

锌(II)配合物 $\text{Zn}(\text{2-PMBBA})_2(\text{Phen})$ 的合成、 电化学、磁性及荧光性能研究

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摘要: 以 2-(对甲基苯甲酰基)苯甲酸 (2-PMBBA) 和 1,10-邻菲罗啉 (Phen) 为配体合成了一个新的锌(II)配合物 $\text{Zn}(\text{2-PMBBA})_2(\text{Phen})$ 。该配合物晶体属正交晶系,空间群 $Pccn$, 晶胞参数: $a=1.371\ 6(4)\ \text{nm}$, $b=1.336\ 8(4)\ \text{nm}$, $c=1.928\ 7(5)\ \text{nm}$, $V=3.536\ 4(17)\ \text{nm}^3$, $D_c=1.360\ \text{g}\cdot\text{cm}^{-3}$, $Z=4$, $\mu(\text{Mo } K\alpha)=0.746\ \text{mm}^{-1}$, $F(000)=1\ 496$, 最终偏离因子 $R_1=0.035\ 8$, $wR_2=0.086\ 1$ 。在标题配合物中,中心锌(II)离子的配位数是 4,处于变形的四面体配位环境中,这是不多见的。本工作还测定了标题配合物的电化学、磁性及荧光性能。结果表明:循环伏安过程中,配合物的电子转移是不可逆的,对应的电极反应是 $\text{Zn(II)}/\text{Zn(0)}$;在 300~7 K,配合物有抗磁性;当激发波长为 224 nm 时,配合物在 450 和 472 nm 处有强的荧光发射峰。

关键词: 锌(II)配合物; 2-(对甲基苯甲酰基)苯甲酸; 晶体结构; 电化学、磁性及荧光性能

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Synthesis, Electrochemical, Magnetic and Fluorescent Properties of a Zinc(II) Complex $\text{Zn}(\text{2-PMBBA})_2(\text{Phen})$

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Abstract: A new zinc(II) complex $\text{Zn}(\text{2-PMBBA})_2(\text{Phen})$ with 2-(*p*-methylbenzoyl)benzoic acid (2-PMBBA) and 1,10-phenanthroline (Phen) as ligands has been synthesized. Crystal data for this complex are as follows: orthorhombic, space group $Pccn$, $a=1.371\ 6(4)\ \text{nm}$, $b=1.336\ 8(4)\ \text{nm}$, $c=1.928\ 7(5)\ \text{nm}$, $V=3.536\ 4(17)\ \text{nm}^3$, $D_c=1.360\ \text{g}\cdot\text{cm}^{-3}$, $Z=4$, $\mu(\text{Mo } K\alpha)=0.746\ \text{mm}^{-1}$, $F(000)=1\ 496$, final discrepancy factors $R_1=0.0358$, $wR_2=0.086\ 1$. In the title complex, it is less common that the central Zn(II) ion is in a four-coordinated distorted tetrahedron coordination environment. The electrochemical, magnetic and fluorescent properties of the title complex were investigated. The results show that its electron transfer is irreversible in the cyclic voltammetric reaction corresponding to $\text{Zn(II)}/\text{Zn(0)}$, and it exhibits diamagnetic property in the temperature range of 300~7 K. In addition, it can give off fluorescent emission bands at around 450 and 472 nm, respectively, with the excitation wavelength of 224 nm. CCDC: 926215.

Key words: zinc(II) complex; 2-(*p*-methylbenzoyl)benzoic acid; crystal structure; electrochemical, magnetic and fluorescent properties

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Owing to versatile topological structures and potential application, the studies of the metal-organic frameworks (MOFs) have captured the interest of chemists^[1-4]. Up to now, a large number of the MOFs are constructed by the coordination of metal ions with carboxylic acids with a variety of coordination modes^[5-10]. In this field, the aromatic carboxylate frameworks of Zn(II) ion with a d^{10} electron configuration have been intensively studied because they have good fluorescent property and the application future^[11-15]. 2-(*p*-methylbenzoyl)benzoic acid (2-PMBBA) is an important aromatic carboxylic acid. As an intermediate, it is widely used in the industry synthesis of reductive dyes and fluorescent paint, and its MOFs have been reported in the literature^[16-17]. Herein, with the aim of preparing novel functional MOFs, a new zinc (II) complex $\text{Zn}(2\text{-PMBBA})_2(\text{Phen})$ with 2-PMBBA and 1,10-phenanthroline (Phen) as a ligand has been synthesized, and its structure was characterized by X-ray diffractometer. we also investigated its electrochemical, magnetic and fluorescent properties. The results show that it is a diamagnetism system at low temperatures, and it has two fluorescence emission bands at around 450 nm and 472 nm, respectively. In addition, its electron transfer is irreversible in the cyclic voltammetric reaction.

