

一维链状镉配合物的合成及结构表征

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摘要: 在甲醇体系中合成了镉配合物 $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{MeOH}$ (**1**) [$\text{L}=1,3,5\text{-tris(3-吡啶基甲氧基)苯}$]。通过元素分析及 X-射线单晶衍射对其进行了表征。结构分析结果表明该化合物属于三斜晶系, $P\bar{1}$ 空间群, 晶胞参数为 $a=1.0571(5)$ nm, $b=1.0590(5)$ nm, $c=1.2708(7)$ nm, $\alpha=87.460(16)^\circ$, $\beta=81.895(17)^\circ$, $\gamma=62.326(14)^\circ$, 晶胞体积 $V=1.2470(11)$ nm³, $Z=1$, $D_{\text{calc}}=1.569$ g·cm⁻³, $F(000)=604$, $\mu=6.26$ cm⁻¹, $R=0.0352$, $wR=0.0664$ 。在化合物 **1** 中, 每个 Cd(II) 的配位环境为变形八面体, 而每个配体 L 通过其两个吡啶基团连接 2 个 Cd(II) 形成一维链状结构, 并进一步通过 O—H \cdots N, O—H \cdots O 和 C—H \cdots O 氢键作用形成了一个具有三维结构的超分子化合物。

关键词: 晶体结构; 镉配合物; 合成

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Synthesis and Crystal Structure of Cd(II) Complex with One-dimensional Chain Structure

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Abstract: The complex $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{MeOH}$ (**1**) [$\text{L}=1,3,5\text{-tris(3-pyridylmethoxy)benzene}$] was synthesized in methanol and characterized by elemental analysis and X-ray crystallography. The results of structural analysis indicate that the complex crystallizes in the triclinic, space group $P\bar{1}$ with $a=1.0571(5)$ nm, $b=1.0590(5)$ nm, $c=1.2708(7)$ nm, $\alpha=87.460(16)^\circ$, $\beta=81.895(17)^\circ$, $\gamma=62.326(14)^\circ$, $V=1.2470(11)$ nm³, $Z=1$, $D_{\text{calc}}=1.569$ g·cm⁻³, $F(000)=604$, $\mu=6.26$ cm⁻¹, the final $R=0.0352$ and $wR=0.0664$. The coordination environment of Cd(II) is a distorted octahedron, and each L ligand links two Cd(II) atoms using two of three pyridyl groups to generate an one-dimensional (1D) chain structure. The 1D chains are further connected by O—H \cdots N, O—H \cdots O and C—H \cdots O hydrogen bonds to give a three-dimensional structure. CCDC: 283825.

Key words: crystal structure; Cd(II) complex; synthesis

0 Introduction

Multidentate organic ligands have been received extensive attention in supermolecular chemistry because of their powerful use in generating a wide range of complexes with specific structures and interesting

properties^[1,2]. A great number of metal-organic frameworks (MOFs) with cage, honeycomb, interpenetration structures have been obtained by using tripodal ligands with aromatic core as building block, for example 1,3,5-tris(1-imidazolyl)benzene and 1,3-bis(1-imidazolyl)-5-(imidazol-1-ylmethyl)-benzene^[3-5]. In fact,

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the formation of MOFs is influenced by factors such as solvent system, template, counterions, geometric requirements of metal ions, and sometimes the ratio between the metal salts and ligands^[6,7]. Therefore, further studies are required to understand the assembly process and to realize the controllable synthesis in the future. In this paper, we report a Cd(II) complex with novel tripodal ligand containing pyridyl groups, rather than the previously reported ones containing imidazol groups^[3-5].

1 Experimental

1.1 General

All commercially available chemicals are of reagent grade and used as received without further purification. Solvents were purified according to the standard methods. C, H and N analyses were made on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker Vector22 FTIR spectrophotometer by using KBr discs. The luminescent spectra in the solid-state were measured at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source.

¹H NMR spectra were recorded on the Bruker DRX-500 spectrometer.

1.2 Structure determinations

A single crystal with dimensions of 0.30 mm × 0.25 mm × 0.25 mm was selected for the experiment. The data collection was carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo *K*α radiation ($\lambda = 0.071\ 07\ \text{nm}$). The structure was solved by direct method with SIR92^[8] and expanded using Fourier technique^[9]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms except for those of water molecules were generated geometrically, while ones of coordinated water molecule were found in the differential Fourier map and located directly. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation^[10]. The crystal parameters, data collection and refinement results for the compound are listed in Table 1. The selected bond lengths and bond angles are listed in Table 2.

