



Copper(II) Complex of 2-Hydroxy-4-oxyacetate-benzoic Acid: Synthesis, Structure and Photoluminescence

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A novel copper(II) complex (**1**) $\text{Cu(L)} \cdot (\text{phen})_2 \cdot 10\text{H}_2\text{O}$ was synthesized from 2-hydroxy-4-oxyacetate-benzoic acid (HL), phenanthroline (phen) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and characterized by elemental analysis, IR and X-ray crystallographically. The single-crystal X-ray diffraction studies demonstrated that complex is crystallize in triclinic system, space group P_1 , with $a = 0.9177(6)$ nm, $b = 1.5123(5)$ nm, $c = 1.5753(3)$ nm, $\alpha = 62.263^\circ$, $\beta = 77.639^\circ$, $\gamma = 80.098^\circ$, $V = 1.883(7)$ nm³, $Z = 2$, $M_r = 814.25$, $F_{(000)} = 850.0$, $D_c = 1.436$ g·cm⁻³, μ (M_0K_α) = 0.675 mm⁻¹. It turned out that four N atoms and one carboxyl O atom coordinate to Cu(II), forming a five-coordination trigonal bipyramid geometry. The complex is luminescent in the solid state, which indicate that it may be an excellent candidate for potential photoactive material. CCDC: 883096.

Key Words: Copper compound, 2-Hydroxy-4-oxyacetate-benzoic acid, Crystal structure, Luminescent.

INTRODUCTION

The design and synthesis of metal-organic compound have undergone rapid development because of their particular topologies¹ and beneficial properties in gas adsorption, separation², catalysis³, magnetism⁴, photochemistry^{5,6}. For having potential applications as sensors⁷, highly selective guest inclusion⁸ and delivery of specific chemicals⁹. Modification of the size and shape of the ligands often leads to a change in the structures and properties of the resulting compound. The selection of organic ligands plays a crucial role in the rational design and construction of coordination polymers, thus we successfully designed a new multicarboxylate ligand 2-hydroxy-4-oxyacetate-benzoic acid (HL) based on the following considerations: (1) the rigidity of the benzene ring and flexibility of substituent groups can provide diversiform coordination modes; (2) further flexible carboxyl groups are feasible to link discrete clusters to give an extended network containing high connected nodes; (3) there are many O atoms can act as hydrogen bonding acceptors, it's easy to assemble supramolecular network¹⁰. Therefore, much work is still necessary to understand the coordination chemistry of this ligand. As far as we know, the complex constructed by 2-hydroxy-4-oxyacetate-benzoic acid ligand has never been reported, this prompted us to exploring the coordination chemistry of 2-hydroxy-4-oxyacetate benzoic acid ligand and creating new materials with

excellent properties. In this paper, we report a novel luminescent complex **1** based on the assembly of 2-hydroxy-4-oxyacetate-benzoic acid (HL) and phenanthroline with copper metal under hydrothermal conditions and fully characterized by infrared spectroscopy, elemental analysis, thermogravimetric analysis and X-ray crystallographically it's worth noting that the complex may be an excellent candidate for potential photoactive material.

EXPERIMENTAL

All reagents and solvents used were of commercially available quality and without purified before using. FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4000–400 cm⁻¹. Elemental analysis was performed on C, H, N elemental analyzer, Elementar Vario EL III. A Mettler Toledo thermal analyzer TGA/SDTA 851^o was used to carry out the thermoanalytical analysis with a heating rate of 10 °C min⁻¹ from 30–800 °C in air atmosphere. Fluorescent spectrum were recorded at room temperature on an Edinburgh FL920 phosphorimeter.

Synthesis of the compound: A mixture of 2-hydroxy-4-oxyacetate-benzoic acid (0.5 mmol, 0.135 g), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.5 mmol, 0.114 g), phenanthroline (0.2 mmol, 0.036 g), NaOH (1.0 mmol, 0.0403 g) and H_2O /ethanol (15 mL) was placed in a 25 mL autoclave and heated at 100 °C for 7 days

and then cooled to room temperature at the speed of 1.5 °C/h. The blue block crystals were obtained. Washed with water and ethanol, then dried in air (37 % yield, based on phen). Anal. calcd. (%) for $C_{33}H_{42}N_4O_{16}Cu$: C, 48.58; H, 5.18; N 6.84. Found (%): C, 48.67; H, 5.20; N, 6.88. IR (KBr, ν_{max} , cm^{-1}): 3414 (s), 3060 (w), 2970 (w), 1701(m), 1686(m), 1609(s), 1518(s), 1427(s), 1341(w), 1253 (w), 1181(m), 1107(m), 1052(s), 852(m), 724(s).

