*Asian Journal of Chemistry* Vol. 20, No. 3 (2008), 1692-1696

# Electrochemical Characteristics of a Cu(II) Schiff Base Complex and Its Interaction with DNA

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The Cu(II) Schiff base was synthesized and characterized by elemental analysis, molar conductivity, IR and UV-Visible spectra. The electrochemical characteristics of a mononuclear Cu(II) complex have been studied and the interaction of copper complex with DNA was also studied by cyclic voltammetry and fluorescence spectrum.

**Key Words: Schiff base, Cyclic voltammetry, DNA.**

## INTRODUCTION

Transition metal complexes attracted considerable attention in view of their physico-chemical properties and potentially therapeutic properties[1-5]. Carter *et al.*[6] first used electrochemical theory to explore the interaction of the complex and DNA through the cyclic voltammetry of the effect of the electrical activity molecule and DNA. Usually, when the DNA and the complex were studied, the method of the fluorescence spectrum of EB was adopted[7]. In this paper, the authors reported the electrochemical property of Cu(II) schiff base and the interactivity of the complex and DNA.

## EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. 2,4-Dihydroxybenzaldehyde was added (with stirring) to anhydrous ethanol (20 mL) to make a elucid solution. Then, it was slowly dripped into the anhydrous ethanol solution (15 mL) containing 0.01 mol glycine (containing 0.01mol KOH) at 55 ºC (pH = 6.0-6.5), a mass of yellow grain was separated out which was collected by filtration and washed several times with anhydrous ethanol, recrystallized with methanol and dried under vacuum (yield of the reaction was 94.7 %). Anal. Calcd. (%) for C, 55.39; H, 4.65; N, 7.18; Found (%): C, 54.98; H, 4.62; N, 7.06. IR data (KBr, $\nu_{max}$, cm$^{-1}$): 1650 (C=N); 1598, 1394 ($COO^-$); 1378 (Ar-O).

**Preparation of the complex:** 0.5 mmol of the cupric acetate in 15 mL of anhydrous ethanol was added dropwise into the solution of Schiff-base (0.5 mmol ) in 15 mL of anhydrous ethanol and was stired at 60 ºC. The dark green solution obtained was filtered and the dark green powder was dried under vacuum. The C, H and N contents were as follows: Anal. Calcd. (%) for C, 39.35; H, 3.30; N, 5.10; Cu, 23.13. Found: C, 40.15; H, 3.20; N, 5.50; Cu, 24.24. IR data (KBr, $\nu_{max}$, $cm^{-1}$): 1623 (C=N), 1610, 1449 ($COO^-$), 1349 (Ar-O).

Elemental analyses were carried out with a model 2400 Perkin-Elmer analyzer. Infrared spectrum was recorded in KBr pellets using a Nicolet 170SX spectrophotometer in the 4000-400 $cm^{-1}$ region. Molar conductivity at room temperature were measured in $10^{-3}$ M DMSO solution using a DDS-11A type conductivity meter at 25 ºC. The thermogravimeteric measurements were made using a Perkin-Elmer TGA7 thermogravimeter. The heating rate was programmed to be 10 ºC/min with the protecting stream of $N_2$ flowing at 40 mL/min.

## RESULTS AND DISCUSSION

The title complex is dark green powder, soluble in DMSO, DMF and a little soluble in water and acetone. The molar conductivity of the complex is 30.15 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ in DMSO. Low molar conductivity for the complex in DMSO corresponds to non-eletrolyte[8].

The shift of $\nu$(C=N) from 1650 $cm^{-1}$ in the ligand to 1623 $cm^{-1}$ in the complex, suggesting that Cu ion is bonded with N atom in Schiff-base. The shift of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ from 1598 and 1394 $cm^{-1}$ in the ligand to 1610 and 1449 $cm^{-1}$ in the complex, respectively, suggests the coordination of the oxygen in the carobxylate group to the metal ion. The value of $\nu[\nu_{as}(COO^-)-\nu_s(COO^-)]$ = 160 $cm^{-1}$ indicates that the -$COO^-$ group is coordinated to the metal ion in a monodentate fashion[9]. A broad absorption band at the range of 3200-3029 $cm^{-1}$ confirms the presence of water in the complex. The appearing of Ar-O frequency (1349) is lower than1378 $cm^{-1}$, which exposes that Ar-O-Cu in the complex. The bands appearing at 845 and 728 $cm^{-1}$ attribute to the water bonded with complex are observed[10].

**Thermal analysis:** Thermogravimetric (TG) analysis and differential thermgravimetric (DTG) analysis show that the thermal decomposition of the title compound includes three transitions. The first and the second weight loss stages have decomposition temperature ranges of 25-1700 and 170-2500, with weight losses of 7.04 % (Calcd. 6.7 %) and 6.3 % (Calcd. 6.7 %), which corresponds to the losses of one molecule of water, respectively. The third weight losses of one molecule of Schiff base (250-10000) decomposed. The weight percentage of 30 % (Calcd. 29 %) of the original sample remained, CuO is the final residue. These changes could be diagnostic for the complex of $[Cu(C_9O_4NH_4)\cdot H_2O]\cdot H_2O$.

**Cyclic voltammetry of glycine-2,4-dihydroxybenzaldehyde Cu(II) complex and the interactivity of the complex and the DNA:** The electrochemical experiment of the title complex was carried out with a glass carbon (GC) working electrode, a Pt plate auxiliary electrode and a AgCl/Ag reference electrode the scanning rate was 0.062 v/s. The curve 1 is a cyclic voltammetry of the title complex in the B-R buffer solution (pH = 4.5). The cyclic voltammetry of the title complex shows that there is one pair of redox peaks: Epc = -0.358V, Epa = -0.785 V.

