



Synthesis and Characterization of Mononuclear Copper(II) Complex with 5,5'-Dihydroxy-2,2'-[1,1'-(propane-1,3-diylldioxydinitrilo)dimethylidyne]diphenol

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Copper(II) complex $[\text{Cu}(\text{H}_4\text{L})]\cdot\text{CH}_3\text{CH}_2\text{OH}\cdot 0.5\text{H}_2\text{O}$ has been synthesized by the reaction of copper(II) acetate monohydrate with 5,5'-dihydroxy-2,2'-[1,1'-(propane-1,3-diylldioxydinitrilo)dimethylidyne]diphenol in anhydrous ethanol medium and characterized by elemental analyses, molar conductance, IR spectra, UV-visible spectra and TG-DTA analyses.

Key Words: Cu(II) complex, Salen-type bisoxime ligand, Synthesis.

INTRODUCTION

The Cu(II) complexes with salen or salen-type bisoxime ligands are extensively studied due to their ease of preparation and structural variety. Salen and its derivatives are very important as versatile ligands, they can accommodate one, or more metal centers to form complexes with interesting properties and applications¹. These complexes have been found to possess effective activities including catalysis², medical imaging³, inorganic biochemistry⁴, thin films⁵ and optical materials⁶. Herein, we report on the synthesis and characterization of Cu(II) complex $[\text{Cu}(\text{H}_4\text{L})]\cdot\text{CH}_3\text{CH}_2\text{OH}\cdot 0.5\text{H}_2\text{O}$ with salen-type bisoxime ligand, 5,5'-dihydroxy-2,2'-[1,1'-(propane-1,3-diylldioxydinitrilo)dimethylidyne]diphenol (H_4L).

EXPERIMENTAL

2,4-Dihydroxybenzaldehyde ($\geq 99.0\%$) was purchased from Alfa Aesar and used without further purification. Copper(II) acetate monohydrate ($\geq 99.0\%$) was purchased from Shanghai Zhenxin Reagent Factory. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. Elemental analysis for Cu was detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. UV-VIS absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. ¹H NMR spectra were recorded on a Mercury-400BB spectrometer. Melting points were measured by the use of a microscopic melting point

apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

Preparation of 5,5'-dihydroxy-2,2'-[1,1'-(propane-1,3-diylldioxydinitrilo)dimethylidyne]diphenol (H_4L): Synthetic route to salen-type bisoxime compound H_4L is shown in Fig. 1.

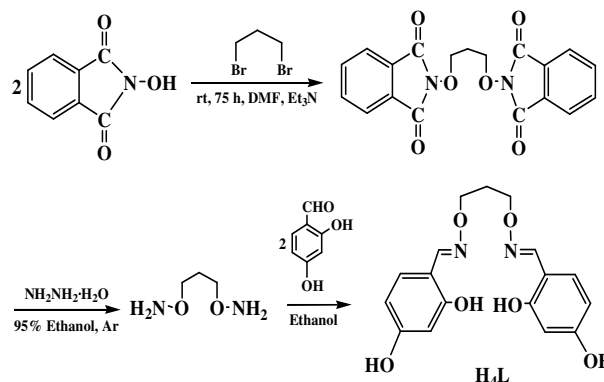


Fig. 1. Synthetic route to 5,5'-dihydroxy-2,2'-[1,1'-(propane-1,3-diylldioxydinitrilo)dimethylidyne]diphenol (H_4L)

1,3-Bis(aminooxy)propane was synthesized according to an analogous method reported earlier⁷⁻¹⁰.

To an ethanolic solution (4 mL) of 2,4-dihydroxybenzaldehyde (138.1 mg, 1 mmol) was added an ethanolic solution (2 mL) of 1,3-bis(aminooxy)propane (53.2 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 4 h. The formed precipitate was separated by filtration and washed successively with ethanol and ether, respectively. The product was dried under reduced pressure to obtain 124 mg pale-pink crystalline ligand (H_4L). Yield, 35.8 %. m.p. 462.5-463.5 K.

