Synthesis, Characterization, and Prohibitive Action on Free Radical O_2^{-} of β -Phenylalanine Schiff Base Binuclear Complexes¹

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Abstract—A new Schiff base ligand as salt (KL) was synthesized using potassium salt of DL- β -phenylalanine and 2-hydroxy-1-naphthaldehyde. Two binuclear complexes of this ligand, $[M_2L_2(CH_3COO)_2]$ (M = Cu(II), Ni(II)) have been synthesized and characterized by elemental analyses, IR, UV spectra, and molar conductance.

Their prohibitive action on the superoxide anion free radical $(O_2^{-\bullet})$ was estimated by the NBT illumination deoxidizing method (Methionine-lactoflavin illumination method). The results suggested that the ligand and its complexes had the prohibitive action on $O_2^{-\bullet}$.

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INTRODUCTION

Some Schiff base complexes derived from amino acids are particularly active in biology. Recently, studies of some metal complexes with α -amino acid Schiff bases have been reported [1–5]. To continue the investigation in this area, a new Schiff base ligand as salt (**KL**) was synthesized using potassium salt of DL- β -phenylalanine and 2-hydroxy-1-naphthaldehyde, and two binuclear complexes [M₂L₂(CH₃COO)₂] (M = Cu(II) (**I**), Ni(II) (**II**); HL— β -phenylalanine-2hydroxy-1-naphthaldehyde Schiff base) were synthesized in 95% ethanol. The prohibitive action on the superoxide anion free radical (O₂⁻⁺) of the ligand and its complexes was also studied.

EXPERIMENTAL

All reagents used in this work were of analytical grade or biological grade.

Preparation of potassium salt of the ligand. Potassium hydroxide (0.281 g, 5.0 mmol) was dissolved in 20 ml ethanol and mixed with DL- β -phenylalanine

 NH_2

(0.826 g, 5.0 mmol) dissolved in 10 ml of ethanol. The reaction proceeded for 1 h at 40°C, and then the reaction mixture was filtered. 2-Hydroxy-1-naphthalde-hyde (0.861 g, 5.0 mmol) dissolved in 15 ml of ethanol was added dropwise to the above filtered solution and the mixture stirred for 6 h at $50-55^{\circ}$ C to give a precipitate. The light yellow precipitate was collected by filtration, washed with ethanol, and dried in vacuum. The yield was 1.40 g (78%).

For $C_{20}H_{16}NO_3K$ (<i>M</i> = 357.4)							
anal. calcd, %:	C, 67.20;	H, 4.51;	N, 3.92.				
Found, %:	C, 67.03;	Н, 4.41;	N, 3.85.				

The synthesis reactions of the KL are shown below:



¹ The text was submitted by the authors in English.

Compound	λ_{max1} , nm	$\epsilon_1 \times 10^{-4},$ mol ⁻¹ l cm ⁻¹	λ_{max2}, nm	$\epsilon_2 \times 10^{-4},$ mol ⁻¹ l cm ⁻¹	λ_{max3} , nm	$\epsilon_3 \times 10^{-4},$ mol ⁻¹ l cm ⁻¹
KL	255	6.16	308	1.15		
$[Cu_2L_2(CH_3COO)_2]$	255	10.5	318	1.82	388	1.44
[Ni ₂ L ₂ (CH ₃ COO) ₂]	258	12.9			413	1.78

UV spectra for the ligand and complexes

Preparation of the complexes I and II. The potassium salt of the Schiff base ligand (1.07 g, 3.0 mmol) dissolved in 30 ml of 95% ethanol was mixed with metal acetate (3.0 mmol) dissolved in 10 ml of anhydrous ethanol, and the mixture stirred for 12 h at 65°C to give precipitates, which were cooled and filtered off. The precipitates were collected, washed with ethanol, and dried in vacuo. The purity of the complexes was higher than 99%.

For $C_{44}H_{38}N_2O_{10}Cu_2$ (I) (*M* = 881.9)

anal. calcd, %:	C, 59.93;	Н, 4.34;	N, 3.18;	Cu, 14.41.			
Found, (%):	C, 59.39;	H, 4.14;	N, 3.21;	Cu, 14.36.			
For $C_{44}H_{38}N_2O_{10}Ni_2$ (II) ($M = 872.1$)							
anal. calcd, %:	C, 60.59;	H, 4.39;	N, 3.21;	Ni, 13.46.			
Found, %:	C, 60.23;	Н, 4.52;	N, 3.35;	Ni, 13.57.			

The synthesis reaction of the complexes may be represented in the following way:

 $2M(CH_3COO)_2 \cdot nH_2O + 2KL$

 \longrightarrow [M₂ L₂(CH₃COO)₂] + 2CH₃COOK + 2*n*H₂O.

Physical measurement of the complexes I and II. Elemental analyses were carried out with a model 240C Perkin Elmer analyzer. The metal content was determined by gravimetry. The UV spectra were recorded on a TU-1901 spectrophotometer in DMSO. The molar conductance was measured with a Shanghai DDSJ-308A conductivity meter. IR spectra of the ligand and complexes were recorded in KBr pellets using a AVATAR 360 FT-IR spectrophotometer. Visible spectra were measured with a 723 spectrophotometer.