X-Ray crystallography: A single crystal of the compound with dimensions of 0.347 mm \times 0.154 mm \times 0.088 mm was selected and mounted on a glass fiber and collected diffraction data on a Bruker Smart APEX II CCD diffractometer with graphite monochromated M_0K_{α} radiation ($\lambda = 0.071073$ nm) at 296(2) K. Structure was solved by direct methods using SHELXS-97¹¹ and refined on the F^2 by full-matrix least-square method with SHELXL-97¹². All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined by using a riding mode. Experimental details for X-ray data collection are presented in Table-1 and the selected bond lengths and angles are listed in Table-2. CCDC No. 883096 of **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The IR spectra of complex **1** exhibit broad strong absorptions at 3414 cm^{-2} , which corresponds to the existence of hydrogen bonds formed by water molecules, as well as the asymmetric stretching vibrations of hydroxyl groups in the complex. Weak absorptions observed at 2970 cm^{-1} can be ascribed to the $\nu(CH_2)$ of the HL ligand. The characteristic band is shown at 1609 cm^{-1} may be assigned to the asymmetric

stretching vibration of the carboxylate groups, While symmetric stretching the feature 1427 cm^{-1} is associated with the symmetric (COO^-) stretching vibrations. The $\Delta\nu$ ($\nu_{as}(COO^-) - \nu_s(COO^-)$) values are 182 cm^{-1} (more than 160 cm^{-1}), indicating the coordination of L^- with Cu(II) in monodentate modes¹³, which is well consistent with the X-ray diffraction structural analysis.

Structural description: The crystal structure of the complex **1** $Cu(L) \cdot (phen)_2 \cdot 10H_2O$ is shown in Fig. 1. Its asymmetric unit consists of one Cu(II), one L^- , two phenanthroline and 10 free water molecules. Cu(II) atom is coordinated by one flexible carboxyl groups from L^- (Cu-O(2) 0.1980(3) nm) and four N donor from two symmetrical independent phen ligand (Cu-N 0.1990(3) to 0.2143(3) nm) to furnish a trigonal bipyramid geometry, the selected coordination bond lengths and angles for **1** are listed in the Table-2. In the coordination environment of Cu(II) (Fig. 2), the O(2), N(1) and N(3) define a trigonal plane, whereas the other two N atoms occupies the axial positions from the opposite direction.

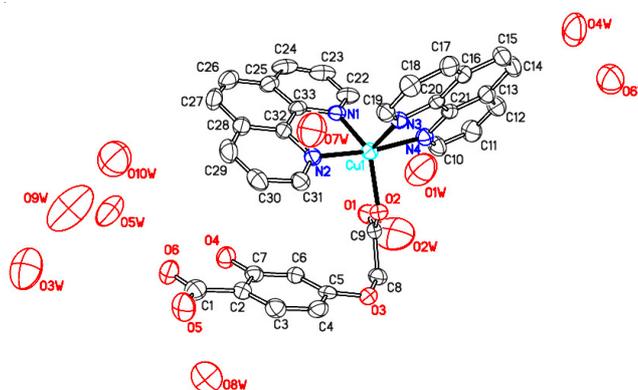


Fig. 1. Thermal eclipse diagram of the nonsymmetrical unit of **1** with ellipsoids at 30 % probability. The hydrogen atoms are omitted

