第 29 卷第 11 期
2013 年 11 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.29 No.11
2465-2469

2-苯甲酰苯甲酸铜配合物的合成、电化学、荧光及磁性研究

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摘要:以 2-苯甲酰苯甲酸(HL)和 1,10-邻菲啰啉(Phen)为配体合成了一个新的铜(Ⅱ)配合物{$[Cu_2(Phen)_4(NO_3)][Cu(Phen)_2(L)]_2(L)_2(NO_3)_3$}·$2H_2O$ (**1**)。该化合物晶体属三斜晶系,空间群 $P\bar{1}$,晶胞参数:a=1.138 57(5) nm,b=1.193 49(7) nm,c=2.615 31(13) nm,α=89.428 0(10)°,β=82.753(2)°,γ=74.537 0(10)°,V=3.3968(3) nm^3,D_c=1.408 g·cm^{-3},Z=1,μ(Mo $K\alpha$)=0.700 mm^{-1},F(000)=1 480,最终偏离因子 R_1=0.057 1,wR_2=0.133 4。在标题配合物分子中,有 2 个单核阳离子$[Cu(Phen)_2(L)]^+$和 1 个双核阳离子$[Cu_2(Phen)_4(NO_3)]^{3+}$,中心铜(Ⅱ)离子的配位数都是五。测定了标题配合物的电化学、荧光和磁性。结果表明:在循环伏安过程中,配合物的电子转移是准可逆的,对应的电极反应是 Cu(Ⅱ)/Cu(Ⅰ);当激发波长为 488 nm 时,配合物在 494 nm 附近有较强的荧光发射峰;在 300~52 K,配合物具有抗磁性。

关键词:铜(Ⅱ)配合物;2-苯甲酰苯甲酸;晶体结构;电化学、荧光和磁性

中图分类号:O614.121 **文献标识码**:A **文章编号**:1001-4861(2013)11-2465-05

DOI:10.3969/j.issn.1001-4861.2013.00.356

Synthesis, Electrochemical, Fluorescent and Magnetic Properties of a Copper(Ⅱ) Complex with 2-Benzoylbenzoic Acid as a Ligand

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Abstract: A new copper(Ⅱ) complex {$[Cu_2(Phen)_4(NO_3)][Cu(Phen)_2(L)]_2(L)_2(NO_3)_3$}·$2H_2O$ (**1**) with 2-benzoylbenzoic acid (HL) and 1,10-phenanthroline (Phen) as ligands has been synthesized. Crystal data for the complex are as follows: triclinic, space group $P\bar{1}$, a=1.138 57(5) nm, b=1.193 49(7) nm, c=2.615 31(13) nm, α=89.428 0(10)°, β=82.753(2)°, γ=74.537 0(10)°, V=3.396 8(3) nm^3, D_c=1.408 g·cm^{-3}, Z=1, μ(Mo $K\alpha$)=0.700 mm^{-1}, F(000)=1 480, final discrepancy factors R_1=0.057 1, wR_2=0.133 4. In **1**, there are two mononuclear cations $[Cu(Phen)_2(L)]^+$ and one dinuclear cation $[Cu_2(Phen)_4(NO_3)]^{3+}$, and the four central Cu(Ⅱ) ions are all penta-coordinated. The electrochemical, fluorescent and magnetic properties of **1** were investigated. The results show that the electron transfer in the electrode reaction of **1** is quasi reversible, and the electrode reaction corresponds to Cu(Ⅱ)/Cu(Ⅰ). When the exciting radiation set at 488 nm, **1** can give off strong fluorescence band at around 494 nm. In addition, **1** displays diamagnetic property in temperatures range of 300~52 K. CCDC: 929034.