RESULTS AND DISCUSSION

The molar conductance values of Cu(II) and Ni(II) complexes are 14.3 and 1.41 Ohm⁻¹ cm² mol⁻¹, respectively, indicating their nonelectrolytic nature [6]. This suggests that two acetate ions are within the coordination sphere. The complexes are stable in air and insoluble in water and ethanol; however, they are soluble in DMF and DMSO.

The shift of the band with v(C=N) from 1636.4 cm⁻¹ in the ligand to 1644.6 and 1633.5 cm⁻¹ in the Cu(II) and Ni(II) complexes, respectively, suggests the formation of a C=N–M bond system. The vibration v(Ar-O)

of the ligand occurs at 1210.5 cm⁻¹. The shift of the band to a higher frequency by about 34 cm⁻¹ in the metal complexes indicates the coordination of hydroxyl oxygen to the metal ion. The shifts of $v_{as}(COO^{-})$ and $v_{c}(COO^{-})$ from 1636.4 and 1451.0 cm⁻¹ in the ligand to 1644.6 and 1434.4, 1633.5 and 1442.8 cm⁻¹ in the Cu(I) and Ni(II) complexes, respectively, suggest the coordination of the oxygen in the carboxylate group to the metal ions. The value of $v_{as}(COO^{-}) - v_{s}(COO^{-}) > 180 \text{ cm}^{-1}$ indicates that the -COO⁻ group in the ligand is coordinated to the metal ions by the monodentate mode [7, 8]. The bands at about 1574 and 1434 cm⁻¹ are assigned to the coordinated $-COO^{-}$ group by the bridged mode [8]. The spectra of the Cu(II) and Ni(II) complexes exhibit a broad band at 3411.6 and 3420.4 cm⁻¹, respectively, which are attributed to v(O-H) of phenol.

The spectral data are shown in the table. The electronic spectra of the Cu(II), Ni(II) complexes in DMSO exhibit three bands (at 255, 318, and 388 nm) and two bands(at 258 and 413 nm), respectively. Two bands occur at 255 and 308 nm in the spectrum of the ligand. Compared with the electronic spectrum of the ligand, there are some changes in the numbers of wave and the molar extinction coefficients, which further indicates the formation of the complexes.

The prohibitive action on the superoxide anion free radical (O_2^{-}) of the Schiff base ligand and its complexes was studied by the NBT illumination deoxidizing method (Methionine-lactoflavin illumination method) [9]. The phosphate buffer solutions (pH 7.8) containing 3.3×10^{-6} mol 1⁻¹ lactoflavin, 0.01 mol 1⁻¹ DL-methionine, 4.6×10^{-5} mol 1⁻¹ NBT, and 0–10 mg 1⁻¹ of the ligand or complexes were made up. This solution was kept at a constant temperature ($30 \pm 0.2^{\circ}$ C) for 10 min and illuminated with a 72-W daylight lamp with invariable intension. Its absorbance was measured with a 723 spectrophotometer at 560 nm per 1 min. The inhibitive percent of compounds (β , %) at some concentration was calculated by the formula:

$$\beta (\%) = \left[(\Delta A / \Delta t)_0 - (\Delta A / \Delta t)_m \right] / (\Delta A / \Delta t)_0 \times 100\%,$$

where $(\Delta A/\Delta t)_0$ is the variety of absorbance in unit time when the concentrations of the ligand or complexes were zero, $(\Delta A/\Delta t)_m$ is the variety of absorbance in unit time when the concentrations of the ligand or complexes were measured.

As seen from the figure, the Schiff base and complexes have a certain inhibitive effect to the free radical

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Percent curve of the complex and Schiff base inhibition to the free radical O_2^{-} : (1) Schiff base KL, (2) $[Cu_2L_2(CH_3COO)_2]$, and (3) $[Ni_2L_2(CH_3COO)_2]$.

 O_2^{-} . The inhibitive rate of the complexes was higher than that of the Schiff base ligand in summary. The inhibitive rate of the ligand increases with the concentration increasing. The inhibitive rate of the $[Cu_2L_2(Ac)_2]$ complex reduces with the concentration increasing; however, the inhibitive percent of the $[Ni_2L_2(Ac)_2]$ complex has a nadir at a concentration of 8 mg/l and is lower than that of the ligand at this concentration. The inhibitive mechanism of the ligand and its complexes to the free radical $O_2^{-\bullet}$ is to be studied in the future.

Thus, the results presented here clearly indicate that copper acetate and nickel acetate can form stable solid binuclear complexes with Schiff base DL- β -phenylala-nine-2-hydroxy-1-naphthaldehyde. The compositions of the complexes are confirmed to be $[M_2L_2(CH_3COO)_2]$ (M = Cu(II), Ni(II)). The structures proposed for the complexes I and II are shown below:



The ligand and its two complexes have prohibitive action on superoxide anion free radical $O_2^{-\bullet}$.

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