



Synthesis and Characterization of Copper(II) Complexes with Salen-Type Bisoxime Chelating Ligand

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Two Cu(II) complexes **1** and **2** have been synthesized by the reaction of copper(II) picrate tetrahydrate and copper(II) perchlorate hexahydrate with a Salen-type bisoxime chelating ligand (H_2L = 6,6'-dimethoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol) and characterized by elemental analyses, IR spectra, UV-visible spectra, TG-DTA analyses and molar conductances. The Salen-type bisoxime is a good tetradentate N_2O_2 -donating ligand and the likely formula of the Cu(II) complexes may be suggested as $CuL \cdot (HPic)_2$ (**1**) and $CuL \cdot 2H_2O$ (**2**).

Keywords: Cu(II) complex, Bisoxime ligand, Synthesis.

INTRODUCTION

Oxime-type compounds have long been used as chelating ligands in the synthesis of transition metal complexes due to their ease of preparation and structural variety. These compounds can accommodate one, two or more metal centers and form homo- and heteronuclear metal complexes with interesting properties¹⁻⁴, 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_2L = 6,6'-dimethoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol) and its Cu(II) complexes **1** and **2** have been synthesized and structurally characterized.

EXPERIMENTAL

3-Methoxy-2-hydroxybenzaldehyde ($\geq 98\%$) was purchased from Alfa Aesar and used without further purification. 1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier⁴. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analysis for Cu 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 (400-4000 cm^{-1}). UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. TG-DTA analyses were carried out at

a heating rate of 5 °C/min on a ZRY-1P thermoanalyzer. Molar conductance value measurement was carried out on a model DDS-11D type conductivity bridge using 1.0×10^{-3} mol dm^{-3} solution in DMF at 25 °C.

Synthesis of ligand (H_2L): The ligand H_2L was synthesized with a slightly modified method reported literature⁴. Reaction of 1,2-bis(aminooxy)ethane (133.7 mg, 1.45 mmol) with 2 equiv. of 3-methoxy-2-hydroxybenzaldehyde (456 mg, 3.00 mmol) in ethanol (10 mL) at 55 °C for 6 h. After cooling 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 colorless micro-crystal. m.p. 120-121 °C.

Synthesis of Cu(II) complex 1: A solution of copper(II) picrate tetrahydrate (59.3 mg, 0.10 mmol) in ethanol (3 mL) was added dropwise to a solution of H_2L (36.2 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. A green solution was obtained and stirred vigorously and refluxed for 3 h. The resulting solid was filtered off, washed with ethanol/ether (1:4) and ether, respectively. The product was dried *in vacuo* and obtained 47.8 mg of pale-green solid.

Synthesis of Cu(II) complex 2: To an ethanol solution (5 mL) of H_2L (35.9 mg, 0.10 mmol) was added an ethanol solution (5 mL) of copper(II) perchlorate hexahydrate (37.1 mg, 0.10 mmol). After the mixture 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 25.5 mg of pale-green solid.

TABLE-1
 COLOUR, YIELDS AND ANALYTICAL DATA OF H₂L AND ITS COPPER(II) COMPLEXES

Comp.	m.f. (m.w.)	Colour	Yield (%)	Found (calcd.) (%)				Molar conductance (S cm ² mol ⁻¹)
				C	H	N	Cu	
H ₂ L	C ₁₈ H ₂₀ N ₂ O ₆ (360.4)	Colorless	83.6	59.97 (59.99)	5.87 (5.59)	7.61 (7.77)	–	–
1	C ₃₀ H ₂₄ N ₈ O ₂₀ Cu (880.1)	Pale-green	54.3	40.89 (40.94)	3.11 (2.75)	12.58 (12.73)	7.15 (7.22)	2.78
2	C ₁₈ H ₂₂ N ₂ O ₈ Cu (457.9)	Pale-green	55.7	47.38 (47.21)	4.66 (4.84)	6.08 (6.12)	13.69 (13.88)	1.53

RESULTS AND DISCUSSION

Composition of Cu(II) complexes: The analytical results of Cu(II) complexes **1** and **2** are given in Table-1. Their compositions agree with the formula CuL·(HPic)₂ for complex **1** and CuL·2H₂O for complex **2**. The molar conductance values of complexes **1** and **2** in 1.0 × 10⁻³ mol dm⁻³ DMF solutions are 2.78 and 1.52 S cm² mol⁻¹ at 21 °C, respectively, indicating that both are non-electrolytes. This implies that all of the picrate groups in complex **1** are present in the coordination sphere maybe through the hydrogen-bonding interactions in solution or solid state.

