

由间苯二甲酸和喹喔啉类配体构筑的一维隔(II) 的配合物的水热合成及晶体结构

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摘要: 采用水热法合成了一种金属-有机配合物 $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ (H_2ipt =isophthalic acid, Medpq =2-methyldipyrido[3,2-f:2',3'-h]quinoxaline), 并对其进行了元素分析、红外光谱、紫外-可见光谱、热重表征、和 X-射线单晶衍射测定。该配合物属于单斜晶系, $C2/c$ 空间群。在晶体结构中, $\text{Cd}(\text{II})$ 原子为六配位与来自于间苯二甲酸配体上的 4 个羧基氧原子, 及 Medpq 配体上的 2 个氮原子配位, 呈现畸变的八面体构型。整个晶体由 ipt-Cd-medpq 单元组成一维结构。

关键词: 配位聚合物; 间苯二甲酸; 晶体结构; 水热合成

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Hydrothermal Synthesis and Crystal Structure of a One-Dimensional Cadmium(II) Complex with Isophthalic Acid and 2-Methyldipyrido[3,2-f:2',3'-h]quinoxaline Ligands

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Abstract: A metal-organic coordination polymer $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ (H_2ipt =isophthalic acid, Medpq =2-methyldipyrido[3,2-f:2',3'-h]quinoxaline) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV-Vis spectrum, TG and single-crystal X-ray diffraction. Title compound crystallizes in the monoclinic system, space group $C2/c$, with $a=2.013\ 6(4)$ nm, $b=1.608\ 9(3)$ nm, $c=1.609\ 3(3)$ nm, $\beta=125.12(3)^\circ$, $V=4.302\ 8(15)$ nm³, $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_6\text{Cd}$, $M_r=558.81$, $D_c=1.725$ g·cm⁻³, $Z=8$, the final $R=0.053\ 1$ and $wR=0.140\ 3$. In the crystal structure, the cadmium is six-coordinated with four carboxylate oxygen atoms from three different carboxylate groups, and two nitrogen atoms from Medpq ligand, showing a slightly distorted octahedral geometry. Furthermore, it exhibits a one-dimensional zigzag structure with ipt-Cd-medpq as building units. CCDC: 800998.

Key words: coordination polymer; isophthalic acid; crystal structure; hydrothermal synthesis

0 Introduction

The rational design and synthesis of metal-organic frameworks (MOFs) are currently of great interest and important in producing new functional materials^[1-8]. In the recent years some studies have dealt with the coordination properties of 1,10-phenanthroline (phen)

and its derivatives in the construction of metal organic complexes^[1-8]. However, Medpq (2-methyldipyrido[3,2-f:2',3'-h]quinoxaline) as an important phen derivative has been given far less attention. On the other hand, isophthalic acid (H_2ipt) as a rigid and versatile bridging ligand may generate multi-dimensional structures^[9-15]. Inspired by the above considerations, we selected

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typical Cd(II) center with distinct coordination preferences to assemble with Medpq and isophthalic acid, adopted a hydrothermal technique and successfully synthesized a novel coordination polymers $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$.

1 Experimental

1.1 Materials

The Medpq ligand was synthesized according to the literature method^[16-17]. $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and isophthalic acid were purchased commercially and used without further purification.

1.2 Instrument and measurements

Transmission mode FTIR spectrum was obtained between 4 000 and 400 cm^{-1} using a Nicolet Nexus 470 infrared spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TG) and differential scanning calorimetric (DSC) analysis of the precursor powders was performed on a Germany Netzsch STA449C with heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$ under flowing nitrogen. UV-Vis absorption spectrum was recorded on a Hitachi UV-2450 spectrophotometer at room temperature.

1.3 Synthesis of the title complex

The compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ was prepared from a mixture of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.267 g, 1 mmol), H_2ipt (0.166 g, 1 mmol), Medpq (0.248 g, 1 mmol) and H_2O (8 mL) in an 18 mL Teflon-lined autoclave

under autogenous pressure at 165 $^\circ\text{C}$ for five days. After cooling to room temperature, Yellow block crystals of $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ were collected by filtration and washed with distilled water in 60% yield (based on Cd). Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_6\text{Cd}$ (%): Cd, 20.11; C, 49.42; H, 3.26; N, 10.04; O, 17.17. Found (%): Cd, 20.12; C, 49.43; H, 3.25; N, 10.03; O, 17.18. IR (KBr, cm^{-1}): 3 370 m (respectively ascribed to the stretching vibrations of H_2O , which indicates the existence of water molecules), 1 600s, 1 550s, 1 440s, 1 370s, 1 080s, 823s, 729s.