TABLE-1
CRYSTALLOGRAPHIC DATA FOR THE COMPLEX

Empirical formula	$C_{33}H_{42}CuN_4O_{16}$	Calculated density (Mg/m^3)	1.436
Formula weight	814.25	Absorption coefficient (mm^{-1})	0.657
Temperature (K)	296(2)	$F_{(000)}$	850.0
Wavelength (nm)	0.071073	Crystal size (mm)	0.347 \times 0.154 \times 0.088
Crystal system	Triclinic	θ range for data collection ($^\circ$)	1.48 to 27.53
Space group	P_1	Limiting indices	$-11 \leq h \leq 11, -16 \leq k \leq 19, -20 \leq l \leq 20$
a (nm)	0.9117(6)	Reflections collected / unique	28406/8468 [R_{int}] = 0.0426]
b (nm)	1.5123(5)	Refinement method	Full-matrix least-squares on F^2
c (nm)	1.5753(3)	Data/restraints/parameters	8468/0/487
α ($^\circ$)	62.263(3)	Goodness-of-fit (on F^2)	0.990
β ($^\circ$)	77.639(3)	Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0644, wR_2 = 0.1541$
γ ($^\circ$)	80.098(3)	R indices (all data)	$R_1 = 0.1560, wR_2 = 0.1931$
Volume (nm^3)	1.88374(2)	$\Delta\rho$ max, $\Delta\rho$ min ($e \text{ nm}^{-3}$)	596 and -395
Z	2		–

TABLE -2
SELECTED BOND LENGTHS (nm) AND ANGLES ($^\circ$)

Bond	Length	Bond	Length	Bond	Length
Cu(1)-O(2)	0.1980(3)	Cu(1)-N(4)	0.1998(3)	Cu(1)-N(3)	0.2143(3)
Cu(1)-N(2)	0.1990(3)	Cu(1)-N(1)	0.2080(3)	–	–
Angle	($^\circ$)	Angle	($^\circ$)	Angle	($^\circ$)
O(2)-Cu(1)-N(2)	91.29(12)	N(2)-Cu(1)-N(1)	81.56(13)	N(4)-Cu(1)-N(3)	79.98(13)
O(2)-Cu(1)-N(4)	96.87(12)	N(4)-Cu(1)-N(1)	94.71(13)	N(1)-Cu(1)-N(3)	114.79(11)
N(2)-Cu(1)-N(4)	171.27(13)	O(2)-Cu(1)-N(3)	109.99(11)	–	–
O(2)-Cu(1)-N(1)	135.02(12)	N(2)-Cu(1)-N(3)	94.36(12)	–	–

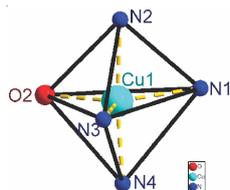


Fig. 2. Coordination polyhedron of Cu(II) in complex 1

In addition, there exists strong intermolecular O-H...O hydrogen bonding interactions between vast free water molecules and uncoordinated oxygen atom of L^- as listed in Table-3. Meanwhile, there are infinite parallel aromatic rings from the L^- and phen. Thus, a 3D supramolecular network has been generated by the hydrogen bonding and π - π stacking interactions (Fig. 3).

TABLE-3 HYDROGEN BOND GEOMETRY FOR TITLE COMPLEX (nm, °)				
D-H...A	D-H	H...A	D...A	D-H...A
O(8W)-H(8WB)...O(5) ^{#1}	0.085	0.199	0.2836(5)	173.3
O(7W)-H(7WA)...O(8W) ^{#2}	0.085	0.200	0.2835(5)	168.9
O(7W)-H(7WB)...O(5W) ^{#3}	0.085	0.224	0.2772(6)	121.1
O(6W)-H(6WB)...O(8W) ^{#4}	0.078	0.203	0.2801(6)	168.7
O(5W)-H(5WA)...O(3W)	0.085	0.221	0.3029(8)	162.6
O(5W)-H(5WB)...O(6)	0.085	0.190	0.2742(5)	168.4
O(4W)-H(4WB)...O(6W)	0.085	0.187	0.2708(7)	169.2
O(4W)-H(4WA)...O(6W)	0.085	0.187	0.2708(7)	169.2
O(9W)-H(9WA)...O(2W) ^{#5}	0.085	0.252	0.2819(12)	101.9
O(9W)-H(9WB)...O(1W) ^{#6}	0.085	0.181	0.2595(11)	152.4
O(3W)-H(3WA)...O(5W)	0.085	0.285	0.3029(8)	93.6
O(3W)-H(3WB)...O(4W) ^{#7}	0.085	0.240	0.2770(7)	107.2
O(2W)-H(2WA)...O(6) ^{#5}	0.085	0.279	0.3105(9)	103.8
O(1W)-H(1WA)...O(10W) ^{#8}	0.085	0.210	0.2736(9)	131.1
O(1W)-H(1WB)...O(4W) ^{#9}	0.085	0.249	0.3091(9)	128.3
O(10W)-H(10W)...O(5W)	0.085	0.202	0.2857(7)	166.9
O(4)-H(20A)...O(6)	0.082	0.179	0.2515(4)	147.0

