

## Synthesis and Characterization of a Ni(II) and Cu(I) Complexes of Schiff Base Derived from Salicylaldehyde

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A new Schiff-base ligand, 2-(3-[2-(6-aminoquino[8,7-b]azin-5-yliminomethyl) phenoxy]propoxy)-benzaldehyde has been synthesized from the reaction of 1,5-bis(2'-formylphenyl)-1,5-dioxapentane with 5,6-diamino-1,10-phenanthroline and its metal complexes with Cu(I) and Ni(II) have been prepared. Molecular structure of Schiff-base and its metal complexes have been investigated and characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, fluorescence, FAB (+) mass spectra, elemental analysis, magnetic measurements and TGA-DSC-DTG techniques.

**Key Words:** Schiff-base, *o*-Diamine, 1,10-Phenanthroline, Imine.

### INTRODUCTION

Schiff base ligands and their complexes derived from the reaction of dialdehydes with *o*-diamines have been extensively studied and a number of them are used as model for complicated biological systems<sup>1-10</sup>. These ligands have an affinity for transition metals such as Mn, Co, Fe and Cu. Some of these complexes have been studied in great deal for their various structures, steric effects and their coordination chemistry<sup>11-13</sup>.

Even though the number of works reported are rather few, ligands derived from 5,6-diamino-1,10-phenanthroline have been proven to show interesting coordinating properties because of the additional donor sites on the aromatic core<sup>14-16</sup>.

Herein, the synthesis and characterization of a new multidonor Schiff base ligand, namely 2-(3-[2-(6-aminoquino[8,7-b]azin-5-ylimino-methyl)-phenoxy]propoxy)benzaldehyde and its diamagnetic Cu(I) and Ni(II) complexes are reported.

### EXPERIMENTAL

All chemicals employed were of the highest grade available. The FT-IR spectra (KBr discs) were recorded in the 4000-325 and 400-300 cm<sup>-1</sup> ranges on a Mattson 1000 FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-200 MHz (MeOH:CHCl<sub>3</sub>, 1:1, v/v) spectrometer. <sup>13</sup>C NMR,

elemental analysis and mass spectra FAB (+) mass were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). Fluorescence spectra were measured on a PTI time master C71 spectrophotometer with 1 cm quartz cell was used. Magnetic property of complexes was measured with a Scherwood Scientific Magnetic Susceptibility Balance. TGA-DSC-DTG curves were obtained with a TA SDT Q600 thermal analyzer apparatus using flowing nitrogen over a temperature range 50-1000 °C at 100 mL min<sup>-1</sup> at a heating rate of 10 °C min<sup>-1</sup>. Melting points were obtained with a Gallenkamp CAP MPD-350 apparatus in open capillaries.

**Synthesis of the ligand:** To a solution 1,5-*bis*(2'-formylphenylenyl)-1,5-dioxapentane (0.3072 g, 1.08 mmol) in absolute methanol (50 mL) was added the solution of 5,6-diamino-1,10-phenanthroline (0.2268 g, 1.08 mmol) in absolute methanol (30 mL). The solution was refluxed for 3 h, evaporated to 10 mL and chromatographed on silica by a mixed solvent of MeOH:CHCl<sub>3</sub> (1:1, v/v) to give the Schiff-base ligand (0.297 g, 60 %) as yellow solid: m.p. 269 °C, IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3412 (NH<sub>2</sub>), 3064 (Ar-CH), 2927-2878 (CH), 1681 (C=O), 1598 (phen C=N), 1585 (imine C=N), 1285-1236 (C-O-Ar) 1049 (C-N) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 2.41 (q, 2H, CH<sub>2</sub>), 4.18 (t, 4H, Ar-O-CH<sub>2</sub>), 6.67- 6.95 (m, 6H, phen.H), 7.15-7.65 (m, Ar. H), 8.21 (s, 1H, C=N), 8.73 (s, 2H, NH<sub>2</sub>), 10.4 (s, 1H, CHO) ppm. <sup>13</sup>C NMR (125.7 MHz in CDCl<sub>3</sub>),  $\delta$  = 28.09 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 63.93 (OCH<sub>2</sub>), 111.57 (aryl C), 120.05 (aryl C), 127.76 (aryl C), 135.35 (aryl C), 147.08 (phen. C=N), 160.13 (aryl C=N) and 189.06 (-CHO) ppm. FAB (+) mass spectrum: m/z: 477 (M+1). Analytical calculated for C<sub>29</sub>H<sub>24</sub>N<sub>4</sub>O<sub>3</sub> (476 g/mol): C, 73.11; H, 5.04; N, 11.76%. Found: C, 73.55; H, 5.52; N, 11.27 %.

