



# Investigation on Kinetics and Mechanism of Metal Exchange Reaction of Copper (II) Ions and NiL

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**Abstract:** In this study, the electron spectrum in UV-Vis region is used to study the kinetics of metal exchange reaction between ion  $\text{Cu}^{2+}$  and additional concentration of NiL complex. This complex is soluble in dimethyl formamid solution with ionic strength of 0.1M  $\text{KNO}_3$ . The kinetic data of this reaction proves that the metal exchange is a two-step reaction. The value of the kinetic constant,  $k$ , is proportional with  $[\text{NiL}]$  at low concentration of NiL. At higher higher concentration of NiL ( $[\text{NiL}] \gg [\text{Cu}^{2+}]$ ), this direct relation does not exist, so  $k$  is independent of  $[\text{NiL}]$ . The second order reaction is converted to pseudo first order reaction with the rate constant of  $k_{obs}$ . Based on the experimental data, the values of  $k_{obs}$  are computed. Then  $k_{obs}$  is expressed as a function of  $[\text{NiL}]$ . According to these results, the mechanism of metal exchange reaction is suggested.

**Keywords:** Metal Exchange Reaction, Kinetics, Rate Constant, Mechanism the Reaction

## 1. Introduction

In recent years, the chemistry of the complexes such as a salen type Schiff base ( $\text{H}_2\text{L}^2$ ) and its derivatives has attracted much attention due to its bioinorganic, catalysis, and analytical applications. Therefore, this subject is useful for researchers to advance in the realm of coordination chemistry. Investigations were begun with the synthesis and the geometry of the salen complexes with bivalent metals. Then studies were about the synthesis and structural properties of the metal complexes that belong to the salen derivatives containing functional groups. The main difference of these components is in the chain lengths that exist in the amine backbone. When the length of the methylene chain increases, the sufficient flexibility of this structure can be obtained. This leads to the formation of a planar with a distorted tetrahedral or species which has a higher coordination number when additional donors exist [1-6].

Ligand or group substitution (exchange) is known as one of the most significant reactions that takes place at the inorganic center of a solution phase. This reaction involves the substitution of the metal ion in the complex with a

solvent-coated metal ion. Also, the substitution of the coordinated ligand with a metal with a free ligand in the solution can result in the substitution reaction. During the substitution reaction, the oxidation number of the metal does not change, but the change in the oxidation number is possible for the reaction products. The kinetic of substitution reactions is important because it can help a researcher to recognize conditions in combinational and decomposition methods. Also, it is possible to understand the behavior of metal and the enzymes which can activate metals [7, 8].

Due to the importance of the substitution reactions, several investigations have been conducted on this subject. Vafazadeh and Bidaki [9] studied the kinetics of a ligand exchange in the system of  $\text{CuL}^4/\text{H}_2\text{L}^n$ . They found that the reaction rate was first-order with respect to  $\text{CuL}^4$  complex and  $\text{H}_2\text{L}^n$  ligand. Moreover, the kinetics of ligand exchange did not have a significant change when  $\text{H}_2\text{O}$  was added to the DMF solvent. However, it increased when  $\text{NEt}_3$  was added to the reaction mixture. Hynes and Doody [10] studied the kinetics and mechanism of removing  $\text{M}^{2+}$  from bis-(heptane-2,4,6-trionato) M (II [ $\text{M}$ ] = Ni, Co). They used ethylenediminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), 1,2-cyclohexanediamine-NN, N 'N, ' - tetraacetic acid

(CyDTA), and ethylenebis (oxyethylenetriolo) tetraacetic acid (EGTA) for their investigation. They suggested an associative mechanism for the kinetics of the reactions.

Investigations on the structure of complexes made up of the salen copper (II) and their derivatives have proved that such complexes are monomers. Their flexibility is due to increasing chain length. According to this, the square-planar geometry of the molecule converts to the distorted tetrahedral geometry. Increasing the number of methylene units (known as  $n$  in the  $H_2L^n$  chain) can reduce the stability of the copper (II) complexes. This decrease in the stability of copper (II) complexes is considered as a driving force for ligand exchange reaction. Moreover, the product of this reaction is a higher stable complex.

In the present study, electronic spectrum in UV-Vis region has been used to determine the kinetics of  $cu^{2+}$  ion exchange reaction. This exchange occurs between  $cu^{2+}$  ions and additional concentration of NiL complex soluble in dimethyl formamid solution with ionic potency of 0.1M  $K(NO_3)$  solution. The value of reaction constant ( $k$ ) in low concentration of NiL has been determined. According to these results, the mechanism of metal exchange reaction is suggested.

