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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A TRINUCLEAR COPPER(II) COMPLEX $Cu_3(TBSSB)_2(BSA)_2(bipy)_2{\cdot}H_2O$

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Abstract： A trinuclear copper(II) complex $Cu_3(TBSSB)_2(BSA)_2(bipy)_2{\cdot}H_2O$ (**1**) with mixed ligands of taurine-5-bromo-salicylaldehyde Schiff base (TBSSB), 5-bromo-salicylaldehyde (BSA) and 2,2'-bipyridine(bipy), was synthesized and characterized by elemental analysis, infrared spectrum, single crystal *X*-ray, photoluminescent, solid-state diffuse reflectance spectrum and molecular orbital analysis. The results of *X*-ray crystallographic analysis indicate that the complex belongs to triclinic and space group $P\bar{1}$ with a = 10.031(2) Å, b = 11.480(2) Å, c = 12.913(3) Å, α = 73.13(3)°, β = 78.58(3)°, γ = 75.24(3)°, V = 1363.6(5) Å^3, Z = 1, M_r = 1533.30, Dc = 1.867 g/cm^3, F(000) = 759, μ = 4.236 mm^{-1}, S = 0.921, R_1 = 0.0488, wR_2 = 0.0471($I > 2\sigma(I)$), R_1 = 0.1812 and wR_2 = 0.0546. Cu(2) atom adopts a square geometry coordinated by two N and two O atoms from two separated TBSSB ligands, while the other two equal Cu(1) atoms exhibit a square-pyramidal environment formed by two N atoms of bipy, one O of TBSSB and two O of BSA. The intramolecular interactions (O−H···Br) and intermolecular interactions (C−H···O) link the molecules into a complicated three-dimensional (3D) supramolecular structure. Photoluminescent investigation reveals that it displays an emission in the blue region. Optical absorption spectra reveals the presence of an energy band gap of 2.19 eV.

Key words: copper complex; crystal structure; taurine; photoluminescence; supermolecule

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三核铜配合物$[Cu_3(TBSSB)_2(BSA)_2(bipy)_2]{\cdot}H_2O$的合成、晶体结构及性质研究

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摘 要：以牛磺酸缩 5-溴水杨醛席夫碱（TBSSB）、5-溴水杨醛（BSA）、2,2'-联吡啶(bipy)为混合配体，合成了三核铜配合物$[Cu_3(TBSSB)_2(BSA)_2(bipy)_2]{\cdot}H_2O$(**1**)，并对该化合物进行了元素分析、红外光谱、*X*-射线单晶衍射、光致发光光谱、固体漫反射光谱及分子轨道分析等表征。晶体结构分析表明，该化合物结晶属三斜晶系，$P\bar{1}$ 空间群，晶胞参数为 a = 10.031(2) Å，b = 11.480(2) Å，c = 12.913(3) Å，α = 73.13(3)°，β = 78.58(3)°，γ = 75.24(3)°，V = 1363.6(5) Å^3，Z = 1, M_r = 1533.30, Dc = 1.867 g/cm^3 , F(000) = 759, μ = 4.236 mm^{-1}, S = 0.921, R_1 = 0.0488, wR_2 = 0.0471($I > 2\sigma(I)$), R_1 = 0.1812, wR_2 = 0.0546。Cu(2)离子与来自于两个 TBSSB 配体的两个氮原子和两个氧原子配位，形成正方形配位构型。Cu(1)离子与来自于一个 2,2'-bipy 的两个氮原子，TBSSB 配体的一个氧原子，以及 BSA 的两个氧原子配位，形成四方锥形配位构型。该化合物分子通过 O−H···Br 分子内氢键和 C−H···O 分子间氢键相互连接形成三维超分子结构。研

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究发现该化合物能够发出蓝色荧光，它的带隙为 2.19 eV。