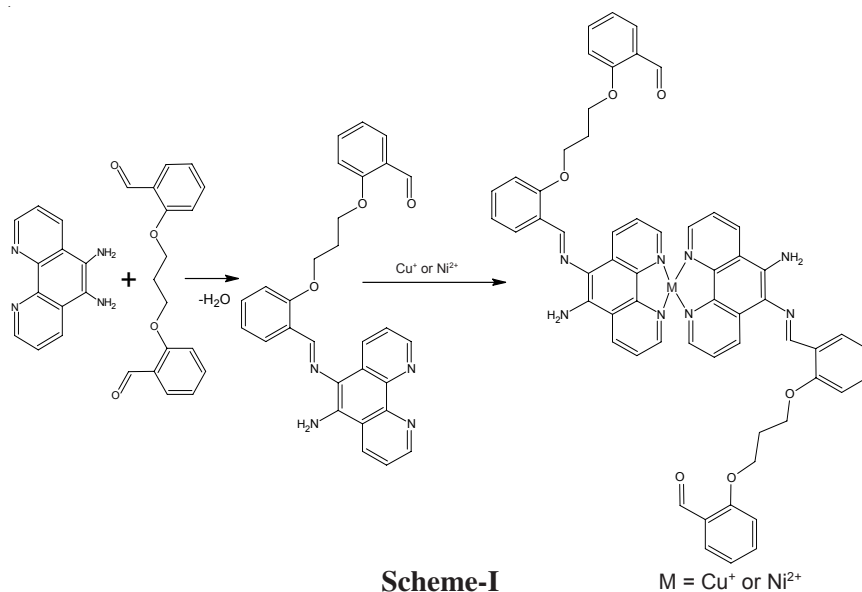
**Synthesis of Cu(I) complex:** To a solution of the ligand (0.571 g, 1.2 mmol) in absolute ethanol (50 mL) was added into solution of CuCl (0.0594 g, 0.6 mmol) in absolute ethanol (10 mL). After addition of 0.05 N NaOH solution in ethanol to raise the pH to 7.5-8, the colour of the solution changed immediately. The mixture was stirred on a water bath at 60 °C for 20 min. The precipitated dark-green complex was filtered, washed with absolute ethanol and then with diethyl ether and dried. The product was slightly soluble in methanol, ethanol and ethyl acetate. Yield: 0.312 g (52 %); m.p. > 360 °C IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3400 (NH<sub>2</sub>), 3075 (Ar-CH), 2923 (CH), 1599 (phen C=N), 1585 (imine C=N), 1240 (C-O-Ar), 1050 (C-N), 342 (Cu-N). Analytical calculated for C<sub>58</sub>H<sub>48</sub>N<sub>8</sub>O<sub>6</sub>CuCl (1052.1): C, 66.54; H, 4.46; N, 10.64%. Found: C, 66.64; H, 4.38; N, 10.49%.

**Synthesis of Ni(II) complex:** To a solution of the ligand (0.571 g, 1.2 mmol) in absolute ethanol (50 mL) was added the solution of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.149 g, 0.6 mmol) in absolute ethanol (10 mL). After addition of 0.05 N NaOH solutions in ethanol to raise the pH to 7.5-8.0, the colour of the solution changed immediately. The mixture was stirred on a water bath

at 60 °C for 20 min. The precipitated dark-green complex was filtered, washed with absolute ethanol and then with diethyl ether and dried. The product was slightly soluble in methanol, ethanol and ethyl acetate. Yield: 0.236 g (39 %); m.p. > 360 °C, IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3400 ( $\text{NH}_2$ ), 3069 (Ar-CH), 2925 (CH), 1599 (phen C=N), 1585 (imine C=N), 1240 (C-O-Ar), 1050 (C-N), 347 (Ni-N). Analytical calculated for  $\text{C}_{58}\text{H}_{48}\text{N}_8\text{O}_6\text{Ni}(\text{OH})_2$  (1045.8) C, 66.60; H, 4.59; N, 10.71 %. Found: C, 66.12; H, 4.62; N, 10.05 %.

