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基于 2-(4-甲基苯甲酰基)苯甲酸及 2,2′-联吡啶的双核铜(Ⅱ)配合物的晶体结构、荧光和磁性

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摘要: 以 2-(4-甲基苯甲酰基)苯甲酸(HL)及 2,2′-联吡啶(2,2′-bipy)为配体合成了一个双核铜(Ⅱ)配合物[$Cu_2(L)_4(2,2'\text{-bipy})_2$]·$H_2O$ (**1**),并对其进行了晶体结构测定。测定结果表明,该配合物晶体属于三斜晶系,空间群为 $P\bar{1}$,晶胞参数:a=1.012 57(15) nm,b=1.312 5(2) nm,c=1.317 0(2) nm,α=82.985(2)°,β=76.437(2)°,γ=88.290(2)°,V=1.688 7(4) nm^3,D_c=1.391 g·cm^{-3},Z=2,F(000)=732,GooF=1.027,最终偏离因子 R_1=0.037 5,wR_2=0.091 4。在配合物分子中相邻的 2 个铜(Ⅱ)离子通过 2 个 2-(4-甲基苯甲酰基)苯甲酸根桥联配位连接起来,其端位各与 1 个 2-(4-甲基苯甲酰基)苯甲酸根和 1 个 2,2′-联吡啶分子配位,整个分子形成了双核结构。测定了标题配合物的荧光和磁性,结果表明:当激发波长为 608 nm 时,配合物在 472 和 476 nm 处有 2 个较强的荧光发射峰;在 2~100 K,配合物具有顺磁性。

关键词: 铜(Ⅱ)配合物; 2-(4-甲基苯甲酰基)苯甲酸; 晶体结构; 荧光和磁性

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Crystal Structure, Fluorescent and Magnetic Properties of One Dinuclear Copper(Ⅱ) Complex with 2-(4-Methylbenzoyl)benzoic Acid and 2,2′-Bipyridine as Ligands

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Abstract: A new dinuclear copper(Ⅱ) complex [$Cu_2(L)_4(2,2'\text{-bipy})_2$]·$H_2O$ (**1**) has been synthesized with 2-(4-methylbenzoyl)benzoic acid (HL) and 2,2′-bipyridine (2,2′-bipy) as ligands. Its crystal belongs to a triclinic system with space group $P\bar{1}$, a=1.012 57(15) nm, b=1.312 5(2) nm, c=1.317 0(2) nm, α=82.985(2)°, β=76.437(2)°, γ=88.290(2)°, V=1.688 7(4) nm^3, D_c=1.391 g·cm^{-3}, Z=2, F(000)=732, GooF=1.027. Final R_1=0.037 5, wR_2=0.091 4. The crystal structure shows that two neighboring copper(Ⅱ) ions are linked together by two bridging 2-(4-methylbenzoyl)benzoic acid anions, and their each end position coordinates with one 2-(4-methylbenzoyl)benzoic acid anion and one 2,2′-bipyridine molecule, forming a dinuclear structure. The fluorescent and magnetic properties of the title complex were discussed. The results show that the title complex has two emission bands at 472 and 476 nm, respectively, with the best excitation wavelength at 608 nm, and it is a paramagnetism system in temperatures range of 2~100 K. CCDC: 918797.

Key words: copper(Ⅱ) complex; 2-(4-methylbenzoyl)benzoic acid; crystal structure; fluorescent and magnetic properties

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0 Introduction

Carboxylic complexes have captured the extensive interest of researchers due to their versatile topological structures and application future in many fields such as magnetism, optics, catalysis and biology[1-7]. Up to now, in this field, much attention has been focused on the aromatic carboxylic acid system. For example, terephthalic acid, isophthalic acid, trimesic acid and 1,2,4,5-benzenetetracarboxylic acid have been found to act as excellent building blocks in the construction of functional complexes[8-17]. 2-(4-methylbenzoyl)benzoic acid is an important aromatic carboxylic ligand, it has be used to generate complexes with versatile structures and properties[18]. In this paper, with the aim of preparing novel functional complexes, a new dinuclear copper (Ⅱ) complex $[Cu_2(L)_4(2,2'\text{-bipy})_2]\cdot H_2O$ (**1**) using 2-(4-methylbenzoyl)benzoic acid (HL) as a ligand has been solvothermally synthesized and structurally determined, and its fluorescent and magnetic properties are also discussed.

1 Experimental

1.1 Materials and instrumentation

All materials were of analytical grade and used without further purification. Crystal structure determination was carried out with a Bruker SMART APEX-Ⅱ CCD Diffractometer. C, H, N analysis was performed on a PE-2400(Ⅱ) apparatus. Fluorescence spectrum was obtained at room temperature on a WGY-10 fluorescence spectrophotometer. Magnetic measurements in the range of 2 ~240 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode.