¹H NMR (400MHz, DMF-*d*₆) δ: 1.98 (s, 2H), 4.12 (s, 4H), 6.28 (s, 4H), 7.27~7.31 (d, 2H), 8.25 (s, 2H), 9.78 (s, 2H), 9.82 (s, 2H).

Preparation of Cu(II) complex: A blue solution of copper(II) acetate monohydrate (20 mg, 0.10 mmol) in ethanol (2 mL) was added dropwise to a pale-pink solution of H₄L (34.6 mg, 0.10 mmol) in ethanol (2mL) at room temperature. The colour of the mixing solution turned to brown immediately. After refluxing and stirring for 3 h, the reaction mixture was cooled and the resulting precipitate was filtered off, washed with ethanol/ether (1:4) and ether, respectively and dried under reduced pressure to obtain 32.6 mg grey crystalline solid. Yield, 70.4 %.

RESULTS AND DISCUSSION

A Salen-type bisoxime compound H₄L and its Cu(II) complex have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible spectra and ¹H NMR data.

The colour, yields and elemental analytical results of the synthesized Salen-type bisoxime compound H₄L and its Cu(II) complex are presented in Table-1. The H₄L is a pale-pink solid, stable in air and soluble in methanol, ethanol, acetone, acetonitrile, DMF and DMSO, slightly soluble in ether and benzene, insoluble in chloroform, dichloromethane and *n*-hexane. The corresponding Cu(II) complex is a grey solid, soluble in chloroform, DMF and DMSO, insoluble in methanol, ethanol, dichloromethane, ether, acetone, acetonitrile, benzene and *n*-hexane. The molar conductance of the Cu(II) complex at 21 °C in 10⁻³ mol/L DMF solution is 2.08 S cm² mol⁻¹, indicating that the Cu(II) complex is non-electrolytes¹¹. The elemental analysis data and the composition of the Cu(II) complex shows that the elemental analysis data of the Cu(II) complex close to the theoretical value, prove accurate results. Copper(II) acetate monohydrate and ligand H₄L formed 1:1 (M:L) type stoichiometric ratio and one complex molecule containing 1 ethanol molecule and 0.5 water molecule. It has quite good stability in air at room temperature.

Infrared spectra of the free ligand H₄L and its Cu(II) complex exhibit various bands in 4000-400 cm⁻¹ region. The IR spectra data of the free ligand H₄L and its Cu(II) complex are given in Table-2. It can be seen from the infrared spectra results, the infrared spectra of the free ligand H₄L and its Cu(II) complex have large difference and indicates that Cu(II) and the free ligand H₄L formed the new complex.

The characteristic C=N stretching band of the free ligand H₄L appears at 1631 cm⁻¹, while the C=N band of the Cu(II) complex is observed at 1612.6 cm⁻¹. The Ar-O stretching band occurs at 1250.7 cm⁻¹ for the free ligand H₄L, whereas that at 1221.3 cm⁻¹ for the Cu(II) complex. This shifting of C=N and Ar-O stretching frequency indicate that the M-N and M-O bonds are formed between the Cu(II) ion and the oxime N and the phenolic oxygen atoms of (H₂L)²⁻ unit^{10a}. Meanwhile, a O-H stretching band of the free ligand H₄L at 3391.8 cm⁻¹ disappears in the Cu(II) complex, indicating the oxygen in phenolic alcohol of the Cu(II) complex has been deprotonated and coordinated to the Cu(II) ion. In the 1363.7-1516.3 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations. In addition, infrared spectrum of the Cu(II) complex shows the expected strong absorption band due to ν(O-H) at *ca.* 3309.3 cm⁻¹, which is the evidence for the existence of ethanol molecules^{10g}.

The absorption spectra of H₄L and its corresponding Cu(II) complex (Table-3) show that the spectrum of the Cu(II) complex is different from the spectrum of the free ligand H₄L. The UV-visible spectrum of the ligand H₄L exhibits two intense peaks at around 278 and 312 nm, The former absorption peak at 278 nm can be assigned to the π-π* transition of the benzene rings, while the latter one at 312 nm can be attributed to the intra-ligand π-π* transition of the C=N bonds¹².