IR spectra of H₂L and Cu(II) complexes: The most important FT-IR spectra data for H₂L and its corresponding Cu(II) complexes are given in Table-2. The characteristic C=N stretching band of the free ligand H₂L appears at 1605 cm⁻¹, while the C=N bands of Cu(II) complexes **1** and **2** are observed at 1608 and 1607 cm⁻¹, respectively. The Ar-O stretching bands occur at 1262 cm⁻¹ for H₂L, whereas those at 1256 cm⁻¹ and 1255 cm⁻¹ for complexes **1** and **2**, respectively. This shifting of C=N and Ar-O stretching frequency indicate that the Cu-N and Cu-O bonds are formed between the Cu(II) ions and the oxime N atoms and the phenolic oxygen atoms of the ligand L²⁻ unit⁴. The O-H stretching band of the free ligand H₂L appears at 3435 cm⁻¹, which disappears in complexes **1** and **2**, indicating the oxygen atoms in the phenolic alcohol groups have been completely deprotonated and coordinated to Cu(II) ions. In addition, the OH out-of-plane bending vibration of the free picric acid at 1150 cm⁻¹ appears in the spectra of complex **1**, indicating that the H-atom of the OH group existed in complex **1**⁹. Free picric acid has ν_{as}(-NO₂) and ν_s(-NO₂) at 1555 and 1342 cm⁻¹, respectively, which split into two bands

at 1576, 1545 cm⁻¹ and 1368, 1337 cm⁻¹. This indicates that some of the nitryl O atoms take part in coordination¹⁰. The broad bands at 3446 cm⁻¹ are ascribed to the vibration of the water mole-cules in complex **2**¹¹.

UV-visible spectra of H₂L and Cu(II) complexes: The absorption spectra of H₂L and its corresponding Cu(II) complexes **1** and **2** (Table-3), in diluted DMF solution show that the spectra of complexes **1** and **2**, are similar to each other, but are different from the spectrum of the ligand (H₂L). The UV-visible spectrum of the free ligand H₂L exhibits two absorption peaks at 272 and 318 nm. The former absorption peak at 272 nm can be assigned to the π-π* transition of the benzene rings and the latter one at 318 nm can be attributed to the intra-ligand π-π* transition of the C=N bonds¹².

Compared with the absorption peak of the ligand, a corresponding absorption peak at 308 and 307 nm is observed in complexes **1** and **2**, respectively, which is hypsochromically shifted by 10 nm, indicating the coordination of Cu(II) ions with the ligand. Meanwhile, the absorption band at about 318 nm disappears from the UV-visible spectra of complexes **1** and **2**, which indicates that the oxime nitrogen atom is involved in coordination to the metal atom^{13,14}. In addition, the new bands observed at 360 and 375 nm for complexes **1** and **2** are 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, which are characteristic of the transition metal complexes with N₂O₂ coordination spheres^{4,15}.

Thermal properties: The thermal decomposition process of complexes **1** and **2** can be divided into three stages. The initial weight loss occurs in the range 152-185 °C for complex **1** and 124-150 °C for complex **2**, corresponding to an endothermic peak and the TG curve shows that the weight loss corresponding to this temperature range is 25.9 and 12.1 % that roughly coincides with the value of 26 and 11.8 %, respectively, calculated for the loss of two picric acid molecules of complex **1** and two water molecules of complex **2**. On further heating, two exothermic peaks successively at 259 and 329 °C for complex **1** (261 and 341 °C for complex **2**) in the DTA curve and a continued weight loss occurs in the TG curve. Then, the second strong exothermic peak at 329 °C for

 TABLE-2
 KEY FT-IR BANDS FOR H₂L
 AND ITS COPPER(II) COMPLEXES (cm⁻¹)

Comp.	ν(C=N)	ν(Ar-O)	ν(O-H)	ν(C=C) benzene ring skeleton
H ₂ L	1605	1262	3435	1594, 1512, 1413
1	1608	1256	3452	1596, 1413, 1415
2	1607	1255	3446	1596, 1413, 1416

 TABLE-3
 UV-VISIBLE SPECTRA DATA OF H₂L AND ITS COPPER(II) COMPLEXES

Comp	Concentration (×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 ₂ L	1.00	272	2.599	318	0.826
1	1.00	308	32.42	360	25.64
2	1.00	307	33.12	375	24.65

complex **1** (at 341 °C for complex **2**) accompanied with further decomposition of the compound and the final solid product is likely to CuO with a residual value of 10.1 % (theoretical value, 9.0 %) for complex **1** and 18.6 (theoretical value, 17.4 %) for complex **2** when the temperature is above 800 °C.

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