1.2 Synthesis of the title complex

A mixture of europium(Ⅲ) nitrate hexahydrate (0.19 mmol, 0.0.086 g) and HL (0.51 mmol, 0.123 g) was dissolved in 6ml mixed solvent of DMF/H_2O (volume ratio 2:1). The solution was poured into a 25 mL hydrothermal reaction autoclave and kept at 150 ℃ for 1 h. when this solution was cooled to room temperature, cuprous chloride (0.60 mmol, 0.057 g) and 2,2′-bipyridine (0.29 mmol, 0.045 g) were added into it. Then, the resultant solution was heated at 150 ℃ for 4 h, and filtered. The filtrate was kept untouched and evaporated slowly at room temperature. Blue single crystals suitable for X-ray analysis were obtained after six weeks. Anal. Calcd. for $[Cu_2(L)_4(2,2'\text{-bipy})_2]\cdot H_2O$ (%): C, 67.93; H, 4.42; N, 3.96. Found (%): C, 67.90; H, 4.41; N, 3.95. Yield: 37.4%.

1.3 Crystal structure determination

Single-crystal X-ray diffraction of complexes **1** was performed on a Bruker SMART APEX-Ⅱ CCD Diffractometer at 173(2) K by using graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). The total 8619 reflections were collected within the range of $1.56° \leqslant \theta \leqslant 25.01°$, of which 5 889 were independent with R_{int}=0.018 0. 5 030 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 a full-matrix least squares method using the SHELXS-97 and SHELXL-97 programs, respectively[19-20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions. The final refinement including hydrogen atoms converged to R_1=0.037 5, wR_2=0.091 4, $(\Delta/\sigma)_{max}$=0.001, S=1.027. The crystallographic data and structure refinement of the title complex are shown in Table 1.

CCDC: 918797.

2 Results and discussion

2.1 Crystal structure

In Table 2 are some selected bond lengths and bond angles of complex **1**. Fig.1 reveals its molecular structure. As shown in Fig.1, complex **1** consists of two copper(Ⅱ) ions, four L^- anions, two 2,2′-bipyridine molecules and one free water molecule. It is noteworthy that europium(Ⅲ) ion does not appear in the final structure while europium (Ⅲ) nitrate hexahydrate has been used in the synthesis of the compound. This is probably because europium (Ⅲ) nitrate hexahydrate functions as a catalytic agent. All other conditions unchanged, we have done the

Table 1 Crystallographic data and structure refinement for complex 1

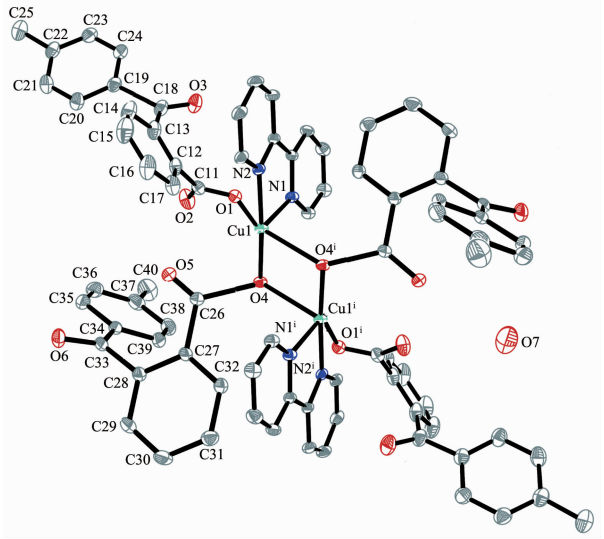
Empirical formula	$C_{40}H_{31}CuN_2O_{6.50}$	γ / (°)	88.290(2)
Formula weight	707.21	V / nm^3	1.688 7(4)
Size / mm	0.13×0.12×0.11	D / (g·cm^{-3})	1.391
θ range for data collection / (°)	1.56 to 25.01	Z	2
Crystal system	Triclinic	F(000)	732
Space group	$P\bar{1}$	μ (Mo $K\alpha$) / mm^{-1}	0.700
a / nm	1.012 57(15)	Reflections collected	8 619
b / nm	1.312 5(2)	Independent reflections	5 889 (R_{int}=0.018 0)
c / nm	1.317 0(2)	Final GooF	1.027
α / (°)	82.985(2)	R_1, wR_2 (I>2σ(I))	0.037 5, 0.091 4
β / (°)	76.437(2)	R_1, wR_2 (all data)	0.046 5, 0.096 8

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

Cu1-O1	0.193 98(17)	Cu1-N2	0.200 65(19)	Cu1-O4	0.196 01(16)
Cu1-O4^i	0.238 28(16)	Cu1-N1	0.200 0(2)	O4-C26	0.128 9(3)
O1-Cu1-O4	88.10(7)	O1-Cu1-O4^i	90.37(6)	O1-Cu1-N1	172.19(8)
O4-Cu1-O4^i	77.14(6)	O4-Cu1-N1	96.99(8)	N1-Cu1-O4^i	96.52(7)
O1-Cu1-N2	93.74(8)	N2-Cu1-O4^i	108.45(6)	O4-Cu1-N2	174.09(7)
Cu1-O4-Cu1^i	102.86(6)	N1-Cu1-N2	80.62(8)	O5-C26-O4	125.1(2)

