

研究简报

由邻苯二甲酸和 Medpq 配体构筑的锌的配合物的水热合成及晶体测定

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Hydrothermal Synthesis and Crystal Structure of A Zinc Complex with Phthalic Acid and Medpq Ligands

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Abstract: A metal-organic coordination polymer $[\text{Zn}(\text{Pht})(\text{Medpq})]_n$ (Pht=phthalic acid, Medpq=2-methyldipyrido [3,2-f:2',3'-h]quinoxaline) (**1**) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG and X-ray single-crystal structure analysis. Title complex crystallizes in the monoclinic system, space group *Cc*, with $a=1.027\ 4(4)$ nm, $b=2.955\ 7(11)$ nm, $c=0.685\ 2(3)$ nm, $\beta=112.941^\circ$, $V=1.916\ 3(13)$ nm³, $\text{C}_{23}\text{H}_{14}\text{N}_4\text{O}_4\text{Zn}$, $M_r=475.75$, $D_c=1.649\ \text{g}\cdot\text{cm}^{-3}$, $\mu(\text{Mo } K\alpha)=1.324\ \text{mm}^{-1}$, $F(000)=968$, $Z=4$, the final $R=0.038\ 8$ and $wR=0.071\ 7$ for 2 697 observed reflections ($I>2\sigma(I)$). In the crystal structure, the Zinc atom is six-coordinated with four carboxylate oxygen atoms from two different carboxylate groups and two nitrogen atoms from Medpq ligand, showing a slightly distorted octahedral geometry. Furthermore, it exhibits a one-dimensional structure with Pht-Zn-Medpq as building units. CCDC: 716600.

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

The rational design and synthesis of metal-directed supramolecular frameworks have received much attention in coordination chemistry because of their interesting molecular topologies and tremendous potential applications in host-guest chemistry, catalysis, molecular selection, nonlinear optics, ion exchange and

microelectronics^[1~10]. On the other hand, it is wellknown that weak interactions are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. In particular, the stacking interactions between suitable aromatic moieties of the twofold coordinating ligands are fascinating^[11], like π - π

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stacking interactions. At the same time, the significance of hydrogen bonding has long been recognized in crystal engineering^[12-14].

Benzenedicarboxylic acids are ideal ligands to design novel coordination polymers and open framework structures^[15-17]. Zinc is a trace element must be contained in the human body, and the active center of some important element, therefore, the zinc complex research has been very active in these field. Furthermore, the synthesis and study of carboxylic acid and zinc complex structure have been more reported^[18-21].

In this paper, we report the hydrothermal synthesis of $[\text{Zn}(\text{Pht})(\text{Medpq})]_n$ (**1**) composed of phthalic acid, Medpq and $\text{Zn}(\text{Ac})_2$ units, and elemental analysis, IR spectrum, TG and X-ray single-crystal structure determination are used to characterize the as-obtained product.

1 Experimental

1.1 Synthesis of ligand

1,10-Phenanthroline-5,6-dione (phendione)^[22] (4.1 g), 1,2-propane diamine (1.5 mL) and alcohol (10 mL) were mixed and refluxed for 2 hours. Then the alcohol was evaporated. The mixture was cooled at room temperature and the light green precipitate was collected by filtration and washed with distilled water in 45% yield.

1.2 Synthesis of the title complex

Compound **1** was prepared from a mixture of $\text{Zn}(\text{Ac})_2$ (0.027 g), isophthalic acid (0.020 g), Medpq (0.027 g)

and H_2O (20 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 180 °C for three days. After cooling to room temperature, brown block crystals of **1** were collected by filtration and washed with distilled water in 70% yield (based on Zn). Anal. Calcd. (%) for $\text{C}_{23}\text{H}_{14}\text{N}_4\text{O}_4\text{Zn}$: Zn, 13.8; C, 58.1; H, 2.8; O, 13.4; N, 11.9. Found(%): Zn, 13.8; C, 58.0; H, 2.9; O, 13.5; N, 11.8. IR (KBr, cm^{-1}): 1 618s, 1 565s, 1 469m, 1 404w, 1 369w, 1 346w, 1 125m, 812w, 751w, 736s, 720m.