关键词：铜配合物；晶体结构；牛磺酸；光致发光；超分子

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0 INTRODUCTION

In the past decades many efforts have been made to synthesis and to investigate polynuclear copper complexes with various bridges between the metal centers[1-3]. In principle, the extended coordination framework solids with desired structural features and/or physicochemical properties greatly depend on the nature of the organic ligands (spacers) and metal ions (nodes). As a consequence, nowadays, utilizing suitable organic units with functional groups that are capable of bridging metal centers to construct such tailored crystalline materials has revealed to be a fast developing field of crystal engineering research[4-6]. The ligands condensation from salicyladehyde or acetylacetone with amine forms the basis of an extensive class of chelating ligands that has enjoyed popular use in the coordination chemistry of transition metal elements[7-9]. Recently, taurine Schiff base complexes have been synthesized by our group[10]. Herein, we describe the preparation and crystal structure of the trinuclear copper complex with new Schiff base. This study has demonstrated that introduction of substitutional group benefits to the growth of polynuclear metals.

1 EXPERIMETAL

1.1 Reagents and physical measurements

All reagents and solvents employed were commercially available and used as received without further purification. The tridentate Schiff base ligand was obtained by following a reported procedure[11]. Infrared spectra on KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer in the range 4000～400 cm^{-1}. Elemental analyses were determined with a Perkin-Elmer model 240C instrument. Photoluminescence experiments are carried out using the solid state powder at room temperature on a F97XP spectrometer. The UV-vis spectra were recorded at room temperature on a computer-controlled TU1901 UV-vis spectrometer equipped with an integrating sphere. $BaSO_4$ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance.

1.2 Synthesis

Solution of taurine-5-bromo-salicylaldehyde Schiff base (6 mmol) in ethanol(15 mL) and $CuCl_2·2H_2O$(4 mmol) in ethanol(15 mL) were magnetically stirred with simultaneous drop-wise addition of 5-bromo-salicylaldehyde(10 mmol). After two hours, an aqueous solution containing 2,2'-bipy(6 mmol) was added into the above-mentioned mixture, the overall solution sequentially stirred for 3 h at 50℃. Finally, the solution was filtered and kept at room temperature for crystallizing. After two weeks, very fine crystals were obtained with 51% yield. Anal. Calcd. (%) for $C_{52}H_{42}Br_4Cu_3N_6O_{13}S_2$: C, 40.87; H, 2.77; N, 5.50. Found (%): C, 40.65; H, 2.96; N, 5.23.

1.3 *X*-ray crystal structure determination

A blue crystal of the title compound having approximate dimensions of 0.28 mm×0.22 mm×0.15 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were preformed with a Mo*K*α radiation (λ = 0.71073 **Å**) on a Bruker Apex II CCD area-detector diffractometer equipped with a graphite-monochromator at 298(2) K. A total of 12051 reflections together with 4888 independent ones (R_{int} = 0.0767) were collected in the range of 1.66 ≤ θ ≤ 25.20° by using the ω-2θ scan mode at room temperature, in which 1651 reflections ($I > 2\sigma(I)$) were observed and used in the succeeding

refinements.

The structure was solved by direct methods (SHELXS-97). Most of the non-hydrogen atoms were located from an *E*-map. The coordinates of remaining non-hydrogen atoms as well as some hydrogen atoms were found by difference Fourier techniques. The structure was refined by full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The final R = 0.0488, wR = 0.0471 ($w = 1/[\sigma^2(F_o^2) + (0.0000P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$), S = 0.921 and $(\Delta/\sigma)_{max}$ = 0.001. The maximum and minimum peaks in the final difference Fourier map are 0.486 e·Å $^{-3}$ and -0.445 e·Å $^{-3}$, respectively. All calculations were performed with SHELXS-97 programe[12] (CCDC:1820165).