1.4 Structure determination

A single crystal with dimensions of 0.2 mm×0.2 mm×0.2 mm was mounted on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using an φ - ω scan mode ($5.94^\circ < 2\theta < 50.7^\circ$) at 293(2) K. The structure was solved by direct methods with SHELXS-97 program^[18] and refined by SHELXL-97^[19] using full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. All H atoms were positioned geometrically (C-H 0.093 nm for CH or 0.096 nm for CH_3) and refined as riding mode, with $U_{\text{iso}}(\text{H})$ values of 1.2 $U_{\text{eq}}(\text{C})$. The detailed crystallographic data and structure refinement parameters for the title complex are summarized in Table 1.

CCDC: 800998.

Table 1 Crystallographic data for the title complex

Empirical formula	$\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_6\text{Cd}$	c / nm	1.609 3(3)
Formula weight	558.81	$\beta / (^\circ)$	125.12(3)
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.725	V / nm^3	4.302 8(15)
$\mu (\text{Mo } K\alpha) / \text{mm}^{-1}$	1.065	Z	8
Crystal system	Monoclinic	$R_1, wR_2 (I > 2\sigma(I))$	0.053 1, 0.140 3
Space group	$C2/c$	$F(000)$	2 240
Crystal size / mm	0.20×0.20×0.20	Collected reflections	9 939
a / nm	2.031 6(4)	Goodness-of-fit (GOF) on F^2	1.052
b / nm	1.608 9(3)		

2 Result and discussion

2.1 Description of crystal structure

Single-crystal X-ray diffraction analysis reveals that compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ crystallizes in $C2/c$

space group and consists of a one-dimensional zigzag chain structure. The minimum asymmetric unit of the compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ is shown in Fig.1. There are one Cd(II) ion, one ipt^{2-} ligand, one Medpq ligand and two dissociating water molecules in the asymmetric

unit. The Cd(II) ion is six-coordinated with six atoms (N(1), N(2), O(1), O(2), O(3), O(4)) from Medpq ligand and ipt^{2-} ligand, showing a slightly distorted octahedral geometry. The selected important bond parameters are given in Table 2. In the compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$, each ipt^{2-} ligand links three Cd(II) ions by means of bridging and chelating coordination mode, and the adjacent Cd atoms are bridged through ipt^{2-} ligands to obtain a one dimensional zigzag chain along the *a* axis, as show in Fig.2.

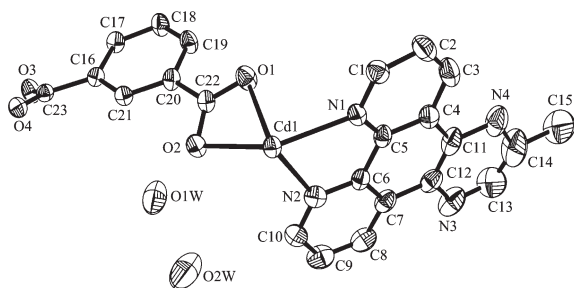


Fig.1 ORTEP drawing of $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ showing the local coordination environment of Cd(II) with thermal ellipsoids at 30% probability

In the one-dimensional infinite chains, intermolecular π - π stacking interactions are found between the aromatic ring of Medpq and its equivalent

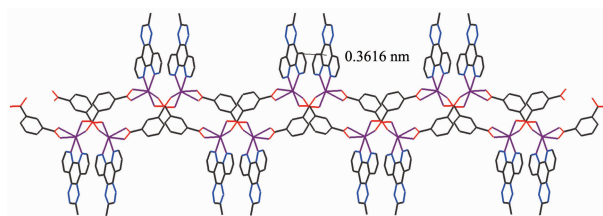


Fig.2 One-dimensional zigzag chain structure of $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ showing π - π stacking interactions

symmetry at $(1-x, y, 1/2-z)$ in an offset fashion. The distances for face-to face and centroid-to centroid are 0.361 6 and 0.367 2 nm, respectively. The relative dihedral angles range from 0° to 2.30° , all of which fall in the reported normal range^[20-21]. The π - π stacking interactions extend along the *a* axis, thus forming the title compound with a 2D layer structure. In compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$, hydrogen bonds are also observed between O (1W) and O (2W). With the help of these hydrogen bonds, the 2D layers spread along the axes, resulting in polymer $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ in an infinite 3D supramolecular structure, and the hydrogen bonds of the compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ are shown in Table 3. Furthermore, the π - π stacking interactions and hydrogen bonds enhance the stability of the polymer^[22-24].