Symmetry transformations used to generate equivalent atoms: ^{i} $-x+2, -y, -z+1$.

experiment without europium(Ⅲ) nitrate hexahydrate. The result is very interesting. We haven′t obtained the title compound. The four L^- anions have two coordination modes: monodentate coordination and monodentate-bridging coordination. Owing to the monodentate-bridging coordination of two L^- anions, two neighboring copper(Ⅱ) ions are linked together and the whole molecule presents a dinuclear structure, where Cu1-Cu1^i distance is 0.340 6 nm. Cu1, O4, Cu1^i and O4^i are coplanar, and their plane equation is $3.453x+10.682y-3.918z=1.494$ 3. Cu1 ion is coordinated by three oxygen atoms from three L^- anions and two nitrogen atoms from one 2,2′-bipyridine molecule to give a penta-coordinated distorted square pyramidal coordination geometry. In this coordination polyhedron, O4^i occupies the vertex, while N1, N2, O1 and O4 define the base plane. Bond angles N1-Cu1-N2, N2-Cu1-O1, O1-Cu1-O4 and O4-Cu1-N1 are 80.62(8)°, 93.74(8)°, 88.10(7)° and 96.99(8)°, respectively, and the sum of the above angles is 359.45°. Bond distances Cu1-O4^i and Cu1-O4 are 0.238 28(16) and 0.196 01(16) nm, respectively. The former is much longer than the latter, which could be attributed to the special position of O4^i at the pyramid vertex. In complex **1**, the Cu-N distances are in the normal range, and their average bond length is 0.200 33 nm.



Symmetry code: ^{i} $-x+2, -y, -z+1$

Fig.1 Molecular structure of complex **1**

2.2 Fluorescent properties

The fluorescent property of complex **1** was measured in the mixture of methanol and water at

room temperature in the range of 375~575 nm. The emission spectrum is shown in Fig.2. Complex **1** exhibits two fluorescence emission bands at 472 and 476 nm, respectively, with the best excitation wavelength at 608 nm. Under the same conditions, the emission band of 2,2′-bipy ligand was investigated, and it displays fluorescence emission bands at 468 and 476 nm, respectively, with the excitation wavelength at 612 nm. Compared with 2,2′-bipy ligand, complex **1** has a similar emission band position, which shows that intraligand is responsible for the fluorescence of complex **1**.

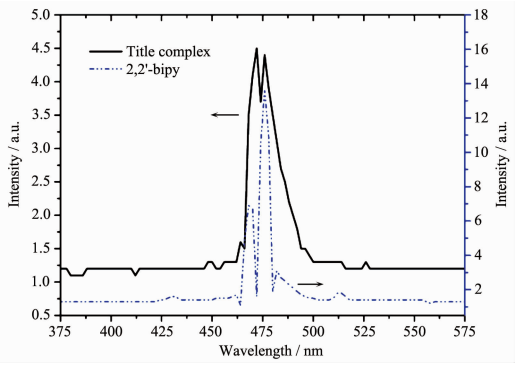


Fig.2　Emission spectra of complex **1** and the ligand in the liquid state at room temperature

2.3　Magnetic properties

The temperature dependence of the molar magnetic susceptibility of complex **1** is presented in Fig.3 in the form of X_mT and $1/X_m$ vs T. The product of X_mT increases slowly from 0.033 23 $cm^3 \cdot K \cdot mol^{-1}$ at 240 K to 0.059 83 $cm^3 \cdot K \cdot mol^{-1}$ at 8 K. when the temperature drops to 2 K, the value of X_mT is significantly increases to 0.06775 $cm^3 \cdot K \cdot mol^{-1}$. Besides, in the ranges of 2 to 100 K, $1/X_m$ is

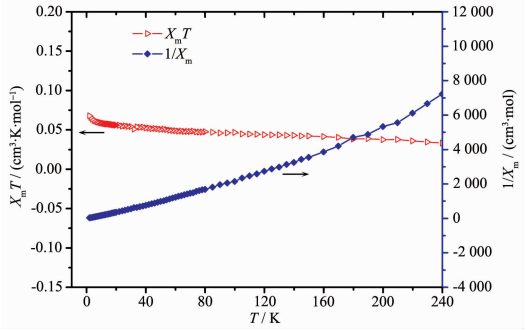


Fig.3　Temperature dependence of the magnetic susceptibility of complex **1** in the form of X_mT and $1/X_m$ vs T

proportional to T, and the linear regression equation is $1/X_m=21.773T-67.073$ with the correlation coefficient of 0.997 6. According to the Curie-Weiss law, $X_m=C/(T-\theta)$, the weiss constant (θ=3.080 5 K) is obtained, and the value of θ is positive. Such magnetic behavior indicates complex **1** is a paramagnetism system in temperatures range of 2~100 K.

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