## 2. Experimental

### 2.1. The Applied Ligands

The first ligand is N'-N-bis (5-bromo-salicylidene) -2,2-dimethyl-1,3-propanediamine known as  $H_2L$ . The second ligand is N'-N-bis (5-bromo-salicylidene)-2,2-dimethyl-1,3-propanediamine copper II known as CuL. The third ligand is N'-N-bis (5-bromosalicylidene) -2,2-dimethyl-1,3-propanediamine of nickel II known as NiL. The synthesis and crystallographic data of these three ligands have already been reported in [11, 12].

### 2.2. The Applied Apparatus

To study the rate of reaction between the ion of Nickel II ions and copper II, the UV-Vis and IR spectroscopies are used for complexes with N, N-bis (5-bromo-salicyclidine) -2,2-dimethyl-1 and 3-propane diamine ligands. All of the IR spectroscopies were conducted by the IR Prestige 21 manufactured by Shimadzu. The dry potassium bromide tablet is used for spectroscopies. The electron spectrum of the complex and the following the metal ion exchange reaction was recorded by using the UV-Vis spectrometer (model 6310) manufactured by Jenway, UK.

### 2.3. The Kinetics of the Reaction

The electron spectra of the NiL and CuL complexes are characterized at equal concentrations in Figure 1. Due to the considerable difference between the maximum wavelengths ( $\max\lambda$ ) of these two complexes, it can be concluded that the metal exchange reaction is possible by using the electron spectrum.

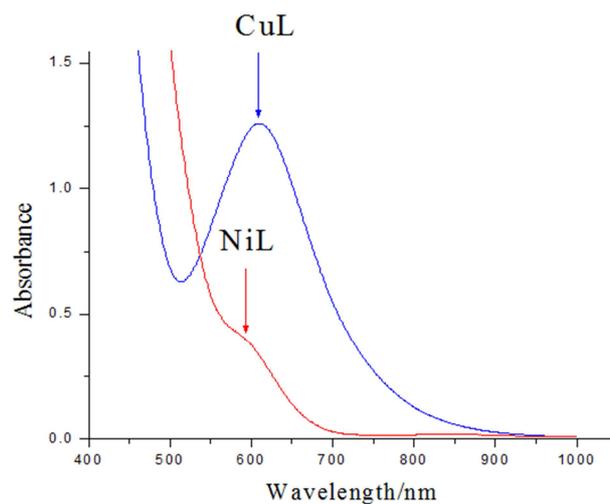


Figure 1. The UV-Vis spectrum of two NiL and CuL complexes at 25°C.

The reaction rate was determined by adding equal volumes of the solution including  $10^{-4}$  M NiL complexes and a solution of  $5 \times 10^{-4}$  M of  $Cu(NO_3)_2 \cdot 3H_2O$  salt to 0.1 M of the  $KNO_3$  salt as electrolyte. The reactions are at 25°C and the changes of absorption with time are followed by the electron spectrum. Figure 2 shows the changes of the electron spectrum for 60 minutes. This change is a result of adding equal volumes of a solution containing  $5 \times 10^{-4}$  M NiL complex soluble in dimethylformamide and  $5 \times 10^{-4}$  M  $Cu(NO_3)_2 \cdot 3H_2O$  salt soluble in dimethylformamide with the ionic strength of 0.1M. In order to prepare a complex solution ionic strength of 0.1M, since the  $KNO_3$  salt is polar and it is insoluble in a nonpolar solvent, such as dimethylformamide, firstly, 0.1 M of the  $KNO_3$  salt was weighted. Then it was inserted into the balon joje with a capacity of 10 ml, 10-20 drops of distilled water was added, and it is dissolved in the water. After we insured that the salt was completely dissolved, the corresponding complex was weighted and added to the solution. Then the dimethylformamide solvent was dissolved and reached to the volume of 10 ml.