2 RESULTS AND DISCUSSION

2.1 Infrared spectra

Infrared spectrum of the title compound is revealed in Fig.1. By comparing the infrared spectra of free ligand to the complex, we can get some information about the coordination nature of the ligand. The broad band centered around 3432cm^{-1} attributable to O-H stretching frequency of water and the bands at 3113, 3035 and 2921 cm^{-1} belong to the N-H stretching vibration. Bands assigned to $\upsilon_{as}(SO_3^-)$ and $\upsilon_s(SO_3^-)$, which are respectively observed for the free ligand at 1201, 1183, 1041 cm^{-1} shift to 1221, 1168, 1029 cm^{-1} in the title complex. This indicates that the deprotonation of sulfonic groupa occurs upon coordination[13]. The strong intensity bands occurring at 1621 cm^{-1} may be assigned to the υ(C=N) absorption of the imine[14]. Besides, the adsorption peaks of 2,2'-bipy shift from 1540, 743 cm^{-1} to 1515, 776 cm^{-1} in the complex, suggesting the existence of coordinate bonds between metal ions and 2,2'-bipy.

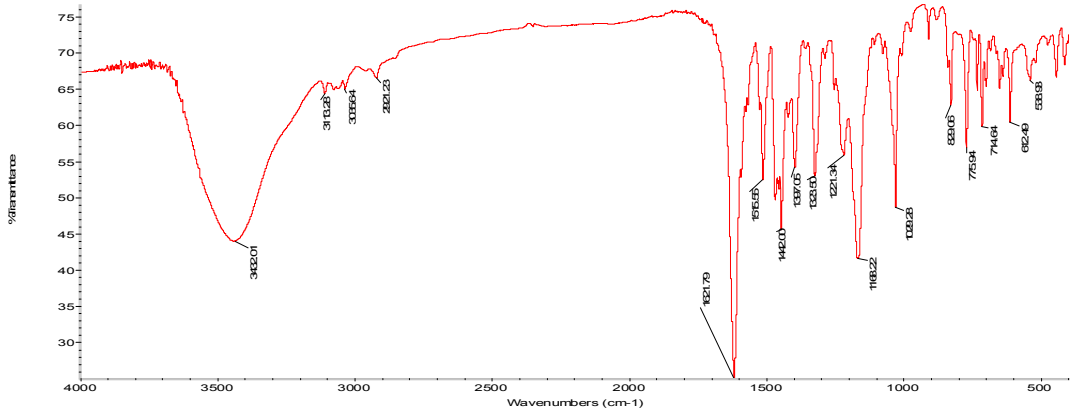

Fig.1 IR spectra of 1

2.2 Crystal structure

The selected bond lengths and bond angles are shown in Table 1. Molecular structure of the title compound is revealed in Fig.2. This complex contains a linear Cu(1)-Cu(2)-Cu(1) core via linking by two sulfonic groups. In contrast with others trinuclear complexes derived from the Schiff base ligand, the structure of complex **1** displays an especial mode[15]. It is an approximate description that the trinuclear cation, which is interconnected through three types of oxygen atoms afforded by the sulfonic groups, hydroxyl groups of Schiff base ligands and carbonyl groups, hydroxyl groups of BSA ligands. The center Cu(2) lays a center symmetrical fashion and is coordinated by two N atoms and two O atoms from two different Schiff base molecules, forming square pyramid coordinated geometry. The Schiff base adopts tridentate mode and forms a five-membered chelate rings coordinating to metal ions. The bond distance Cu(2)-O(4)(1.884(4) Å) and Cu(2)-N(3)(1.964(5) Å), which are consistent with those values reported copper complexes with Schiff base[16]. While other two copper atoms (Cu(1)) with $[N_2O_3]$ coordinated spheres are defined by the phenolic oxygen atoms, sulfonic oxygen atoms, two chelating N atoms of pyridine rings, as well as carbonyl oxygen atoms. This coordinated fashion is rare in reported

complexes due to the presence of BSA molecules. The average bond distance Cu-O and Cu-N are 1.971 **Å** and 1.976 **Å**, respectively, which are comparable to those observed in other copper Schiff base complexes[17-18]. The coordination geometry was determined by the τ values varying from 0 for an idealized square pyramid to 1 for an idealized trigonal bipyramid. On the basis of the τ value of 0.005, the coordination geometry represents a square pyramid. The equatorial plane consists of phenolic oxygen (O(6)), carbonyl oxygen (O(5)) and pyridine nitrogen atoms (N(1) and N(2)). The other sulfonic oxygen (O(3)) is located at the axis position. Cu(1) atom is always from its basal plane by 0.276 **Å**. The C(17)-N(3) bond distance is 1.294(6) **Å**, consistent with the form of the amidogen functionality in the complexes[19-22].