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Table 1 Crystallographic data for complex 1

Empirical formula	C ₄₉ H ₅₀ CdC ₁₂ N ₆ O ₁₇	<i>V</i> / nm ³	1.247 0(11)
Formula weight	1 178.25	<i>Z</i>	1
Temperature / K	200	<i>D</i> _{calc} / (g·cm ⁻³)	1.569
Crystal system	Triclinic	Absorption coefficient / cm ⁻¹	6.26
Space group	<i>P</i> $\bar{1}$	<i>F</i> (000)	604
<i>a</i> / nm	1.057 1(5)	θ range / (°)	3.24~27.43
<i>b</i> / nm	1.059 0(5)	Reflections collected	12 325
<i>c</i> / nm	1.270 8(7)	Independent reflections	5 623
α / (°)	87.460(16)	Goodness of-fit on <i>F</i> ²	0.92
β / (°)	81.895(17)	<i>R</i> [<i>I</i> >2σ(<i>I</i>)]	0.035 2
γ / (°)	62.326(14)	<i>wR</i>	0.066 4

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

Cd1-N11	0.238 8(2)	Cd1-O10	0.230 91(19)	Cd1-N31#2	0.234 4(2)
O10-Cd1-O10#1	180.0	O10-Cd1-N31#3	88.36(7)	O10-Cd1-N11#1	86.71(8)
O10-Cd1-N31#2	91.64(7)	O10-Cd1-N11	93.29(8)	N31#3-Cd1-N31#2	180.0
N31#3-Cd1-N11	90.11(7)	N31-Cd1-N11#2	89.89(7)	N11-Cd1-N11#1	180.0

Symmetry transformation used to generate equivalent atoms: #1: -*x*, -*y*+2, -*z*; #2: *x*, *y*, *z*-1; #3: -*x*, -*y*+2, -*z*+1.

1.3 Synthesis of ligand L

Ligand L was synthesized by a similar method reported for the synthesis of α, α' -bis-(3,5-bis(phenylthiamethyl)phenoxy)- α'' -phthalimidomesitylene^[11]. A mixture of 3-picolyl chloride hydrochloride (6 g, 36 mmol) and K_2CO_3 (6 g, 43.2 mmol) in DMF was stirred 20 min at room temperature. Then a mixture of phloroglucinol (1.5 g, 12 mmol) and K_2CO_3 (6 g, 43.2 mmol) in DMF, which was stirred 1 h, was added. The suspension was stirred overnight. After the evaporation of DMF, the distilled water was added. The crude product L was obtained by filtration, and was recrystallized from ethanol to give a pale yellow powder in 35% yield. Calcd. for $C_{24}H_{21}N_3O_3$ (%): C, 72.17; H, 5.30; N, 10.52; found (%): C, 72.18; H, 5.29; N, 10.53. IR data (KBr pellet, cm^{-1}): 1 608s, 1 578m, 1 483 m, 1 431m, 1 165s, 1 071m, 805m, 708m. 1H NMR (500 MHz, $CDCl_3$): δ 5.04 (s, 6H); 6.27 (s, 3H); 7.33 (q, 3H); 7.75 (d, 3H); 8.59 (d, 3H); 8.66 (s, 3H).

1.4 Synthesis of $[Cd(L)_2(H_2O)_2](ClO_4)_2 \cdot MeOH$ (**1**)

A solution of L (102 mg, 0.27 mmol) in methanol (10 mL) was added slowly to an acetonitrile (10 mL) and water (2 mL) solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (56.6 mg, 0.135 mmol). The mixture was stirred for half an hour and filtrated. The filtrate was stood at room temperature. Pale-yellow block single crystals suitable for single crystal X-ray diffraction analysis were obtained after several weeks in 46% yield. Calcd. for $C_{48}H_{50}Cl_2N_6O_{17}Cd$: C, 49.95; H, 4.23; N, 7.13; found (%): C, 49.84; H, 4.32; N, 7.23. IR data (KBr pellet, cm^{-1}): 1 609s, 1 598 s, 1 462m, 1 385m, 1 160s, 1 110s, 1 075s, 795m, 704m.

2 Results and discussion

2.1 Structure description

The crystal structure of the cation part of complex **1** is shown in Fig.1. It can be clearly seen that each Cd(II) atom is in an octahedral coordination environment, with four nitrogen atoms from four different L ligands, and the two oxygen atoms from two water molecules at the axial positions. The bond distances of Cd1-O10, Cd1-N11 and Cd1-N31B are 0.230 91(19) nm, 0.238 8(2) nm and 0.234 4(2) nm, respectively. The O-Cd-N angles are in the range of 86.71(8) $^\circ$ to 93.29(8) $^\circ$ as listed in Table 2. On the other hand, each ligand L links two Cd(II) atoms using its two of three arms, and two L ligands and two Cd(II) atoms

generate an M_2L_2 28-membered macrocyclic motif, and such motifs are joined together by the metal atoms to give an infinite one-dimensional (1D) chain as illustrated in Fig.1 through the Cd-N coordination bonds. There is a T-type edge-to-face π - π interaction within the M_2L_2 macrocircle since the distance between the C atom of one pyridine ring and the centroid of another one is 0.386 nm^[12,13]. It is noteworthy that the third arm with pyridyl group containing N51 does not participate the coordination with the metal atom, instead to form O10-H22 \cdots N51 hydrogen bond (vide post).