Key words: copper(Ⅱ) complex; 2-benzoylbenzoic acid; crystal structure; electrochemical, fluorescent and magnetic properties

收稿日期:2013-03-20。收修改稿日期:2013-06-11。

国家自然科学基金(No.21102040),湖南省自然科学基金(No.12JJ6013,11JJ9005,13JJ3112),湖南省科学技术厅科技计划项目(No.2012GK3030,2012FJ3020),湖南省教育厅科学研究项目(No.11C0186),衡阳市科技计划项目(NO.2011kG28),湖南省高校青年骨干教师培养对象资助,湖南省重点建设学科资助项目。

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0 Introduction

The study of metal-organic complexes has attracted much attention not only for their novel structure, but also for their application such as gas sorption, fluorescence, catalysis, molecular magnetism, nonlinear optics and ion-exchange[1-7]. In the synthesis of metal-organic complexes, the organic ligands play very important role. The aromatic carboxylic acids with a variety of coordinating modes are often used as ligands to construct metal-organic complexes because the aromatic carboxylic acid complexes can exhibit high thermal and good physical and chemical properties in practical use[8-15]. 2-Benzoylbenzoic acid (HL) is an important aromatic carboxylic acid, and it is a main raw material of anthraquinone dyes intermediates to manufacture anthraquinone and 1-aminoanthraquinone. As a rigid organic ligand, the complexes of HL have been reported in the literature[16-20]. In this paper, a new copper(Ⅱ) complex $\{[Cu_2(Phen)_4(NO_3)][Cu(Phen)_2(L)]_2(L)_2(NO_3)_3\}\cdot 2H_2O$ (**1**) by assembly reaction of HL and cuprous acetate has been solvothermally synthesized and structurally determined. We also report our preliminary results of the electrochemical, fluorescent and magnetic properties of **1**.

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. Fluorescence spectra was performed on a WGY-10 fluorescence spectrophotometer. Magnetic measurements were performed on a MPMS-SQUID magnetometer on a crystalline sample in the temperature settle mode.

1.2 Synthesis

A mixture of cuprous acetate (0.088 g, 0.44 mmol), HL (0.089 g, 0.40 mmol) and Phen (0.117 g, 0.59 mmol) was dissolved in 10 mL mixed solvent of dimethyl sulfoxide and water (volume ratio 2:8). The pH value of the solution was adjusted to about 7~8 by adding dilute NaOH solution. Then, the resultant solution was poured into 25 mL hydro-thermal reaction autoclave and kept at 140 ℃ for 24 h, and filtrated. The filtrate was put at room temperature for slow volatilization. Blue single crystals suitable for X-ray diffraction analysis were obtained after five weeks. Yield: 37%. IR (KBr, cm^{-1}): 3 437(w), 1 657(vs), 1 381(vs), 1 105(m), 851(s), 724(s), 432(m).

1.3 Structure determination

A crystal with dimensions of 0.17 mm×0.16 mm×0.15 mm was chosen to be measured on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) by using ω-φ scan mode at 173(2) K. The total 18 852 reflections were collected within the range of $1.57°\leqslant\theta\leqslant 26.00°$, of which 13 195 were independent with R_{int}=0.028 5. 9 523 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the programs SHELXS-97[21] and SHELXL-97[22]. Corrections for Lp factors and empirical adsorption adjustment were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to R_1=0.057 1, wR_2=0.133 4; $w=1/[\sigma^2(F_o^2)+(0.06P)^2+1.99P]$, where $P=(F_o+2F_c^2)/3$, $(\Delta/\sigma)_{max}$=0.000, S=1.03. Crystallographic data of the complex are shown in Table 1.

CCDC: 929034.

2 Results and discussion

2.1 Crystal structure analysis

The crystal structure of **1** is revealed in Fig.1. Selected bond lengths and bond angles are shown in Table 2. Complex **1** consists of two mononuclear cations $[Cu(Phen)_2(L)]^+$, one dinuclear cation $[Cu_2(Phen)_4(NO_3)]^{3+}$, two L^- anions, three NO_3^- anions and two lattice water molecules. In mononuclear cation $[Cu(Phen)_2(L)]^+$, Cu(1) ion is coordinated with four nitrogen atoms from two Phen moleculars, and one oxygen atom from one L^- anion to give a distorted square-pyramidal coordination geometry, where N(1), N(2), O(1) and N(3)