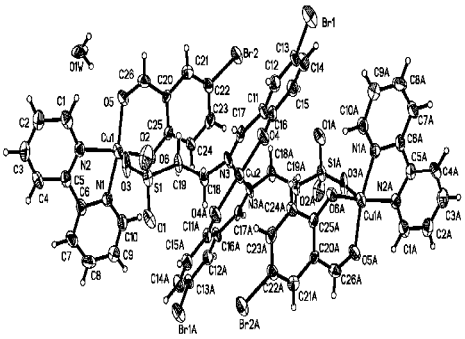

Fig.2 Molecular structure of 1

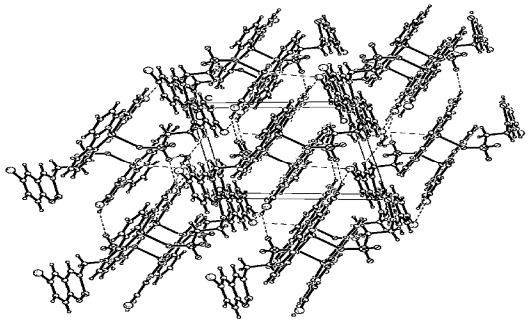

Fig.3 Packing drawing of 1

There are extensive hydrogen-bonding interactions in the crystal system (Table 2). Uncoordinated Br(1) ion hydrogen bonds strongly to O(1w) of sulfonic group with 3.123 Å. The interact by way of π–π stacking interactions in the sequence of benzyl rings with the neighboring bipy planes separated by 3.72 **Å**. In addition, the intramolecular hydrogen bondings (O−H···Br) and intermolecular hydrogen bondings (C−H···O) link the molecules into a complicated three-dimensional (3D) supramolecular structure (Fig.3), which play an important role in stabilizing of the compound.

Table 1 Selected bond lengths (Å) and angles (°)

Bond	Dist	Bond	Dist	Bond	Dist
Cu(1)-O(6)	1.881(4)	S(1)-O(1)	1.433(4)	N(1)-C(6)	1.370(7)
Cu(1)-O(5)	1.963(4)	S(1)-O(2)	1.444(4)	O(6)-C(25)	1.307(6)
Cu(1)-N(2)	1.982(5)	S(1)-O(3)	1.450(4)	C(26)-O(5)	1.2693(6)
Cu(1)-N(1)	1.995(5)	S(1)-C(19)	1.749(5)	N(3)-C(18)	1.508(6)
Cu(1)-O(3)	2.245(4)	N(2)-C(1)	1.332(7)	C(17)-N(3)	1.294(6)
Cu(2)-O(4)	1.884(4)	N(2)-C(5)	1.350(7)	C(16)-O(4)	1.302(7)
Cu(2)-N(3)	1.964(5)	N(1)-C(10)	1.310(7)		
Angle	(°)	Angle	(°)	Angle	(°)
O(4)-Cu(2)-O(4)	180.000(1)	O(5)-Cu(1)-N(2)	93.5(2)	N(1)-Cu(1)-O(3)	99.89(18)
O(4)-Cu(2)-N(3)	88.15(19)	O(6)-Cu(1)-N(1)	90.5(2)	O(1)-S(1)-O(2)	112.0(3)
O(2)-S(1)-C(19)	105.8(3)	O(5)-Cu(1)-N(1)	166.6(2)	O(1)-S(1)-O(3)	115.1(3)
O(3)-S(1)-C(19)	106.0(3)	N(2)-Cu(1)-N(1)	80.2(3)	O(2)-S(1)-O(3)	110.7(3)
N(3)-Cu(2)-N(3)	180.000	O(6)-Cu(1)-O(3)	102.65(15)	O(1)-S(1)-C(19)	106.4(3)
O(6)-Cu(1)-O(5)	93.50(17)	O(5)-Cu(1)-O(3)	91.66(17)		
O(6)-Cu(1)-N(2)	166.6(2)	N(2)-Cu(1)-O(3)	88.53(17)		

