	Zn(2)-S(3A)#2	0.233 57(10)	S(1)-C(5)	0.171 7(4)
S(2)-C(6)	0.171 9(3)	S(3)-C(15)	0.171 7(3)	S(4)-C(16)	0.171 9(3)
S(2)-Zn(1)-S(2A)#1	112.97(6)	S(2)-Zn(1)-S(1A)#1	100.36(4)	S(2A)#1-Zn(1)-S(1A)#1	114.99(4)
S(2)-Zn(1)-S(1)	114.99(4)	S(2A)#1-Zn(1)-S(1)	100.36(4)	S(1A)#1-Zn(1)-S(1)	113.89(6)
S(4)-Zn(2)-S(4A)#2	99.52(5)	S(4)-Zn(2)-S(3)	117.70(4)	S(4A)#2-Zn(2)-S(3)	117.75(4)
S(4)-Zn(2)-S(3A)#2	117.76(4)	S(4A)#2-Zn(2)-S(3A)#2	117.70(4)	S(3)-Zn(2)-S(3A)#2	87.84(5)
C(5)-S(1)-Zn(1)	102.96(14)	C(6)-S(2)-Zn(1)	101.26(13)	C(15)-S(3)-Zn(2)	109.51(11)
C(16)-S(4)-Zn(2)	106.06(13)				

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

unbound 2-mercaptopyridine, Zn1 atom is in a near-perfect tetrahedral coordinated environment with the

Fig.3 SBUs in complex **1**

H atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level

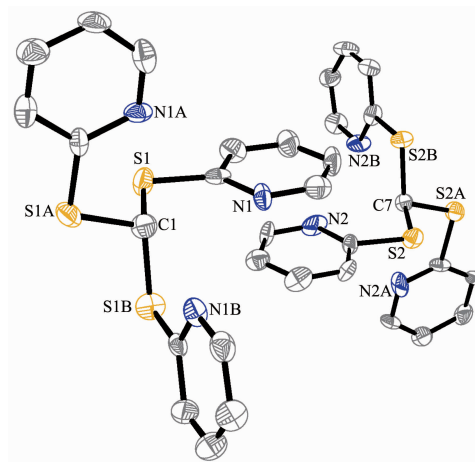
Fig.4 Coordination modes of Zn in **2**

Zn1-S bond distances of 0.234 53 and 0.235 37 nm, while Zn2 is in a distorted tetrahedron with the Zn2-S bond distances of 0.232 10 and 0.233 57 nm. There is no π - π interaction between pyridine rings.

2.2 Study on the cleavage mechanism of C-S bond in **L**

2.2.1 Structure of ligand **L**

X-ray single-crystal diffraction study reveals that the ligand **L** have tripodal structure (Fig.5). The



H atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level

Fig.5 Structure of ligand **L**

Table 3 Crystallographic data and structure refinements for L

Empirical formula	C _{10.67} H _{8.67} N ₂ S ₂	Crystal size / mm	0.30×0.28×0.26
Formula weight	228.98	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.380
Temperature / K	273(2)	μ / mm^{-1}	0.447
System	Trigonal	$F(000)$	2 136
Space group	$R\bar{3}c$	θ range / (°)	3.09~25.01
a / nm	1.203 26(17)	Final GOF	1.065
b / nm	1.203 26(17)	R_{int}	0.066 4
c / nm	3.956 0(8)	R indices (all data)	$R_1=0.048$ 8, $wR_2=0.086$ 4
V / nm^3	4.960 2(14)	Largest peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	242 and -177
Z	18		

Table 4 Selected bond lengths (nm) and bond angles (°) for L

C(1)-S(1A)#1	0.181 6(6)	C(1)-S(1A)#2	0.181 6(6)	C(1)-S(1)	0.181 6(6)
C(1)-H(1)	0.098 00	C(7)-S(2A)#3	0.182 8(5)	C(7)-S(2A)#4	0.182 8(5)
S(1A)#1-C(1)-S(1A)#2	108.6(5)	S(1A)#1-C(1)-S(1)	108.6(5)	S(1A)#2-C(1)-S(1)	108.6(5)
S(1A)#1-C(1)-H(1)	110.3	S(1A)#2-C(1)-H(1)	110.3	S(2A)#3-C(7)-S(2)	108.1(4)
S(2A)#3-C(7)-S(2A)#4	108.1(4)	S(2)-C(7)-S(2A)#4	108.1(4)	S(2A)#3-C(7)-H(7)	110.8
S(2A)#4-C(7)-H(7)	110.8				

