



Synthesis and Characterization of 5,5',6,6'-Tetrahydroxy-2,2'-[ethylene-1,2-diylidioxy]bis(nitrilomethylidene)diphenol and its Copper(II) Complexes

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A series of copper(II) complexes have been synthesized by the reaction of several Cu(II) salts with a Salen-type bisoxime chelating ligand ($H_6L = 5,5',6,6'$ -tetrahydroxy-2,2'-[ethylene-1,2-diylidioxy]bis(nitrilomethylidene)diphenol) in anhydrous ethanol medium. All the copper(II) complexes were characterized by elemental analyses, IR spectra, UV-visible spectra and molar conductance measurements.

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

INTRODUCTION

Salen (N,N' -bis(salicylaldehyde)ethylenediamine) and its derivatives are well-known chelating ligands in modern coordination chemistry¹⁻³. During the past few decades, metallo-salen complexes have been of considerable current interest due to their interesting properties⁴, such as excellent catalytic activity for epoxidation and aziridination⁵. In addition, they are also used as models for reaction centers in metalloenzymes⁶, non-linear optical materials⁷ and molecular recognition and biological activity⁸. Herein, a new Salen-type bisoxime chelating ligand ($H_6L = 5,5',6,6'$ -tetrahydroxy-2,2'-[ethylene-1,2-diylidioxy]bis(nitrilomethylidene)diphenol) and its Cu(II) complexes have been synthesized and structurally characterized.

EXPERIMENTAL

2,3,4-Trihydroxy benzaldehyde ($\geq 98.5\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. 1,2-Bis(aminoxy)ethane was synthesized according to an analogous method reported earlier⁶. Copper(II) acetate monohydrate ($\geq 98.5\%$), copper(II) chloride dihydrate ($\geq 99\%$), copper(II) nitrate tetrahydrate ($\geq 99\%$), the other reagents and solvents were purchased from Tianjin Chemical Reagent Factory and were used without further purification. Copper was detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. FT-IR

spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr ($4000-400\text{ cm}^{-1}$). UV-VIS absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Molar conductance value measurements were carried out on a model DDS-11D type conductivity bridge using $1.0 \times 10^{-3}\text{ mol}\cdot\text{dm}^{-3}$ solution in DMF at $25\text{ }^\circ\text{C}$.

Synthesis of ligand H_6L : The ligand H_6L was synthesized with a slightly modified method reported literature⁴. Synthetic route to salen-type bisoxime ligand H_6L is shown in Fig. 1.

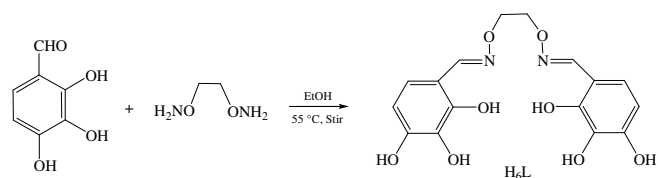


Fig. 1. Synthetic route to 5,5',6,6'-tetrahydroxy-2,2'-[ethylene-1,2-diylidioxy]bis(nitrilomethylidene)diphenol (H_6L)

Reaction of 1,2-bis(aminoxy)ethane (133.5 mg, 1.45 mmol) with 2 equivalents of 2,3,4-trihydroxy benzaldehyde (462.4 mg, 3 mmol) in ethanol (10 mL) at $55\text{ }^\circ\text{C}$ for 6 h. After cooled to room temperature, the resulting solid was filtered and washed with ethanol and ethanol/hexane (1:4), respectively. The product was dried *in vacuo* and obtained 483.7 mg of white microcrystal. Yield: 79.8 %.

Synthesis of complex 1: A solution of copper(II) acetate monohydrate (20 mg, 0.10 mmol) in ethanol (3 mL) was added

dropwise to a solution of H₆L (36.6 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. A green solution was obtained and stirred vigorously and refluxed for 12 h. The resulting reaction solution was concentrated under reduced pressure. After cooled to room temperature, the precipitation formed was filtered and washed with ethanol/ether (1:4) and ether, respectively. The product was dried *in vacuo* and obtained 19 mg of black solid (Yield 29.0 %).