1 Experimental

1.1 Materials and instrumentation

All materials were of analytical grade and used without further purification. Crystal structure determination was carried out on a Bruker SMART APEX CCD diffractometer. Cyclic voltammogram was measured on a CHI660D electrochemical workstation from Shanghai Chen Hua. Magnetic measurements in the range of 300~7 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode. Fluorescence property was performed on a WGY-10 fluorescence spectrophotometer.

1.2 Synthesis

A mixture of 2-(*p*-methylbenzoyl)benzoic acid (0.201 g, 0.84 mmol) and terbium(III) nitrate hexahy-

drate (0.114 g, 0.25 mmol) was dissolved in 7 mL mixed solvent of DMF/H₂O (volume ratio 2:5). The solution was heated in water bath, and keep at 80 °C for 1 h. After this solution was cooled to room temperature, zinc acetate dihydrate (0.039 g, 0.18 mmol) and 1,10-phenanthroline (0.032 g, 0.16 mmol) were added into it. Then, the resultant solution was heated at 50 °C for 4 h, and filtered. The filtrate was evaporated slowly at room temperature. Colorless single crystals suitable for X-ray analysis were obtained after a month. Yield: 33.3%.

1.3 Structure determination

A crystal with dimensions of 0.18 mm×0.17 mm×0.16 mm was put on Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using ω - φ scan mode at 296(2) K. Of the total 17 078 reflections collected in the range of $2.11^\circ \leq \theta \leq 25.01^\circ$, 3 120 were independent with $R_{\text{int}}=0.049\ 9$, of which 2 084 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The absorption correction was carried out by the program SADABS^[18]. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the programs SHELXS-97^[19] and SHELXL-97^[20]. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. The final refinement including hydrogen atoms converged to $R_1=0.035\ 8$, $wR_2=0.086\ 1$; $w=1/[\sigma^2(F_o^2)+(0.048\ 3P)^2+0.330\ 5P]$, where $P=(F_o^2+2F_c^2)/3$, $(\Delta/\sigma)_{\text{max}}=0.000$, $S=1.019$. Details of the crystal parameters, data collection and refinements are summarized in Table 1.

CCDC: 926215.

2 Results and discussion

2.1 Crystal structure analysis

The crystal structure of the title complex is revealed in Fig.1. Selected bond lengths and bond angles are shown in Table 2. The crystal structure of the title complex consists of one Zn(II) ion, two 2-(*p*-methylbenzoyl)benzoic acid anions and one Phen molecular. The central Zn(II) ion is coordinated with two nitrogen atoms from one Phen molecular, and two

Table 1 Crystallographic data of the title complex

Empirical formula	$\text{C}_{42}\text{H}_{30}\text{N}_2\text{O}_6\text{Zn}$	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.360
Formula weight	724.05	Z	4
Size / mm	0.18×0.17×0.16	$F(000)$	1496
θ range for data collection / (°)	2.11 to 25.01	$\mu (\text{Mo K}\alpha) / \text{mm}^{-1}$	0.746
Crystal system	Orthorhombic	Reflections collected	17 078
Space group	$Pccn$	Independent reflections	3 120 ($R_{\text{int}}=0.049\ 9$)
a / nm	1.37 16(4)	Final GooF	1.019
b / nm	1.336 8(4)	$R_1, wR_2 (I > 2\sigma(I))$	0.035 8, 0.086 1
c / nm	1.928 7(5)	R_1, wR_2 (all data)	0.064 6, 0.099 2
V / nm ³	3.536 4(17)	Largest difference peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	232, -302

Table 2 Selected bond lengths (nm) and bond angles (°) of the complex

Zn(1)-O(2A)	0.196 76(17)	Zn(1)-N(1)	0.209 1(2)	O(1)-C(7)	0.123 1(3)
Zn(1)-O(2)	0.196 76(17)	Zn(1)-N(1A)	0.209 1(2)	O(2)-C(7)	0.126 8(3)
O(2A)-Zn(1)-O(2)	129.51(10)	O(2)-Zn(1)-N(1)	111.46(7)	O(2)-Zn(1)-N(1A)	106.77(8)
O(2A)-Zn(1)-N(1)	106.77(8)	O(2A)-Zn(1)-N(1A)	111.46(7)	N(1)-Zn(1)-N(1A)	79.81(13)
O(1)-C(7)-O(2)	122.3(2)	O(3)-C(8)-C(2)	119.9(2)	C(6)-C(1)-C(7)	119.9(2)