Table 2 Bond lengths (Å) and angles (°) for the hydrogen bonds

D-H	d(D-H)	d(H-A)	d(D-A)	∠DHA	A
O(1W)-H(1WA)	0.85(2)	2.7600	3.1232	108.00	Br(1)
O(1W)-H(1WA)	0.85(2)	2.9100	3.6591	148.00	Br(2)
O(1W)-H(1WB)	0.86(2)	2.4100	3.2255	158.00	O(2)
C(1)-H(1A)	0.9300	2.4700	2.9983	116.00	O(5)
C(4)-H(4A)	0.9300	2.4200	3.3273	164.00	O(1)
C(10)-H(10A)	0.9300	2.3900	2.9038	114.00	O(6)
C(17)-H(17A)	0.9300	2.4600	3.2211	139.00	O(1W)
C(18)-H(18B)	0.9700	2.3400	2.7602	105.00	O(4)
C(19)-H(19A)	0.9700	2.5500	3.1162	117.00	O(4)
C(23)-H(23A)	0.9300	2.5300	3.3129	142.00	O(2)

2.3 Photoluminescent property

Taking into account the possible photoluminescent property of TBSSB, BSA and bipy, the photoluminescence of **1** was investigated at room temperature (Fig.4). The solid-state excitation spectra of **1** show that the effective energy absorption mainly takes place in the ultraviolet region of the range 250~350 nm of the light spectrum. The excitation band of **1** under the blue emission of 418 nm possesses one band at 277 nm. We further measured the corresponding emission spectrum and it was shown as the red line in Fig. 4. As for **1**, the emission spectrum shows one main emission peak at 418 nm and three side peaks locating at 435 nm, 466 nm and 487 nm, respectively, upon the excitation of 277 nm. As a result, complex **1** is a possible candidate for blue light emission materials.

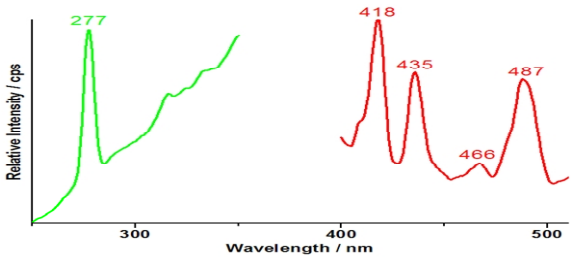

Fig. 4 Solid-state photoluminescent spectra of 1: red plot for emission spectrum and green plot for excitation spectrum

In order to reveal the nature of the photoluminescence of **1**, the photoluminescent spectra of the ligands Bipy, TBSSB and BSA were also performed with solid-state samples at room temperature, as shown in Fig. 5. The excitation spectra of Bipy show that the effective energy absorption mainly takes place in the ultraviolet region of the range 300~400 nm of the light spectrum. The excitation band of Bipy under the green emission of 565 nm possesses one band at 349 nm. We further measured the corresponding emission spectrum and it was shown as the purple line in Fig.5. As for Bipy, the emission spectrum show one broad emission band centered at 565 nm, upon the excitation of 349 nm. The excitation spectra of TBSSB show that the effective energy absorption mainly takes place in the ultraviolet region of the range 250~300 nm of the light spectrum. The excitation band of TBSSB under the blue emission of 472 nm possesses one band at 284 nm. As for TBSSB, the emission spectrum show one broad emission band at 456 and 472 nm, upon the excitation of 284 nm. The excitation spectra of BSA show that the effective energy absorption mainly takes place in the ultraviolet region of the range 250~300 nm of the light spectrum. The excitation band of BSA under the blue emission of 481 nm possesses one band at 272 nm. As for BSA, the emission spectrum show three sharp emission bands at 440, 465 and 481 nm, upon the excitation of 272 nm. As a result, the photoluminescence of **1** is not originated from these ligands.