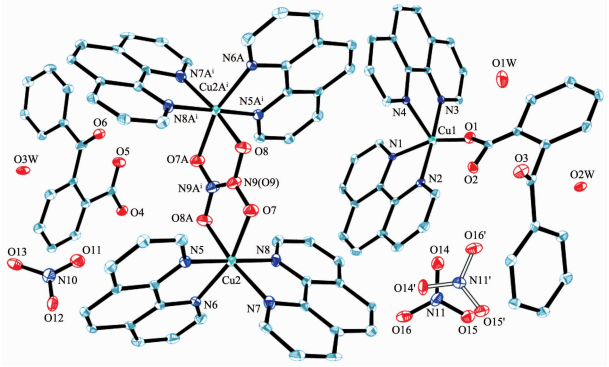
Table 1　Crystallographic data of the title complex

Empirical formula	$C_{152}H_{104}Cu_4N_{20}O_{26}$	γ / (°)	74.537 0(10)
Formula weight	2 880.71	V / nm^3	3.396 8(3)
Color	Blue	D_c / (g·cm^{-3})	1.408
Size / mm	0.17×0.16×0.15	Z	1
θ range for data collection / (°)	1.57 to 26.00	F(000)	1 480
Crystal system	Triclinic	μ (Mo $K\alpha$) / mm^{-1}	0.700
Space group	$P\bar{1}$	Reflections collected	18 852
a / nm	1.138 57(5)	Independent reflections	13 195 (R_{int}=0.028 5)
b / nm	1.193 49(7)	Final GooF	1.030
c / nm	2.615 31(13)	R_1, wR_2 (I>2σ(I))	0.057 1, 0.133 4
α / (°)	89.428 0(10)	R_1, wR_2 (all data)	0.079 7, 0.140 9
β / (°)	82.753(2)	Largest difference peak and hole / (e·nm^{-3})	925, –492

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

Cu(1)-O(1)	0.199 1(2)	Cu(2)-O(7)	0.198 7(5)	Cu(2)-N(7)	0.213 6(3)
Cu(1)-N(2)	0.199 4(3)	Cu(2)-N5	0.200 1(3)	O(7)-N(9)	0.125 8(6)
Cu(1)-N(3)	0.201 4(3)	Cu(2)-N(8)	0.200 8(3)	O(8)-N(9)	0.127 2(6)
Cu(1)-N(1)	0.204 4(3)	Cu(2)-O(8)	0.206 1(5)	O(1)-C(55)	0.127 5(4)
Cu(1)-N(4)	0.217 2(3)	Cu(2)-N(6)	0.211 1(3)	O(2)-C(55)	0.125 5(4)
O(1)-Cu(1)-N(2)	90.68(10)	N(1)-Cu(1)-N(4)	98.72(10)	N(8)-Cu(2)-N(6)	101.04(11)
O(1)-Cu(1)-N(3)	92.55(10)	O(7)-Cu(2)-N(5)	89.10(18)	O(8)-Cu(2)-N(6)	86.65(17)
N(2)-Cu(1)-N(3)	176.77(11)	O(7)-Cu(2)-N(8)	89.41(18)	O(7)-Cu(2)-N(7)	98.21(18)
O(1)-Cu(1)-N(1)	159.34(10)	N(5)-Cu(2)-N(8)	177.17(12)	N(5)-Cu(2)-N(7)	97.00(12)
N(2)-Cu(1)-N(1)	81.91(11)	O(7)-Cu(2)-O(8)	78.8(2)	N(8)-Cu(2)-N(7)	80.83(12)
N(3)-Cu(1)-N(1)	94.99(10)	N(5)-Cu(2)-O(8)	91.99(18)	O(8)-Cu(2)-N(7)	170.50(18)
O(1)-Cu(1)-N(4)	101.54(10)	N(8)-Cu(2)-O(8)	90.09(18)	N(6)-Cu(2)-N(7)	97.76(11)
N(2)-Cu(1)-N(4)	99.70(10)	O(7)-Cu(2)-N(6)	162.12(18)	O(7)-N(9)-O(8)	115.5(4)
N(3)-Cu(1)-N(4)	79.80(10)	N(5)-Cu(2)-N(6)	81.01(12)	O(2)-C(55)-O(1)	123.1(3)