Compared with the absorption peak of the free ligand H₄L, the former absorption peak at 286 nm is observed in the Cu(II) complex, which is bathochromically shifted by 8 nm. This indicates that the coordination of Cu(II) ion with the (H₂L)²⁻ unit. Meanwhile, the absorption band at *ca.* 312 nm disappears from the UV-visible spectrum of the Cu(II) complex, which indicates that the oxime nitrogen atom is involved in

TABLE-1
COLOUR, YIELDS, ELEMENTAL ANALYSIS AND COMPOSITION OF H₄L AND ITS Cu(II) COMPLEX

Compound	m.f. (m.w.)	Colour	Yield (%)	Elemental analysis (%) found (calcd.)			
				C	H	N	Cu
H ₄ L	C ₁₇ H ₁₈ N ₂ O ₆ (346.3)	Pale-pink	35.8	59.07 (58.96)	5.31 (5.24)	7.61 (8.09)	-
[Cu(H ₂ L)]·CH ₃ CH ₂ OH·0.5H ₂ O	CuC ₁₉ H ₂₃ N ₂ O _{7.5} (462.9)	grey	70.4	49.45 (49.29)	5.00 (5.01)	5.59 (6.05)	13.86 (13.73)

TABLE-2
IR SPECTRAL DATA FOR H₄L AND ITS CU(II) COMPLEX (CM⁻¹)

Compound	ν(C=N)	ν(Ar-O)	ν(O-H)	ν(C=C) benzene ring skeleton
H ₄ L	1631.0	1250.7	3391.8	1516.3, 1470.7, 1434.6
[Cu(H ₂ L)]·CH ₃ CH ₂ OH·0.5H ₂ O	1611.6	1221.3	3309.3	1537.4, 1446.5, 1363.7

TABLE-3
UV SPECTRAL DATA OF H₄L AND ITS CU(II) COMPLEX

Compound	C (×10 ⁻⁴ mol L ⁻¹)	First band		Second band	
		λ _{max1} (nm)	ε ₁ (×10 ⁴ L mol ⁻¹ cm ⁻¹)	λ _{max2} (nm)	ε ₂ (×10 ⁴ L mol ⁻¹ cm ⁻¹)
H ₄ L	1.00	278	2.45	312	1.94
[Cu(H ₂ L)]·CH ₃ CH ₂ OH·0.5H ₂ O	1.00	286	2.41	355	1.09

coordination to the metal atom^{13,14}. In addition, the new band observed at 355 nm for the Cu(II) complex is assigned to the n- π^* charge transfer transition from the filled p π orbital of the bridging phenolic oxygen to the vacant d-orbital of the Cu(II) ion, which is characteristic of the transition metal complexes with N₂O₂ coordination spheres^{10,15}.

Thermal properties: The thermal stability studies were performed for the free ligand H₄L and the Cu(II) complex. The thermal decomposition process of the Cu(II) complex compared with the free ligand H₄L is significantly different. The ligand H₄L has a sharp endothermic peak at 190 °C in the DTA curve, with no weight loss in the TG curve. And has an exothermic peak at 240 °C, weight loss occurs at 230 °C in the corresponding TG curve, the ligand H₄L decomposed completely by one step. However, the DTA curves of the Cu(II) complex has endothermic peaks in the range of 88-147 °C, with weight loss in the TG curve. The weight loss values of the Cu(II) complex are 10.3 and 2.2 %, respectively, which are close to the theoretical values (10.0 and 1.9 %) of losing corresponding ethanol and water molecules. The Cu(II) complex has two exothermic peaks at about 230 and 239 °C, with apparent weight loss, which are staged oxidative decomposition of the Cu(II) complex. On further heating, the final solid product is likely to CuO with a residual value of 17.8 % (theoretical value, 17.2 %) when the temperature is above 800 °C.

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