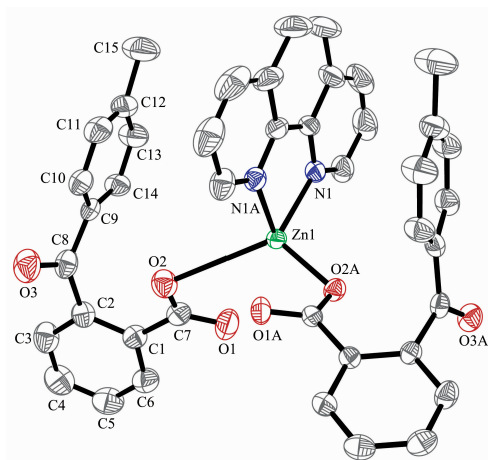
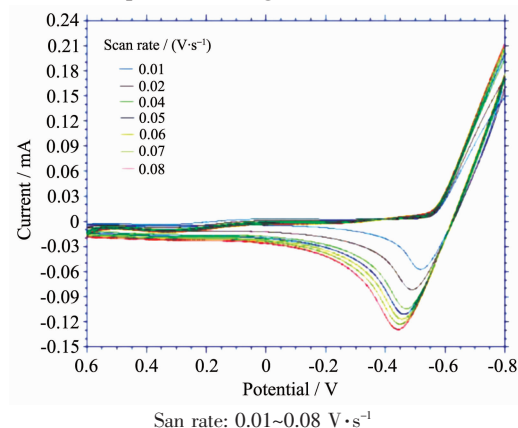
Symmetry transformations used to generate equivalent atoms: A: $-x+3/2, -y+1/2, z$.

oxygen atoms from two 2-(*p*-methylbenzoyl)benzoic acid anions to give a distorted tetrahedron coordination geometry. The bond angles O (2A)-Zn (1)-O(2), O(2A)-Zn(1)-N(1), O(2)-Zn(1)-N(1) and N(1)-Zn(1)-N(1A) are 129.51(10)°, 106.77(8)°, 111.46(7)° and 79.81 (13)°, respectively. The bond lengths of Zn(1)-O(2) and Zn(1)-N(1) are 0.196 76(17) and 0.209 1(2) nm, respectively, which are in the normal range. In addition, the bond lengths of O(2)-C(7) and O(1)-C(7) are 0.126 8(3) and 0.123 1(3) nm, respectively. Their difference value is 0.003 7 nm, and it is larger than

0.000 3 nm, which indicates that after eliminating the hydrogen atom of carboxyl, 2-(*p*-methylbenzoyl)benzoic acid coordinates with Zn(II) ion in a monodentate form^[21]. The above discussion is consistent with the structural determination. Besides, there are weak hydrogen bonding interactions in the title complex such as C(4)-H(4)⋯O(1) (0.324 5(4) nm, 149°) and C(20)-H(20)⋯O(1) (0.312 9(4) nm, 119°). Hydrogen bonds interactions contribute to the stabilization of the whole structure.

2.2 Electrochemical property

Fig.2 shows the cyclic voltammogram (CV) curve of the title complex, and Fig.3 reveals the influence of

**Fig.1** Molecular structure of the title complex**Fig.2** Cyclic voltammogram of the title complex

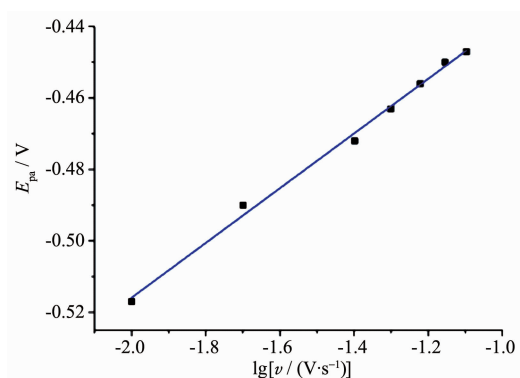


Fig.3 Effect of the potential scan rate (v) on the oxidation peak potential (E_{pa})

the potential scan rate (v) on the oxidation peak potential (E_{pa}) in the potential scan rate range of $0.01 \sim 0.08 \text{ V} \cdot \text{s}^{-1}$.