## RESULTS AND DISCUSSION

5,6-Diamino-1,10-phenanthroline (**I**) was synthesized according to the reported procedures<sup>14-17</sup>. 1,5-Bis(2'-formylphenyl)-1,5-dioxapentane (**II**) was synthesized by Williamson condensation of salicylaldehyde and 1,3-dibromopropane<sup>18</sup>. The ligand was obtained as yellow microcrystalline solid by condensation of 5,6-diamino-1,10-phenanthroline with 1,5-bis(2'-formylphenyl)-1,5-dioxapentane. Its Cu(I) and Ni(II) complexes were prepared by treating the ligand with the corresponding metal salt in 2:1 ratio (**Scheme-I**).



<sup>1</sup>H NMR spectrum of the ligand in MeOH:CHCl<sub>3</sub> (1:1, v/v); The chemical shift of azomethine (-CH=N), -NH<sub>2</sub> and -CHO groups, appeared at 8.21, 8.73 and 10.4 ppm as singlet. The phenanthroline protons appear at 6.67-6.95 ppm as multiplet, aryl protons in salicylaldehyde appear at 7.15-7.65 ppm as multiplet, aryl-O-CH<sub>2</sub> at 4.18 ppm as a triplet. Since the solubility of the Cu(I) and Ni(II) complexes in organic solvents are very low, <sup>1</sup>H NMR spectra could not be taken.

$^{13}\text{C}$  NMR spectrum of the ligand in  $\text{CDCl}_3$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $\text{OCH}_2$ , phent.  $-\text{C}=\text{N}$ , aryl  $\text{C}=\text{N}$  and  $-\text{CHO}$  groups, appeared at 28.09, 63.93, 147.08, 160.13, 189.06 ppm and aryl groups appeared at 111.57, 120.05, 127.76, 135.35 ppm. These observation indicate that one group  $-\text{NH}_2$  reacted with one group  $-\text{CHO}$ , shown in **Scheme-I**.

Schiff-base ligand was verified by  $m/z$ : 477.1 ( $\text{M}+1$ ) in the mass spectrum obtained by FAB (+) mass technique in DMSO.

Magnetic susceptibility of Ni(II) and Cu(I) complexes was measured at 25 °C. The magnetic moment measurement suggests that these both of complexes are diamagnetic and a square-planar structure. The geometry around Cu(I) and Ni(II) are square-planar with four equivalent Cu-N and Ni-N. Due to the insufficient solubility of the complexes in suitable solvents, their  $^1\text{H}$  NMR spectra could not be investigated.

FTIR data give further useful information on the structure of the ligand and complexes. The free ligand show characteristic imine stretching bands at  $1585\text{ cm}^{-1}$ . In the complexes, this band does not shift to the lower or higher wave numbers, suggesting that this imine group is not coordinated to the metal ions. Nitrogens of 1,10-phenanthroline stretching bands at  $1599\text{ cm}^{-1}$  shift to the higher wave numbers and the Cu-N and Ni-N bands of the complexes are observed at  $342$  and  $347\text{ cm}^{-1}$ , respectively. IR spectrum, suggesting that these nitrogen are coordinated to the metal ions. We consider two aromatic  $\text{C}=\text{O}$  groups at  $1681\text{ cm}^{-1}$  disappeared in Cu(I) and Ni(II) complexes, because of equal and opposite dipole moment. In general, molecular vibrations symmetric with regard to the center of symmetry are forbidden in the infrared spectrum and the intensity of an IR absorption band depends on the change of the dipole moment ( $\mu$ )<sup>19</sup>. As shown in Fig. 1, the phenolic C-O, aliphatic C-H and C-N bands of the free ligand is observed at  $1285$ - $1236\text{ cm}^{-1}$ ,  $2927$ - $2878$  and  $1049$ , respectively as strong in the complexes  $1240$ ,  $2926$  and  $1050\text{ cm}^{-1}$  as weak peaks.

Fluorescence property of the synthesized Schiff-base ligand which has conjugated carbon atoms and imine groups were reported. The range of  $1.0 \times 10^{-3}$ - $0.5 \times 10^{-5}$  mol/L of the ligand concentration with the change in fluorescence intensity is shown in Fig. 2. The concentration of Schiff-base for study was chosen as  $1 \times 10^{-5}$  mol/L. The emission peak is at 427 nm and the fluorescence intensity is 243.65 in  $1 \times 10^{-5}$  mol/L in mixed solvent of MeOH: $\text{CHCl}_3$  (1:1, v/v). The effect of Cu(I) and Ni(II) ions ( $0.2 \times 10^{-3}$  mol/L) on fluorescence intensity of the Schiff-base ligand were tested and the results showed that Cu(I) and Ni(II) decrease the fluorescence intensity of the system, between which Cu(I) has the highest decrease as shown in Fig. 3.