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for the title complex

Cd(1)-N(1)	0.231 0(4)	Cd(1)-N(2)	0.237 4(5)	Cd(1)-O(1)	0.238 9(4)
Cd(1)-O(2)	0.235 0(4)	Cd(1)C-O(3)A	0.226 9(4)	Cd(1)-O(4)B	0.227 2(4)
N(1)-Cd(1)-N(2)	71.08(16)	N(1)-Cd(1)-O(1)	86.95(14)	N(1)-Cd(1)-O(2)	136.97(14)
N(1)-Cd(1)-O(3)A	113.21(16)	N(1)-Cd(1)-O(4)B	115.65(14)	N(2)-Cd(1)-O(1)	97.35(16)
N(2)-Cd(1)-O(2)	92.53(15)	N(2)-Cd(1)-O(3)A	171.57(16)	N(2)-Cd(1)-O(4)B	84.59(14)
O(1)-Cd(1)-O(2)	55.09(13)	O(1)-Cd(1)-O(3)A	90.24(15)	O(1)-Cd(1)-O(4)B	156.38(13)
O(2)-Cd(1)-O(3)A	88.78(14)	O(2)-Cd(1)-O(4)B	101.37(12)	O(3)A-Cd(1)-O(4)B	86.98(14)

Symmetry codes : A: $x+1/2, -y+1/2, z+1/2$; B: $-x+1/2, -y+1/2, -z+1$; C: $x-1/2, -y+1/2, z-1/2$.

Table 3 Hydrogen bond parameters for the title complex

D-H $\cdots$ A	<i>d</i> (D-H) / nm	<i>d</i> (H $\cdots$ A) / nm	<i>d</i> (D $\cdots$ A) / nm	$\angle$ (D-H $\cdots$ A) / ($^\circ$)
O(1W)-H(1a) $\cdots$ O(3)A	0.085	0.211	0.295 2(6)	168.3
O(1W)-H(1b) $\cdots$ O(2)	0.085	0.206	0.290 7(6)	179.0
O(2W)-H(2a) $\cdots$ O(1W)	0.085	0.218	0.279 0(9)	128.6
O(2W)-H(2b) $\cdots$ O(1)B	0.085	0.254	0.300 5(9)	115.6

Symmetry code: A: $-x, y, -z+1/2$; B: $x, -y+1, z-1/2$.

2.2 Thermal analysis

The TG curve of $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ is shown in Fig.

3. It shows that the first weight loss of 4.5% from 80 $^\circ\text{C}$ to 170 $^\circ\text{C}$ corresponds to the removal of coordination

water molecules which are out of order (calcd. 6.45%). Upon further heating, an obvious weight loss (32.67%) occurs in the temperature range of 390 ~458 °C, corresponding to the release of the Medpq ligand (calcd. 44.38%). Obvious weight loss (22.13%) occurs in the temperature range of 470~1 200 °C, corresponds to the release of the ipt ligand (calcd. 29.37%). No weight loss is observed after 1 000 °C, indicating the complete decomposition of $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$. The residual weight 40.7% (calcd. 19.8%) corresponds to CdN_7 and CdO .

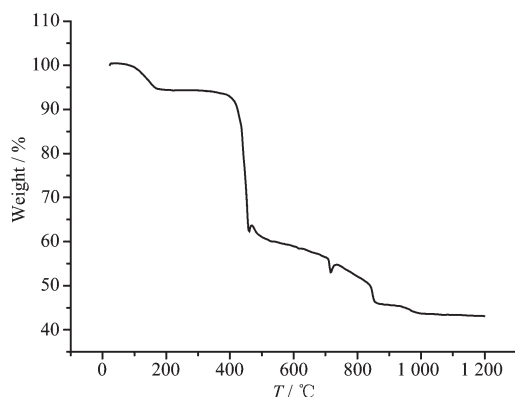


Fig.3 TG curve of the complex $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$

2.3 UV-Vis spectrum analysis

The compound of $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$ is characterized by UV-Vis spectrum at room temperature in solid state, as shown in Fig.4. The experimental bands in the 200 ~343 nm region result from ligand-metal charge transfer and ligand-ligand charge transfer transitions. The absorption band at 427 nm is assigned to the electronic transitions (metal-ligand charge transfer)^[25]. The results indicate the good optical quality of the compound $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$.

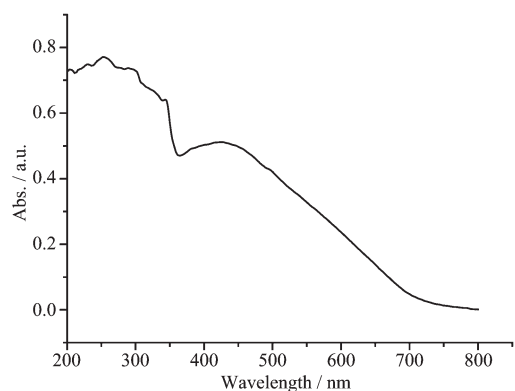


Fig.4 UV-Vis spectrum of the complex $[\text{Cd}(\text{ipt})(\text{Medpq})]_n$

3 Conclusions

In summary, we have prepared a metal-organic polymers by the combination of isophthalic acid and 2-methyldipyrido[3,2-f:2',3'-h]quinoxaline ligands, it has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV-Vis spectrum, TG and single-crystal X-ray diffraction. Our research demonstrates that the new ligand Medpq could be a potential building block to construct novel coordination polymers with unusual architectures and interesting physical properties.

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