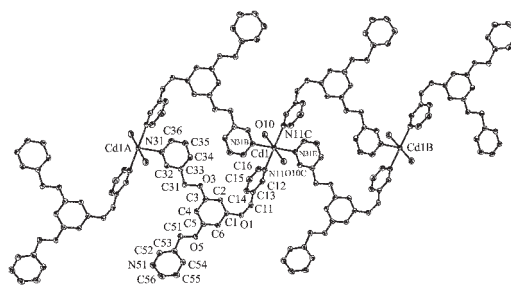


Fig.1 1D chain structure of the cation part of complex **1**

The thermal ellipsoids are drawn at 50% probability and hydrogen atoms were omitted for clarity.

The 1D chains are further connected by O-H \cdots N, O-H \cdots O and C-H \cdots O hydrogen bonds to give a three-dimensional (3D) structure^[14]. The hydrogen bonding data of **1** are summarized in Table 3. First, the O10-N51 distance of 0.271 8(3) nm and O10-H22-N51 angle of 170 $^\circ$ indicate the formation of O10 (water)-H22 \cdots N51 (uncoordinated pyridyl nitrogen atom) hydrogen bond between the neighboring 1D chains, which links the 1D chains to produce a two-dimensional (2D) network (Fig.2). In addition, the ClO_4^- anions and uncoordinated methanol molecules act as linkages to generate 3D framework through the O-H \cdots O and C-H \cdots O hydrogen bonds (Table 3) as exhib-

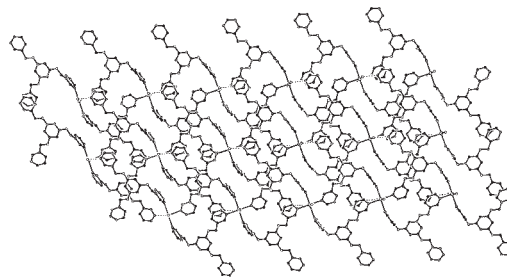


Fig.2 2D network structure of complex **1** linked by O-H \cdots N hydrogen bonds

Table 3 Hydrogen bonding data for complex 1

D-H...A	Distance of D...A / nm	Angle of D-H-A / (°)
O10-H22...N51#1	0.271 8(3)	170
O10-H23...O11#2	0.314 2(4)	126
O10-H23...O101#3	0.262 9(5)	149
O101-H27...O11#1	0.305 9(6)	155
O101-H27...O12#1	0.285 6(6)	121
C11-H4...O11#4	0.347 5(4)	160
C16-H9...O101#3	0.341 8(6)	161
C56-H21...O13#5	0.346 6(5)	165

Symmetry transformation used to generate equivalent atoms: #1: $1-x, 1-y, 1-z$; #2: $-1+x, y, -1+z$; #3: $-x, 1-y, -z$; #4: $x, y, -1+z$; #5: $1+x, -1+y, z$.

ited in Fig.3. The result indicates that the hydrogen bonds play important role in stabilizing the whole structure of complex 1.

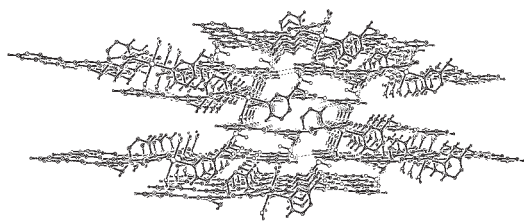


Fig.3 Crystal packing diagram of complex 1 with hydrogen bonds indicated by dashed lines

2.2 Luminescent properties

The Fig.4 shows the emission spectrum of 1 in the solid state measured at ambient temperature. The blue emission with a maximum at *ca.* 436 nm was observed for the complex under the excitation wavelength of 352 nm, while the free ligand L displays a maximum at *ca.* 420 nm under the same conditions. The emission of complex 1 may be from the intraligand emission excited state. Such a difference of emission maximum between the complex and ligand

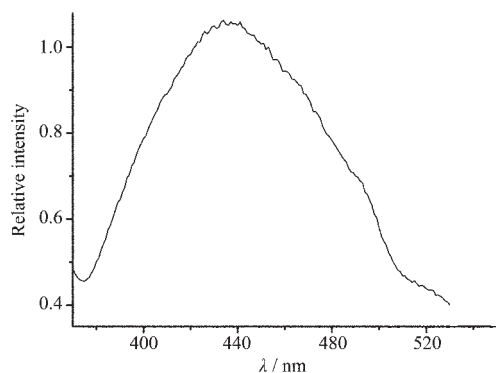


Fig.4 Photo-induced emission spectrum of 1 in the solid state at room temperature with $\lambda_{\text{ex}}=352$ nm

was considered to mainly originate from the influence of the coordination of Cd(II) atom to the L ligand.

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