1.3 Structure determination

A single crystal with dimensions of 0.228 mm × 0.196 mm × 0.117 mm was selected for data collection on a Bruker Apex2 CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using an ω scan mode ($4.52^\circ < 2\theta < 52.24^\circ$) at 293(2) K. A total of 8 219 reflections were collected and 3 674 were independent ($R_{\text{int}}=0.038\ 8$), of which 2 697 reflections with $I > 2\sigma(I)$ were considered as observed. Correction for Lp factors was applied. The structure was solved by direct methods with SHELXS-97 program^[23] and refined using full-matrix least-squares techniques on F^2 with SHELXL-97^[24]. All non-hydrogen atoms were refined anisotropically. 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 final $R=0.048\ 2$ and $wR=0.104\ 8$ ($w=1/[\sigma(F_o)^2+(0.05P)^2]$, where $P=(F_o^2+2F_c^2)/3$). $S=0.983$, $(\Delta\rho)_{\text{max}}=2.73$, $(\Delta\rho)_{\text{min}}=-2.06\ \text{e}\cdot\text{nm}^{-3}$ and $(\Delta/\sigma)_{\text{max}}=0.000$. The selected bond parameters are given in Table 1.

CCDC: 716600.

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

Zn-O(1)	0.221 2(1)	Zn-O(2)	0.235 4(1)	Zn-N(1)	0.210 3(6)
Zn-O(3)	0.206 5(1)	Zn-O(4)	0.197 8(1)	Zn-N(2)	0.208 4(2)
O(1)-Zn-O(3)	96.63(13)	O(3)-Zn-N(1)	105.00(13)	O(2)-Zn-N(2)	93.73(16)
O(1)-Zn-N(1)	98.97(14)	O(3)-Zn-N(2)	113.26(15)	O(2)-Zn-O(4)	87.93(12)
O(1)-Zn-N(2)	149.58(16)	O(3)-Zn-O(2)	137.86(12)	O(4)-Zn-N(1)	160.15(12)
O(1)-Zn-O(2)	58.32(12)	O(3)-Zn-O(4)	58.37(12)	O(4)-Zn-N(2)	96.83(17)
O(1)-Zn-O(4)	94.06(14)	O(2)-Zn-N(1)	111.65(13)	N(1)-Zn-N(2)	79.30(18)

2 Result and discussion

2.1 Crystal structure

Single-crystal structure reveals that compound

$[\text{Zn}(\text{Pht})(\text{Medpq})]_n$ crystallizes in Cc space group and consists of a two-dimensional network structure. The molecular structure of the complex **1** is shown in Fig.1. There are one Zn(II) ion, one Pht ligand and one Medpq

ligand in the asymmetric unit. The Zn(II) ion is hexacoordinated with four carboxylate oxygen atoms [O(1), O(2), O(3), O(4)] from two different carboxylate groups and two nitrogen atoms [N(1), N(2)] from Medpq ligand, assuming a slightly distorted octahedral geometry. The Zn-O bond distances in compound **1** are in the range of 0.197 8(1)~0.235 4(1) nm, The Zn-N bond distances in the crystal are in the range of 0.208 4(2)~0.210 3(6) nm. The N(O)-Zn-O(N) angles range from 58.32(12)° to 160.15(12)°.