In the CV measurement, we employed a conventional three-electrode system, where a saturated calomel electrode (SCE) as the reference electrode, and two platinum electrodes were chosen as the working electrode and the counter electrode, respectively. The title complex was dissolved into the mixture solvent of methanol and water (volume ratio 1:6) with the resulted solution concentration of $2.5 \text{ mmol} \cdot \text{L}^{-1}$. A NaOH- KH_2PO_4 ($\text{pH}=6.2$) solution and a KCl solution of $0.2 \text{ mol} \cdot \text{L}^{-1}$ were used as the buffer solution and supporting electrolyte, respectively. The scanning range is $-0.8 \sim 0.6 \text{ V}$. As revealed in Fig.2, there exists only one oxidation peak in every CV curve, demonstrating that the electron transfer of the title complex is irreversible in the electrode reaction. In addition, the oxidation peak potential (E_{pa}) shifts to a more positive value with increasing scan rate (v), and it is proportional to $\lg v$ in the range of $0.01 \sim 0.08 \text{ V} \cdot \text{s}^{-1}$. The linear regression equation is $E_{pa} (\text{V}) = 0.076 \lg[v / (\text{V} \cdot \text{s}^{-1})] - 0.3627$ with the correlation coefficient 0.9957 (Fig.3). Based on the slope of E_{pa} with $\lg v$, the number of electrons involved in the oxidation of the title complex can be evaluated. The αn is calculated to be 0.77. Generally, in the totally irreversible electrode process, the electron transfer coefficient α is about 0.5. So, n is about 2, indicating that two electrons are involved in the the electrode reaction corresponding to $\text{Zn(II)}/\text{Zn(0)}$.

2.3 Magnetic properties

The magnetic susceptibility of the title complex was measured with an applied magnetic field of 2 kOe ($1 \text{ kOe} = 79.6 \text{ kA} \cdot \text{m}^{-1}$) in the temperature range of $300 \sim 7 \text{ K}$. The temperature dependence of the molar magnetic susceptibility of is revealed in Fig.4 in the form of $1/X_m$ vs T . The value of $1/X_m$ changes less from $-2.17 \times 10^3 \text{ cm}^{-3} \cdot \text{mol}$ at 300 K to $-2.18 \times 10^3 \text{ cm}^{-3} \cdot \text{mol}$ at 53 K. When the temperature drops to about 7 K, the value of $1/X_m$ is $-1.51 \times 10^4 \text{ cm}^{-3} \cdot \text{mol}$, which significantly reduces. In 300 to 7 K, the value of $1/X_m$ is always negative, which indicates that the title complex is a diamagnetism system at low temperatures.

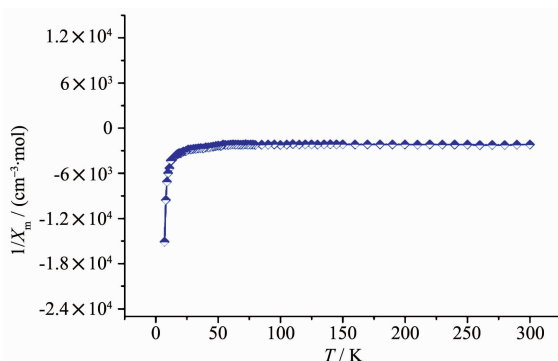


Fig.4 Temperature dependence of the magnetic susceptibility of the title complex in the form of $1/X_m$ vs T

2.4 Fluorescent property

In the range of $400 \sim 520 \text{ nm}$, the fluorescent properties of the title complex was measured in the mixture of methanol and water (volume ratio 1:6) at room temperature, and its emission spectrum is showed in Fig.5. When the exciting radiation is at 224

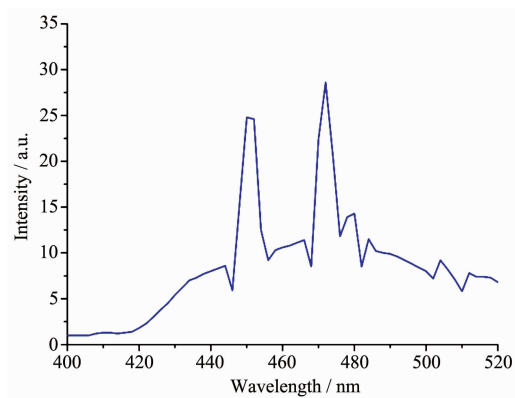


Fig.5 Emission spectra of the title complex in the liquid state at room temperature

nm. the title complex displays two intense emission bands at around 450 and 472 nm, respectively. Comparably, under the same conditions and with the same exciting radiation, we measured the fluorescence properties of the 2-(*p*-methylbenzoyl)benzoic acid and Phen ligands, and the results show that they haven't fluorescent emission band. Such fluorescent behavior indicates that the excitation of the title complex itself is responsible for its fluorescent emission.

3 Conclusions

In the present work, a new zinc(II) complex $\text{Zn}(\text{2-PMBBA})_2(\text{Phen})$ has been synthesized by assembly reaction of 2-(*p*-methylbenzoyl)benzoic acid (2-PMBBA) and Phen as ligands, and characterized by X-diffractometer. The property tests of the title complex show that its cyclic voltammetric reaction corresponds to $\text{Zn}(\text{II})/\text{Zn}(\text{0})$, and its electron transfer is irreversible. In addition, it is diamagnetic system at low temperatures, and when the excitation wavelength being at 224 nm, it has fluorescent emission bands at around 450 and 472 nm, respectively.

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