Symmetry codes: ^{#1}-x+1, -y+1, -z+1; ^{#2}x+1, y, z; ^{#3}-x+2, -y+1, -z+1; ^{#4}x+1, y+1, z; ^{#5}-x+1, -y+1, -z+2; ^{#6}x, y-1, z; ^{#7}x-1, y-1, z; ^{#8}-x+2, -y+1, -z+2; ^{#9}-x+2, -y+2, -z+2.

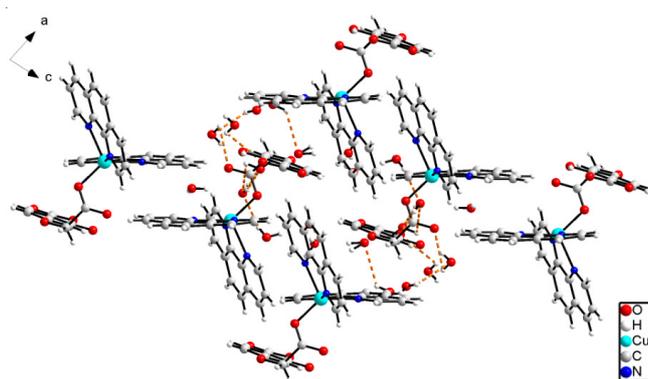
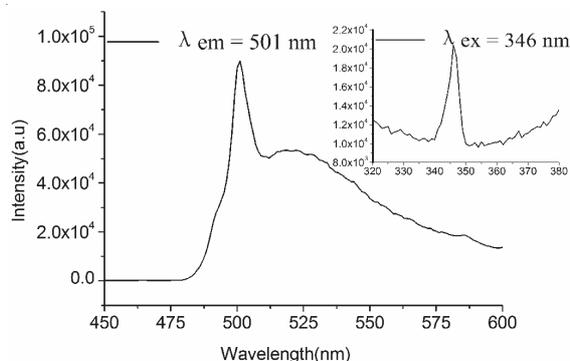


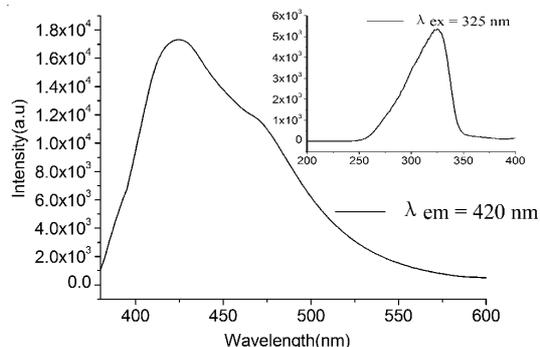
Fig. 3. Packing plot of complex 1

Fluorescent property: Considering the formed Cu(II) center is inclined to transfer an electron to the chromophore after deprotonation¹⁴. The solid luminescent of complex 1 and HL ligand were investigated at room temperature. As depicted in Fig. 4, complex 1 exhibit fluorescent emission with the maxima at 501 nm ($\lambda_{ex} = 346$ nm). Such fluorescence behaviour may be attributed to the intraligand transition of coordinated ligand. Since similar emission at 420 nm ($\lambda_{ex} = 325$ nm) was

observed for the free HL ligand. The red-shifted fluorescence spectra of 1 was attributed to both the deprotonated effect of HL and the coordination interactions of the organic ligands to Cu(II), in this case, the Cu(II) complex will take part in the π -system¹⁵, effectively increasing the conformational rigidity and asymmetry of the ligand and reduces the loss of energy by nonradiative decay of the intraligand (π - π^*) excited state.



(a)



(b)

Fig. 4. Excitation and emission spectra in the solid state at room temperature: (a) complex 1 (b) HL ligand

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