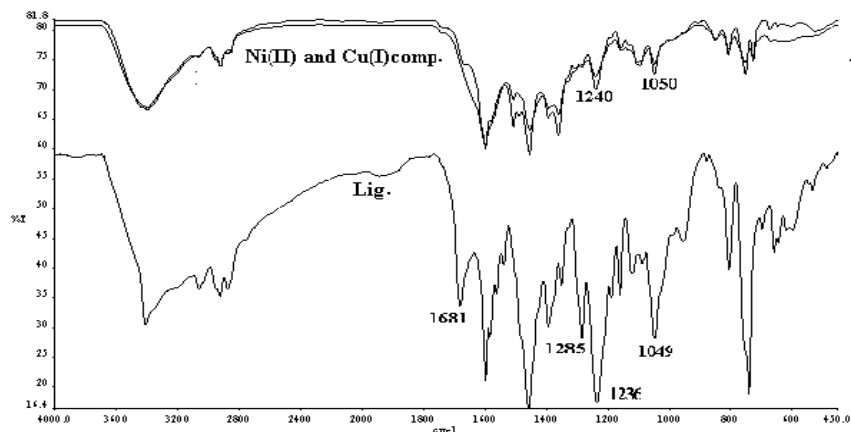


Fig. 1. FT-IR spectra of the ligand and its Cu(I), Ni (II) complexes

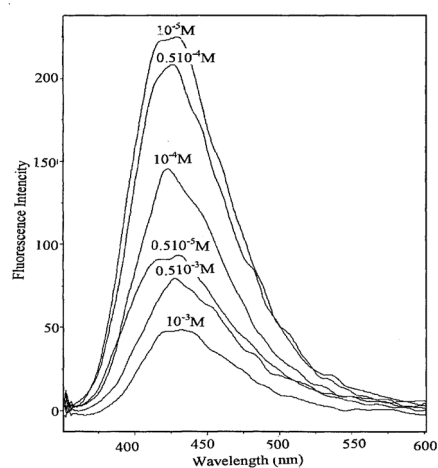
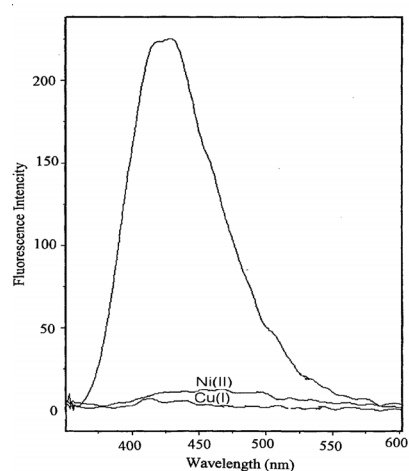


Fig. 2. Fluorescence intensity of the ligand versus concentration

Fig. 3. Fluorescence intensity of the ligand ( $10^{-5}$  M) and their Cu(I) and Ni(II) complexes

The TGA-DSC-DTG curves of the ligand and its Cu(I) and Ni(II) complexes were obtained. Decomposition of the ligand showed many lost step but four loss step were selected, three exothermic pick and weight loss at 139-205 °C (1.79 %), 205-376 °C (15 %) and 376-441 °C (12 %) and broad endothermic pick at 846-935 °C (18 %), residue is 49 %, there only remained black carbon at the end. The representative TGA-DSC-DTG curves of the thermal decomposition of the Cu(I) and Ni(II) complexes showed many loss steps, which can be classified into four temperature ranges 65-87 (2.5 %, Cl<sup>-</sup>), 154-280 (14 %), 280-473(13 %), 473-1000 °C

(28 %), residue 34 % ( $C_{16}H_{24}N_4Cu_{1/2}O$ ) and 66-83 (3 %, anionic  $OH^-$ ), 143-247 (12 %), 247-444 (14 %), 444-1000 °C (35 %), residue 34 % ( $C_{16}H_{24}N_4NiO$ ), respectively.

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