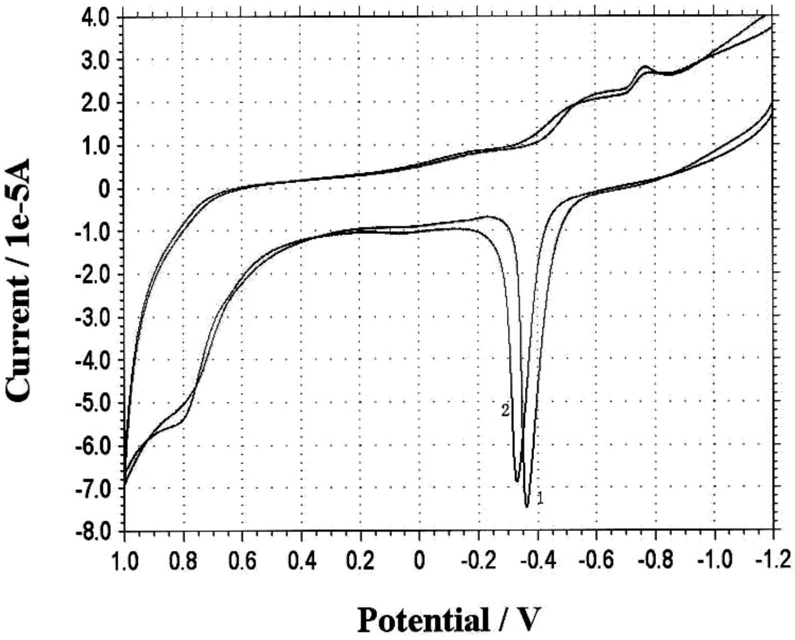

Fig. 1. The cyclic voltammetry of glycine-2,4-dihydroxybenzaldehyde Cu(II) complex and the interactivity of the complex and the DNA C: $6.00 \times 10^{-5}$ mol $L^{-1}$, $C_{DNA}$: (1) 0 (2) $1.40 \times 10^{-1}$ mol $L^{-1}$

The curve 2 is a cyxlic voltammetry of the mixed solution of DNA and complex in the B-R buffer solution (pH = 4.5), from which we can induce that the electric current of oxidation peak decreased and had no new oxidation peak occur, through which we can presume DNA and complex formed the new compound that wasn't electric activity compound. Due to the new compound didn't conducted, the concentration of the complex reduced so that the number of the molecule of the complex moved to the surface of electrodem declined, which lead to the electric currents became weak. It is generally accepted that there are three kinds of binding modes for small molecules to DNA, which refer to intercalative binding, groove binding and electeostatic binding. Carter *et al.*[6] deemed that when the molecule inserts into the inner of DNA bi-helix structure, the peak currents of the oxidation of the voltammetry decreased with positive shifts of the peak potential. On the other way around, when the molecule interacted with DNA in the form of static effect, the peak currents of the voltammetry curves of the oxidation of the voltammetry decreased with negative shifts of the peak potential. The author concluded that the complex interact with DNA in the form of inset.

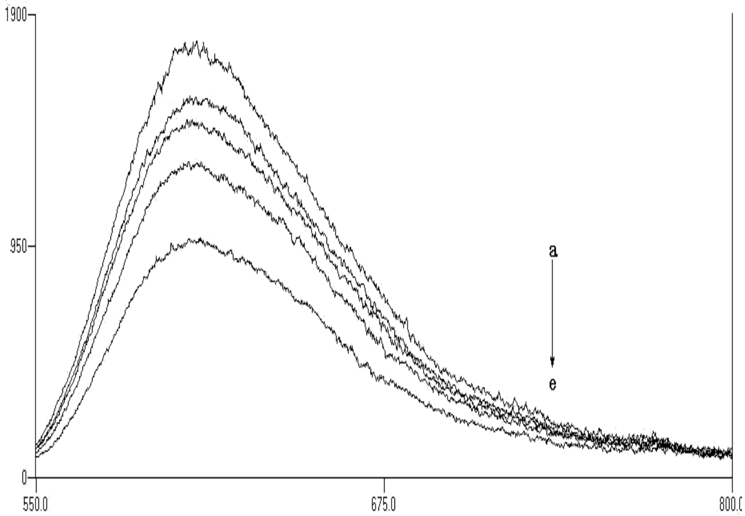

Fig. 2. Fluorescence spectra of different concentration complex interaction with EB-DNA system(unit: nm) (a) $C_{Comp} = 0$ mol/L; (b) $C_{Comp} = 3.00 \times 10^{-5}$ mol/L; (c) $C_{Comp} = 6 \times 10^{-5}$ mol/L; (d) $C_{Comp} = 8 \times 10^{-5}$ mol/L; (e) $C_{Comp} = 1.0 \times 10^{-4}$ mol/L

Fig. 2 shows different concentration of complex interacted with EB-DNA (excitation wavelength: 540 nm pH = 4.5). From Fig. 2, we concluded that when added the complex into the system of EB-DNA, the fluorescence of the system of EB-DNA obviously trailed off, indicated complex combined with DNA, competing with EB. When added the complex in the system of EB-DNA, the EB replace by the complex, According, the complex and EB may combine with DNA at the same spot and proved the complex inserted into the inner of DNA bi-helix structure.

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(*Received*: 23 October 2006; *Accepted*: 22 October 2007) AJC-6029