Synthesis of complex 2: To an ethanolic solution (5 mL) of H₆L (36.5 mg, 0.10 mmol) was added an ethanolic solution (5 mL) of copper(II) picrate tetrahydrate (59.2 mg, 0.10 mmol). After the mixture solution had been stirred at 55 °C for 10 h, the formed precipitate was separated by filtration and washed successively with ethanol/ether (1:4) and ether, respectively. The product was dried under reduced pressure to obtain 32.4 mg of yellow solid (Yield 39.3 %).

Synthesis of complex 3: A solution of copper(II) nitrate trihydrate (24.2 mg, 0.10 mmol) in ethanol (6 mL) was added dropwise to a solution of H₆L (36.3 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. A green solution was obtained and stirred vigorously and refluxed for 8 h. The resulting reaction solution was concentrated under reduced pressure. After cooled to room temperature, the precipitate formed was filtered and washed with ethanol/ether (1:4) and ether, respectively. The product was dried *in vacuo* and obtained 25.6 mg of black solid (Yield 48.9 %).

Synthesis of complex 4: To an ethanolic solution (5 mL) of H₆L (36.4 mg, 0.10 mmol) was added an ethanolic solution (6 mL) of copper(II) chloride dihydrate (17.1 mg, 0.10 mmol). A green solution was obtained and stirred vigorously and refluxed for 10 h. The formed precipitate was separated by filtration and washed successively with ethanol/ether (1:4) and ether, respectively. The product was dried under reduced pressure to obtain 11.8 mg of black solid (Yield 21.4 %).

RESULTS AND DISCUSSION

A Salen-type bisoxime compound H₆L and its Cu(II) complexes have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible spectra and molar conductances.

Composition of Cu(II) complexes: The colour, yields and analytical results of the Cu(II) complexes are given in Table-1.

Their compositions agree with the formula [Cu₃(HL)(CH₃COO)]·EtOH for complex **1**, [Cu₃(HL)(pic)]·EtOH for complex **2**, [Cu₃(HL)(NO₃)]·H₂O for complex **3** and [Cu₃(HL)Cl]·2H₂O for complex **4**. The molar conductance values of the Cu(II) complexes in 1.0 × 10⁻³ mol dm⁻³ DMF solutions at 21 °C are shown in Table-1. Compared with the molar conductance values about different types of electrolytes in organic solvents, we can consider that the formed Cu(II) complexes are non-electrolytes, indicating the anions in the Cu(II) complexes are coordinated to the Cu(II) ions⁹.

IR spectra of H₆L and Cu(II) complexes: The most important FT-IR spectra data for H₆L and its Cu(II) complexes are given in Table-2. From the results of IR spectra, the ligand and its Cu(II) complexes are very different, which proves that Cu(II) ions have been in coordination with the (HL)⁵⁻ unit and new complexes formed. The characteristic C=N stretching band of the free ligand H₆L appears at 1615.7 cm⁻¹, while the C=N stretching bands of the Cu(II) complexes are observed at 1591.0-1606.2 cm⁻¹. The C=N stretching frequency shifted to lower frequency by 24.7-9.5 cm⁻¹ upon complexation, indicating a decrease in the C=N bond order due to the coordinated bonds of the Cu(II) atoms with the oxime nitrogen lone pair¹⁰. The Ar-O stretching frequency appears as a strong band within 1263-1213 cm⁻¹ range as reported for similar ligands¹¹⁻¹³. This band occurs at 1219 cm⁻¹ for H₆L and at 1264.5-1240.2 cm⁻¹ for the Cu(II) complexes. The Ar-O stretching frequency is shifted to lower frequency, indicating that the Cu-O bond was formed between the Cu(II) ion and oxygen atom of phenolic group^{10,14}. In addition, the O-H stretching band of the free ligand H₆L appears at 3453.1 cm⁻¹ and a very broad absorption band at 3431.3-3406.5 cm⁻¹ in the Cu(II) complex is assigned to phenolic alcohol group of the (HL)⁵⁻ unit and -OH groups of non-coordinated ethanol or water molecules.