define the base plane, and N (4) occupies the vertex. The bond angles N(1)-Cu(1)-N(2), N(2)-Cu(1)-O(1), O(1)-Cu(1)-N(3) and N(3)-Cu(1)-N(1) is 81.91(11)°, 90.68(10)°, 92.55(10)° and 94.99(10)°, respectively. Their sum is 360.13°. In dinuclear cation $[Cu_2(Phen)_4(NO_3)]^{3+}$, Cu(2) ion and Cu(2A) ion link through the bridging coordination of one disordered NO_3^- anion, in which N(9) and O(9) occupies the same position, and the share of each is 0.5. Compared with Cu(1) ion, Cu(2) ion is also in a five-coordinated distorted square-pyramidal coordination environment, The sum of bond angles N(5)-Cu(2)-N(6)(81.01(12)°), N(6)-Cu(2)-N(8)(101.04(11)°), N(8)-Cu(2)-O(7)(89.41(18)°) and O(7)-Cu(2)-N(5)(89.10(18)°) is 360.56°, which indicates that N(5), N(6), N(8) and O(7) are nearly coplanar. The Cu-N bond lengths differ to some extent. The bond lengths Cu(1)-N(1), Cu(1)-N(2), Cu(1)-N(3), Cu(1)-N(4), Cu(2)-N(5), Cu(2)-N(6) and Cu(2)-N(7) are 0.204 4(3), 0.199 4(3), 0.2014(3), 0.217 2(3), 0.200 1(3), 0.211 1(3)



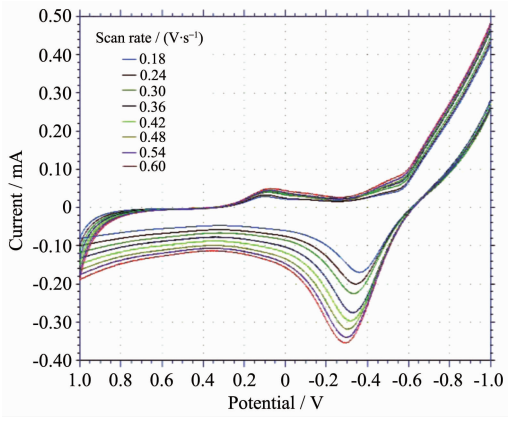
^{i} –x, 2–y, 1–z

Fig.1　Crystal structure of the title compound

and 0.213 6(3) nm, respectively, and their average length is 0.206 7(3) nm, which is in the normal range. It is clear that the bond length of Cu(1)-N(4) (0.217 2(3) nm) is longer than that of the other Cu-N probably because N(4) is in the top of a distorted square-pyramidal coordination geometry. In addition, in **1**, there are one disordered uncoordinated NO_3^- anion and one disordered lattice water molecule. The disordered lattice water molecule occupies three positions, and the share is 0.3, 0.3 and 0.4, respectively.

2.2 Electrochemical property

The cyclic voltammogram (CV) curves of **1** are shown in Fig.2 in the potential scan rate range of 0.18~0.60 V·s^{-1}. In the CV measurement of **1**, we employed a conventional three-electrode system where a saturated calomel electrode was chosen as the reference electrode, and two platinum electrodes as a working electrode and a counter electrode, respectively. **1** was dissolved into the mixture solvent of methanol and water (volume ratio 1∶5), and the concentration of the resulted solution is 1.5 mmol·L^{-1}. A NaOH-KH_2PO_4 (pH=6.2) solution was used as the buffer solution and a KCl solution (0.2 mol·L^{-1}) as the supporting electrolyte. The scanning range is −1.0 ~ 1.0 V. There are a pair of redox peaks in every CV curve, demonstrating that the electron transfer of **1** is quasi-reversible in the electrode reaction. In addition, the oxidation peak potential (E_{pa}) shifts to a more positive value with increasing scan rate (v). E_{pa} is proportional to lg[v/(V·s^{-1})] in the range of 0.18~0.60 V·s^{-1}, and the linear regression equation is E_{pa}(V)= 0.127 6lg [v/(V·s^{-1})]−0.267 5 with the correlation coefficient of 0.997 4 (Fig.3). Based on the slope of E_{pa} with lg [v/(V·s^{-1})], the number of transferred electrons involved in the electrode reaction can be evaluated. The αn is calculated to be 0.46. Generally, in the quasi-reversible electrode process, the electron transfer coefficient α is about 0.5. So, n is about 1, indicating that one electron is involved in the electrode reaction corresponding to Cu(Ⅱ)/Cu(Ⅰ).