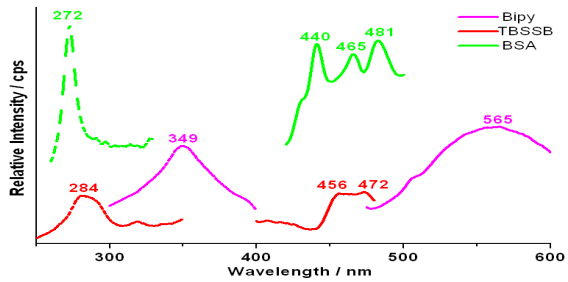

Fig. 5 Solid-state photoluminescent spectra of Bipy, TBSSB and BSA: dashed lines plots for emission spectra and solid lines plots for excitation spectra

2.4 Moleular orbital analysis

The molecular orbital were obtained at the B3LYP/level with the basis set of 6-311G(d, p) for C, N, O, and H, and that of DGDZVP for Cu atoms. The calculations were carried out with the Gaussian 09 program package[23].

To further understand the emission of **1**, the calculated frontier molecular orbitals are shown in Fig. 6. From Fig. 6, it can be found that the electron clouds in the highest occupied orbital (HOMO) are mainly located in one sulfonic group, while that in the lowest unoccupied orbital (LUMO) are mainly located in one molecular plane of Cu1 with $[N_2O_3]$ coordinated spheres. These obviously different localizations of the electron clouds suggest that the interesting inter-layer charge transfer occurs.

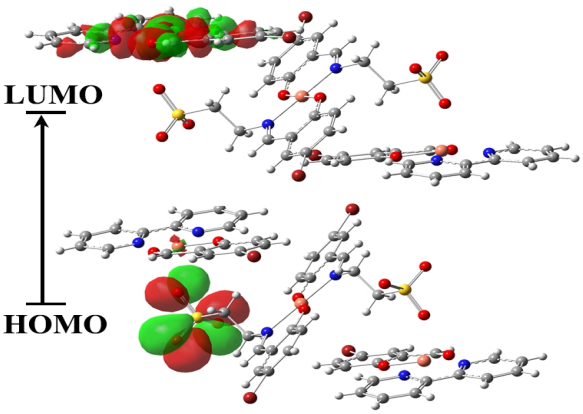

Fig. 6 Frontier molecular orbital of 1

2.5 Solid-state diffuse reflectance spectrum

The solid-state diffuse reflectance spectrum of complex **1** was recorded at room temperature with powder samples. The value of the energy band gaps for this complex was determined by extrapolating from the linear part of the absorption edges. Optical absorption spectra reveal the presence of an energy band gap of 2.19 eV (Fig.7), which suggests that this complex may be a potential narrow-gap semiconductor. The slow slope of the optical absorption edge for the complex is indicative of the existence of indirect transitions[24]. The energy band gap of 2.19 eV for the complex is larger than those of GaAs (1.4 eV), CdTe (1.5 eV) and $CuInS_2$ (1.55 eV), which are well-known for highly efficient photovoltaic compounds [25-26].

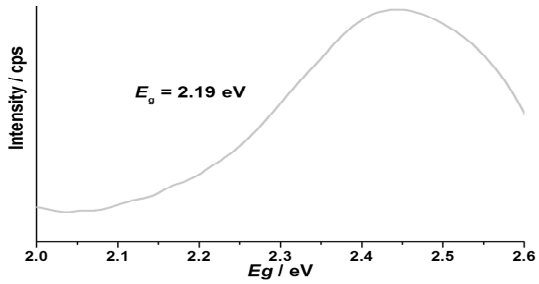

Fig. 7 Solid-state diffuse reflectance spectrum of 1

In brief, the trinuclear copper(II) complex with mixed ligands was synthesized and characterized. Photoluminescent investigation reveals that it displays an emission in the blue region. Optical absorption spectra reveal the presence of an energy band gap of 2.19 eV. Therefore, the title complex is a possible candidate for photoluminescent or semiconductive materials.

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