UV-visible spectra of H₆L and Cu(II) complexes: The UV-visible absorption spectra of H₆L and its Cu(II) complexes in diluted DMF solution are presented in Table-3. The absorption spectra of the Cu(II) complexes are similar to each

TABLE-1
COLOUR, YIELDS AND ANALYTICAL DATA OF H₆L AND ITS Cu(II) COMPLEXES

Compound	m.f. (m.w.)	Colour	Yield (%)	Found (calcd.) (%)			Molar conductance (S cm ² mol ⁻¹)
				C	H	N	
H ₆ L	C ₁₆ H ₁₆ N ₂ O ₈ (364.3)	White	79.8	53.00 (52.75)	4.39 (4.43)	7.37 (7.69)	–
[Cu ₃ (HL)(CH ₃ COO)]·EtOH	C ₂₀ H ₂₀ Cu ₃ N ₂ O ₁₁ (655.0)	Black	29.0	36.60 (36.62)	2.84 (3.23)	4.16 (4.27)	6.62
[Cu ₃ (HL)(pic)]·EtOH	C ₂₄ H ₁₉ Cu ₃ N ₅ O ₁₆ (824.1)	Yellow	39.3	34.88 (34.98)	2.28 (2.32)	8.60 (8.50)	8.87
[Cu ₃ (HL)(NO ₃)]·H ₂ O	C ₁₆ H ₁₃ Cu ₃ N ₅ O ₁₂ (627.8)	Black	48.9	30.54 (30.51)	2.29 (2.08)	6.68 (6.67)	1.15
[Cu ₃ (HL)Cl]·2H ₂ O	C ₁₆ H ₁₅ ClCu ₃ N ₂ O ₁₀ (618.8)	Black	21.4	30.49 (30.93)	2.55 (2.43)	4.87 (4.51)	2.34

TABLE-2
IR SPECTRAL (cm⁻¹) DATA FOR H₆L AND ITS Cu(II) COMPLEXES

Compound	v(C=N)	v(Ar-O)	v(O-H)	v(C=C) benzene ring skeleton
H ₆ L	1615.7	1292.0	3453.1	1595.2, 1525.0, 1471.1
[Cu ₃ (HL)(CH ₃ COO)]·EtOH	1594.6	1250.7	3406.5	1585.3, 1489.6, 1450.5
[Cu ₃ (HL)(pic)]·EtOH	1606.2	1264.5	3430.1	1586.2, 1490.4, 1451.9
[Cu ₃ (HL)(NO ₃)]·H ₂ O	1599.8	1256.4	3431.3	1587.0, 1493.8, 1440.2
[Cu ₃ (HL)Cl]·2H ₂ O	1591.0	1240.2	3410.2	1572.6, 1478.1, 1446.4

TABLE-3
UV-VISIBLE SPECTRAL DATA OF H₆L AND ITS Cu(II) COMPLEXES

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 ₆ L	1.00	283	13.01	386	4.18
[Cu ₃ (HL)(CH ₃ COO)]·EtOH	1.00	268	1.70	332	1.60
[Cu ₃ (HL)(pic)]·EtOH	1.00	261	2.08	330	1.78
[Cu ₃ (HL)(NO ₃)]·H ₂ O	1.00	258	1.68	334	1.55
[Cu ₃ (HL)Cl]·2H ₂ O	1.00	263	1.85	338	1.68

other, but are different from the spectrum of the free ligand H₆L. The UV-visible spectrum of the free ligand H₆L exhibits one absorption peak at 283 nm, which can be assigned to the π-π* transition of the benzene rings¹⁵. Compared with the absorption peak of the free ligand H₆L, a corresponding absorption peak at 258-268 nm is observed in the Cu(II) complexes, which is shifted by 15-25 nm, indicating the coordination of the Cu(II) ions with the (HL)⁵⁻ unit. Meanwhile, a new absorption peak is observed at 330-338 nm in the Cu(II) complexes, which is assigned to the n-π* charge transfer transition from the filled pπ orbital of the bridging phenolic oxygen to the vacant d-orbital of the Cu(II) ions^{16,17}.

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