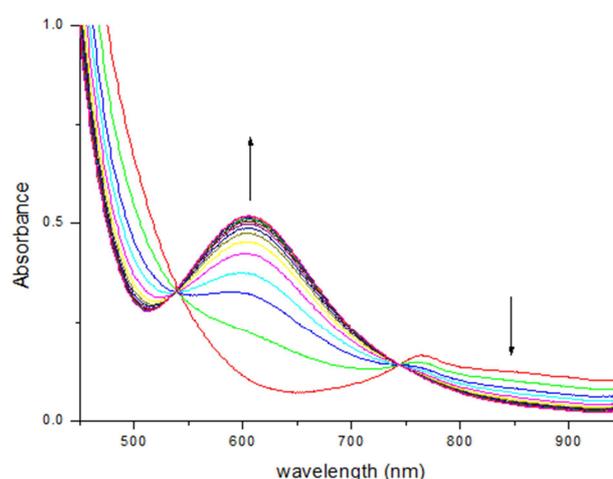
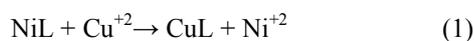


Figure 2. The UV-Vis spectrum of the metal exchange reaction in the NiL complex and copper salt with a concentration of  $5 \times 10^{-4}$  M at the temperature of 25°C.

According to Figure 2, since the wavelength of 650nm shows the highest absorption changes, it is suitable for studying the reaction rate. The values of  $\lambda_{\max}$  (the highest wavelength) are 589 nm and 609 nm for NiL and CuL, respectively.



### 2.3.1. Conversion of Reaction to Lower Order

The reaction between the NiL complex and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  salt depends on the concentration of the complex and copper salt. If we want to convert this reaction to a lower order reaction, we need significant increase in the concentration of one of the reactants. In this case, the reaction rate will depend on the lower concentration of the reactant.

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y \quad (2)$$

If the concentration of A in Eq.(2) increases, the following equation can be written:

$$\text{Rate} = k_{\text{obs}}[\text{B}]^y \quad (3)$$

where

$$k_{\text{obs}} = k[\text{A}]^x \quad (4)$$

To convert the reaction of the desired metal exchange to a lower-order reaction, the concentration of the NiL complex was increased in an additional and variable manner, while the concentration of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was constant in all experiments. The changes of adsorption data versus time were analyzed and the values of  $k_{\text{obs}}$  were obtained for each concentration. The results of a quasi-first-order two-step reaction with a reversible element were obtained. Each experiment was carried out at a minimum of three times the constant concentration and temperature. The average values of  $k_{\text{obs}}$  were reported.

### 2.3.2. Confirming the One-sided Reaction

In order to know that the metal exchange is equilibrium or one-sided reaction, the reverse reaction was examined. The reaction of the NiL complex and the  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  salt produces the CuL complex. If the equilibrium reaction exists, the inverse reaction, the reaction between the CuL and Ni  $(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  complex in the presence of the electrolyte, will result in producing NiL. To investigate this reaction, first, 10 ml of  $5 \times 10^{-3}$  M solution, corresponding to 0.265 gr of CuL, and 10 ml of  $5 \times 10^{-3}$  M solution, corresponding to 0.145 grams of Ni  $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were added to a solution of 0.15 mg of electrolyte prepared with the 0.1M solution. Then the reverse reaction was checked. Firstly, 1 ml of CuL solution was injected into the cell. Then 1 ml of Ni  $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution was added with ion strength of 0.1 M. The spectrum was taken from this sample. From this moment, the spectrum was repeated with the device every two minutes. Finally, it was observed that the first spectrum taken from this sample is exactly the same as the spectrum taken in the next few moments. This indicates that no reverse reaction is

performed, so the reaction between the NiL complex and the  $\text{Cu}^{2+}$  ion is one-sided. This can be attributed to the stability of the Cu metal complex compared to nickel.

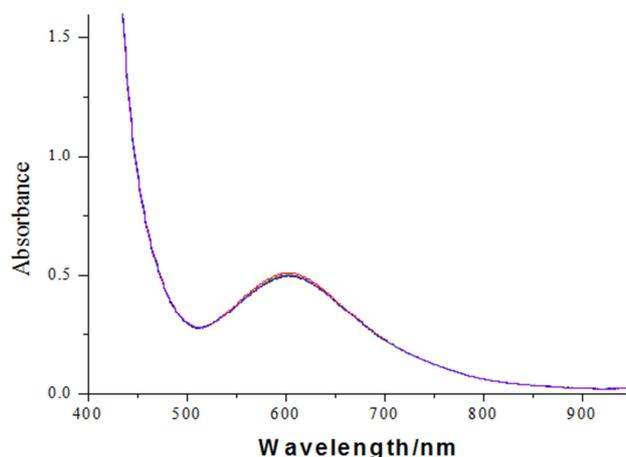


Figure 3. The UV-Vis spectrum of metal exchange in the CuL complex and nickel II salt at a concentration of  $4 \times 10^{-5}$  M at the temperature of 25 °C.