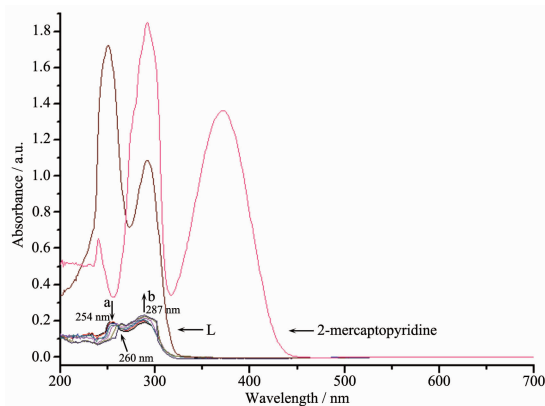
Symmetry transformations used to generate equivalent atoms: #1: $-y+1, x-y+1, z$; #2: $-x+y, -x+1, z$; #3: $-x+y+2, -x+1, z$; #4: $-y+1, x-y-1, z$

crystal data and data collection details for ligand L are summarized in Table 3, and selected bond distances and angles are given in Table 4.

2.2.2 UV-Vis analysis

Taking complex **2** as the example, We tried to use the UV-Vis spectral titration method to track the reaction process. The UV-Vis spectra for the solution of tripodal ligand L and $\text{Zn}(\text{ClO}_4)_2$ according to the different molar ratios of 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4 are summarized in Fig.6. As can be seen, the UV-Vis absorption curves of reaction solution are different from that of ligand L and 2-thiopyrine. In the curves of mixture, as L concentration decrease and Zn^{2+} concentration increase, the absorption peaks centered at 254 nm and 287 nm which can be assigned to the ligand-to-metal charge transfer^[13] are reduction and increase as shown by the arrows respectively, and the absorption at 260 nm appear isosbestic point, which can be assigned to the 2-thiopyrone, the isomer of 2-thiopyrine^[14-15]. Compare the isosbestic point with L and 2-thiopyridine, it exhibits red shift and blue shift respectively. This transformation suggest that the

tripodal ligand L cleave into 2-thiopyridine, and the 2-thiopyridine transfer to 2-thiopyrone^[16-18]. This can also be proved by the bond lengths of C-S in complexes. The bond lengths of C-S in complexes **1** and **2** are 0.173 6, 0.171 8 nm and 0.171 7, 0.171 9 nm respectively. They are shorter obviously than the length of C-S (0.177 ~0.180 nm) in the thiol ligand with S deprotonated in complexes. The mechanism details



Curves at left corner represent the absorption of reaction solution with different molar ratios of tripodal ligand L and $\text{Zn}(\text{ClO}_4)_2$; Arrow a represent the absorption at 254 nm are reducing; Arrow b represent the absorption at 287 nm are increasing

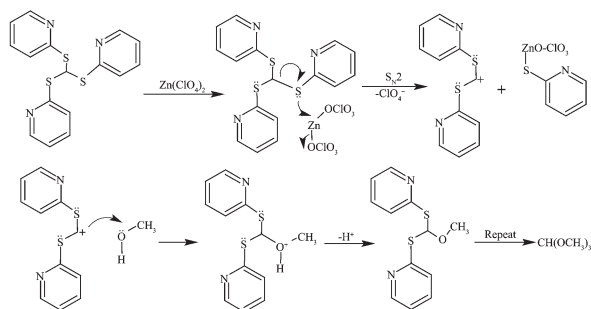
Fig.6 UV-Vis absorption curve

have been studied and confirmed further by ESI-MS spectra.

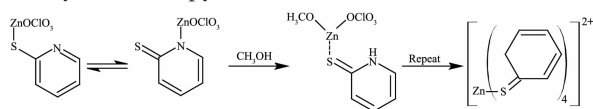
2.2.3 ESI-MS spectra and cleavage mechanism studies

After the complex was separated from the reaction system of tripodal ligand L with the metal salt, the mother solution was taken to carry out ESI-MS in order to detect other product molecules. Taking complex **2** as the example, there is a moderate intensity peak of $m/z+H$ at 107.20 (intensity: 4×10^5) assigned to $CH(OCH_3)_3$ in the ESI-MS spectra. A weaker peak of $m/z-H$ at 109.4 assigned to 2-thiopyridone was also observed. The result further proves that the tripodal ligand L cleaved into 2-thiopyridone coordinated to the metal ion. It is consistent with the result of UV-Vis spectral titration method.

These results indicate that the tripodal ligand L cleaved in the solution contained Zn^{2+} and Cd^{2+} . We speculate that it generated via a S_N2 -like mechanism. The S from L attack metal ion and the $-OCH_3$ groups from methanol attack carbenium ion to generate $CH(OCH_3)_3$ molecules. The reaction can be described as follows (Scheme 2):



The following process occurs because of the more stability of 2-thio-pyridone^[14]:



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