San rate: 0.18~0.60 V·s^{-1}

Fig.2 Cyclic voltammograms of the title complex

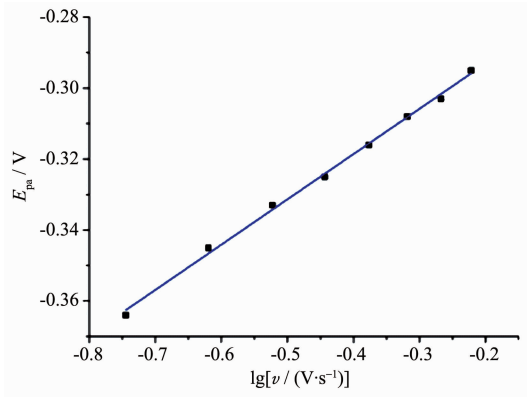


Fig.3 Effect of the potential scan rate (v) on the oxidation peak potential (E_{pa})

2.3 Fluorescent property

Fig.4 shows the fluorescent emission spectra of **1**. In the range of 420 ~570 nm, we measured the fluorescent property of **1** in the mixture of methanol and water (volume ratio 1∶5) at room temperature. **1** exhibits one intense emission band at around 494 nm with the exciting radiation set at 488 nm. Under the same condition and with the same exciting radiation, the fluorescence properties of the HL and Phen ligands were investigated, and the results show that

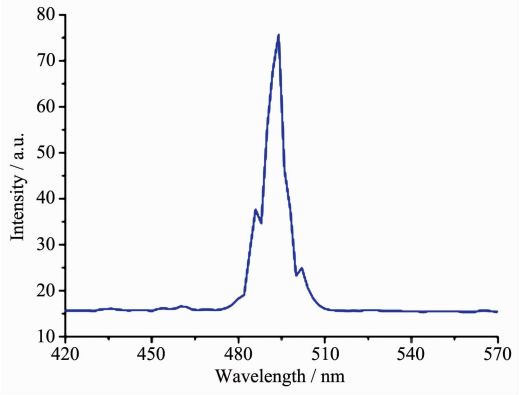


Fig.4 Emission spectra of the title complex in the liquid state at room temperature

they display fluorescence emission bands at about 492 and 488 nm, respectively. Compared with the ligands, **1** has a similar fluorescence emission band position, which indicates that intraligand excitations are responsible for the fluorescence emission of **1**.

2.4 Magnetic properties

The magnetic susceptibility of **1** was measured with an applied magnetic field of 2 kOe in the temperature range of 300 ~2 K. The temperature dependence of the molar magnetic susceptibility of **1** is revealed in Fig.5 in the form of X_m vs T. The value of X_m increases less from -1.68×10^{-3} $cm^3\cdot mol^{-1}$ at 300 K to -1.01×10^{-3} $cm^3\cdot mol^{-1}$ at 90 K. When the temperature drops to 2 K, the value of X_m is 5.145×10^{-2} $cm^3\cdot mol^{-1}$, which significantly increase. The date of X_m is $-3.058\ 67\times10^{-5}$ $cm^3\cdot mol^{-1}$ at 52 K. In 300~52 K, the value of X_m is always negative, which indicates that **1** is a diamagnetism system at low temperaturs.

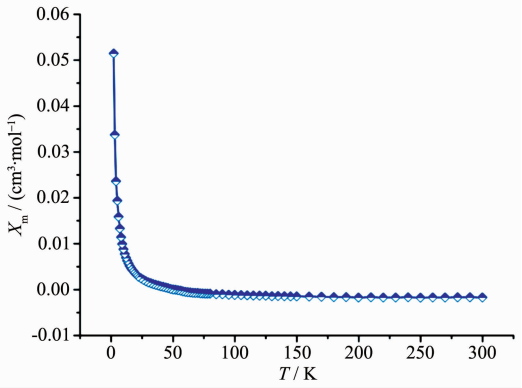


Fig.5 Temperature dependence of the magnetic susceptibility of the title complex in the form of X_m vs T

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