## 3. Results and Discussion

In this study, the metal exchange reaction in the Ni-Cu Complex was studied by using a UV-Vis device as well as measurements of adsorption changes at different times. Then, by using these data, the corresponding calculations were conducted to obtain the constant of the metal exchange reaction rate. Finally, with respect to the above data, a mechanism was proposed for the reaction. Before determining the rate of the metal substitution reaction, we will briefly mention the spectral properties of the ligands and complexes used in this study.

### 3.1. Investigation of the Following Sub-red Spectra (IR)

#### 3.1.1. Study of the IR Spectrum of the $\text{H}_2\text{L}$ Ligand

The comparison of the vibrational spectrum of this ligand (Figure 4) with the initial vibrational diamines and primary salicylic acid shows that the peaks of  $3401\text{cm}^{-1}$  and  $3316\text{cm}^{-1}$ , corresponding to diammonium  $\text{NH}_2$  and the peak region of  $1672\text{cm}^{-1}$ , which are related to the initial tensile frequency of the carbonyl salicycloid group, are removed. A peak appears in the  $1633\text{cm}^{-1}$  region, which is related to the tensile bonding frequency of the bond (C = N). This is the reason for the synthesis of the Schiff open ligand. The frequency and vibrational patterns of this ligand are shown in Table 1.

Table 1. Frequency and important vibrational modes of  $\text{H}_2\text{L}$  Ligand.

Vibration method	Vibration frequency in terms of $\text{cm}^{-1}$
C=N (tensile)	1633
C=C (tensile)	1475 1570,
C-O (tensile)	1274

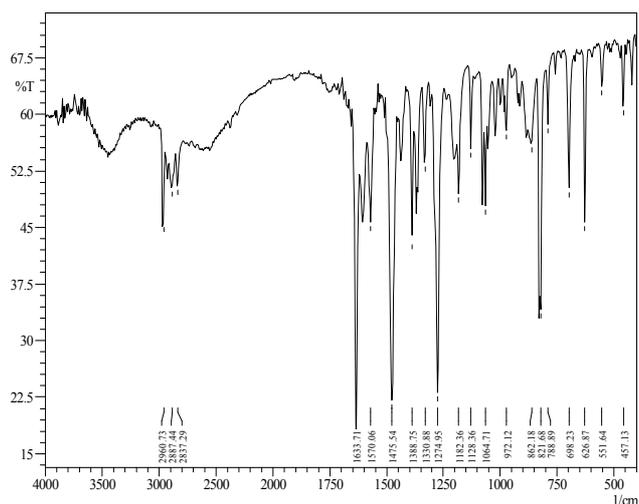


Figure 4. IR spectrum of the  $H_2L$  ligand.

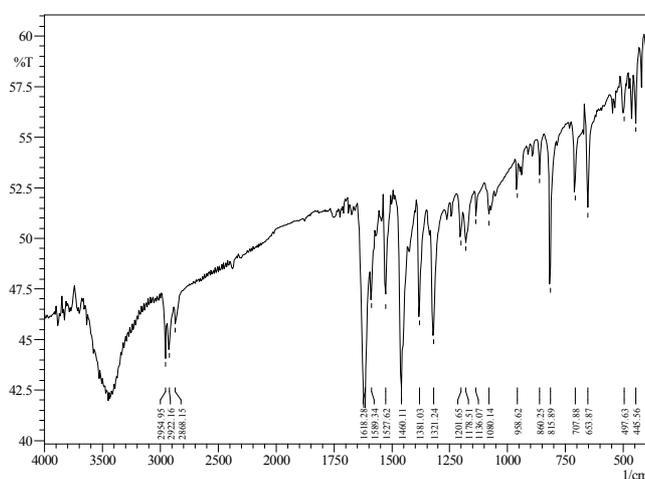


Figure 5. IR spectrum of the NiL complex.

### 3.1.2. Review of the IR spectrum of the NiL Complex

In the IR spectrum of this complex (Figure 5), a sharp peak appears at  $1618\text{ cm}^{-1}$ , which is related to the tensile vibration of the adhesive bond of (C = N). One can see that the peak of the tensile vibration of the (C = N) bond in the nickel complex has been converted to a lower wave number of  $15\text{ cm}^{-1}$ . This shows the coordination of the ligand to the metal. This decrease in frequency relates to the free ligand is due to  $\pi$  the acceptance of the C = N group by  $\pi$  orbitals. This reduces the order of C=N bond. Consequently, it reduces its vibrational frequency. The tensile frequency of the C-O bond appears in the free ligand region is  $1274\text{ cm}^{-1}$ . This frequency is increased up to a higher value of  $1321\text{ cm}^{-1}$  by coordination of the metal. The reason for this increase in the frequency relates to the free ligand that exists in the formation of the complex.