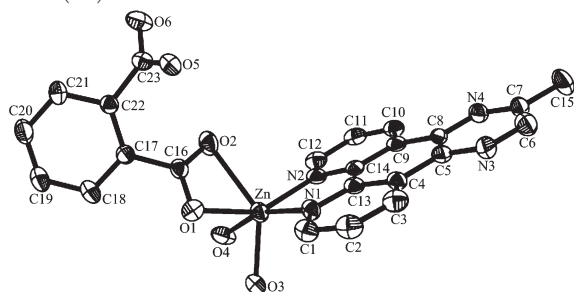
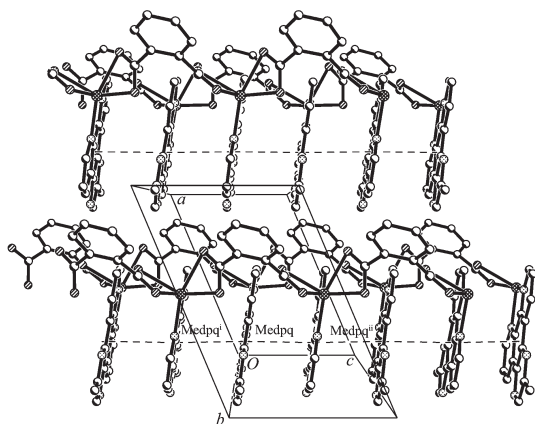


Fig.1 ORTEP drawing of **1** showing the local coordination environment of Zn(II) with thermal, Ellipsoids at 30% probability

In complex **1**, aromatic ring of Medpq ligand and symmetry of the two adjacent equivalent of aromatic ring (symmetry codes: $x, -y, 0.5+z$ and $x, y, -0.5+z$) have π - π interactions with a centroid-to-centroid distance of 0.350 6(2) nm, a vertical face-to-face distance of 0.339 2(3) nm. These adjacent aromatic columns are piled up, along the C axis to form one-dimensional chain (Fig.2). There are atypical hydrogen bonds which



Symmetry codes: ⁱ $x, -y, -0.5+z$; ⁱⁱ $x, y, 0.5+z$

Fig.2 View of three-dimensional network along the b axis in **1** showing π - π stacking interactions between the adjacent aromatic ring of Medpq ligand along the c axis

extend the compound **1** into a 3D supramolecular framework, The atypical hydrogen bond of the compound **1** is shown in Table 2. The atypical hydrogen bond distances in compound **1** are in the range of 0.245 4(1)~0.455 4(1) nm.

Table 2 Hydrogen bond lengths (nm)

Bond	Dist.
C(6)-H(4)···O(2)	0.245 4(1)
C(10)-H(8)···O(3)	0.255 5(1)
C(10)-H(8)···O(2)	0.255 5(1)
C(11)-H(9)···O(2)	0.255 5(1)
C(20)-H(12)···O(1)	0.455 4(1)

2.2 Thermal analysis

The TG curve of **1** is shown in Fig.3. It shows that the first weight loss of 30.06% from 54.9 to 421.2 °C corresponds to the removal of Pht ligand (calcd: 34.47%). Upon further heating, an obvious weight loss (37.52%) occurs in the temperature range of 421.2~888.5 °C, corresponding to the release of Medpq ligand (calcd: 40.10%). After 888.5 °C no weight loss is observed, indicating the complete decomposition of **1**. The residual weight 30.02% (calcd: 25.43%) corresponds to Zn_6N_6 and Zn_3N_2 .

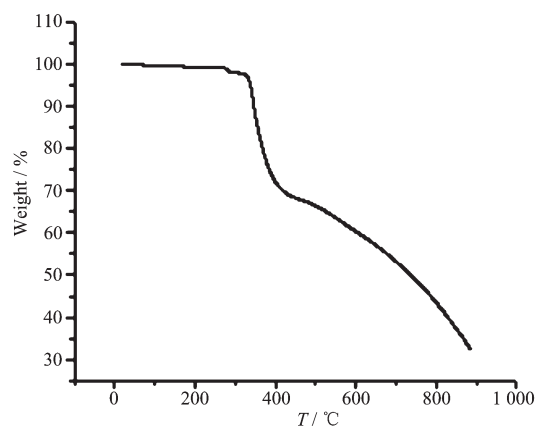


Fig.3 TG of the complex **1**

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