The Schiff ligand acts by losing two phenol protons as an anionic ligand, which increases the electron charge density on oxygen. As a result, the tensile frequency of CO increases. The frequency and vibrational modes of this complex are presented in Table 2.

Table 2. Frequency and important vibrational processes of NiL complex.

Vibration method	Vibration frequency in terms of $\text{cm}^{-1}$
C=N (tensile)	1618
C=C (tensile)	1460 1589,
C-O (tensile)	1321

### 3.1.3. The IR Spectrum of the CuL Complex

In the IR spectrum of this complex (Figure 6), a sharp peak in  $1624\text{ cm}^{-1}$  appears that relates to the tensile vibration of the adhesive bond (C=N). One can see that the peak of the tensile vibration of the (C=N) bond in the copper complex is about  $9\text{ cm}^{-1}$  to the lower wave numbers, which shows the coordination of the ligand into the metal. This decrease in frequency relative to the free ligand is due to  $\pi$  acceptance of the C=N group by  $\pi^*$  orbitals which reduces the order of C = N bond. Therefore, it reduces vibrational frequency. The tensile frequency of the C-O bond in the free ligand region is  $1274\text{ cm}^{-1}$ , which increases to  $1313\text{ cm}^{-1}$  by coordination of the metal into this frequency. The reason for this increase in frequency relates to free ligand in the formation of the complex. The Schiff ligand reacts with the loss of two phenolic protons as an anionic ligand, which increases the electron charge density on oxygen. Consequently, the C-O tensile frequency increases. The frequency and vibrational modes of this complex are presented in Table 3.

Table 3. Frequency and important vibrational processes of CuL complex

Vibration method	Vibration frequency in terms of $\text{cm}^{-1}$
C=N (tensile)	1624
C=C (tensile)	1454 1589,
C-O (tensile)	1313

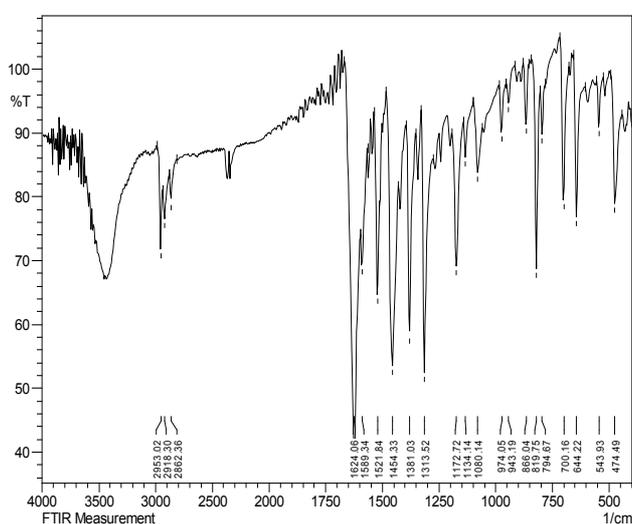


Figure 6. IR spectrum of the CuL complex.

## 3.2. Electron Spectroscopy (UV-Vis)

### 3.2.1. The UV-Vis Spectrum of the $H^2L$ Ligand

In the spectrum of UV-Vis ligands (Figure 7), in the methanol solvent, there are three absorbing strips, an absorption band in the  $414\text{ nm}$  region that is related to the  $n \rightarrow \pi^*$  transfer of an electron-nitrogen electron to the  $\pi^*$  molecular orbital. Two other adsorbent strips exist. The first

one is in 329 nm for transitions from the C = N group to the benzene ring. The other one is at 254 nm, relates to the transfer of phenol orbital to the benzene ring.

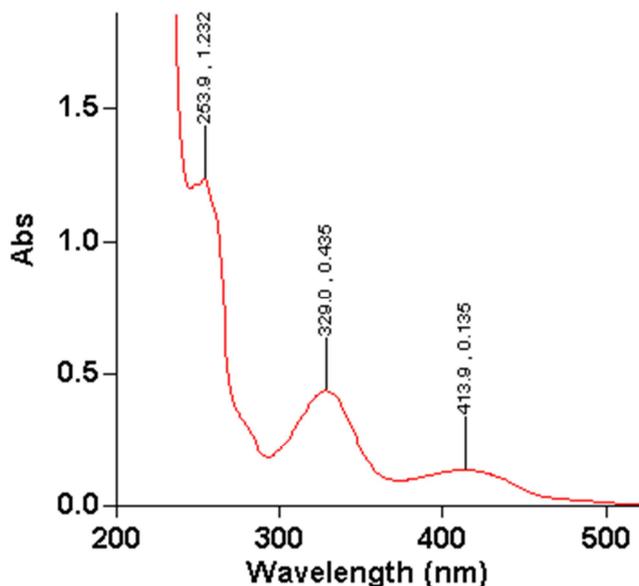


Figure 7. UV-Vis spectrum of the  $H_2L$  ligand.

### 3.2.2. The UV-Vis Spectrum of the NiL Complex

In the UV-Vis complex (Figure 8) in the methanol solvent, the absorbance strip of  $n \rightarrow \pi^*$  at 414 nm was removed due to the coordination of the nitrogen into the removed metal. Instead, a low-intensity peak at 577 nm, which is related to the  $d \rightarrow d$  metal ion transfer, can be seen. Also, with the formation of a complex due to the bond between the ligand and metal, the energy of the  $\pi \rightarrow \pi^*$  transfer from the C = N group to the benzene ring and the  $\pi \rightarrow \pi^*$  transfer to the benzene ring, the resonance of the system decreases.

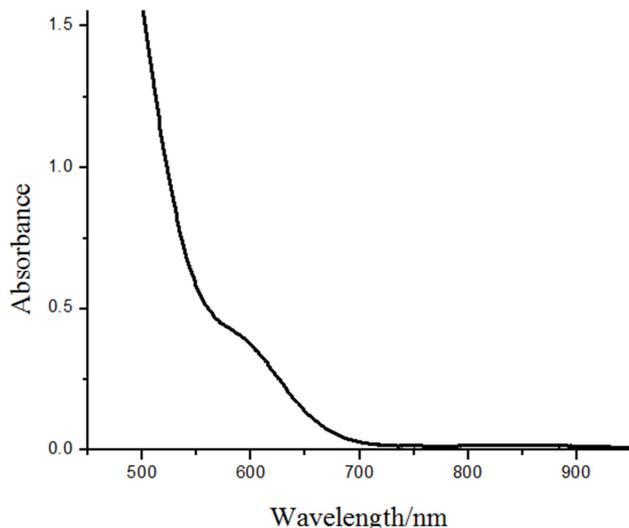


Figure 8. UV-Vis spectrum of the NiL ligand.

### 3.2.3. The UV-Vis Spectrum of the CuL Complex

In the UV-Vis complex (Figure 9) in the methanol solvent,

the absorbance strip of  $n \rightarrow \pi^*$  at 414 nm was removed due to the coordination of the nitrogen into the removed metal. Instead, a low-intensity peak at 597 nm, which is related to the  $d \rightarrow d$  metal ion transfer, can be seen. Also, with the formation of a complex due to the bond between the ligand and metal, the energy of the  $\pi \rightarrow \pi^*$  transfer from the C = N group to the benzene ring and, the resonance of the system decreases.

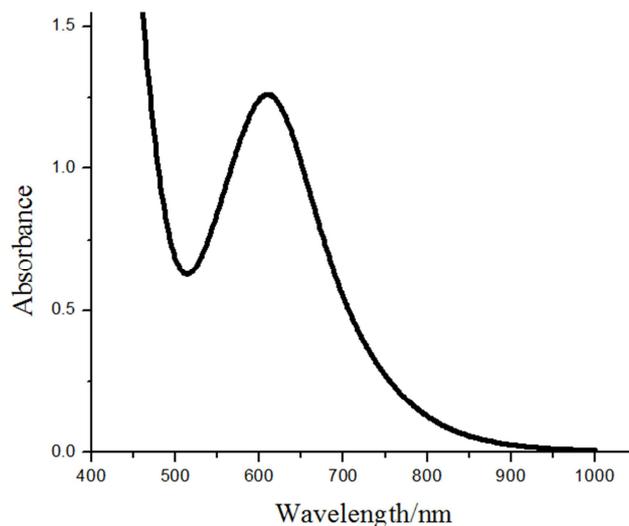


Figure 9. UV-Vis spectrum of the CuL ligand.

### 3.3. The Kinetics of the Reaction

The reaction of the NiL complex with concentrations of  $5 \times 10^{-4}$  M and  $Cu(NO_3)_2$  at 10 additional concentrations of the complex was investigated in this section. The kinetics of the first-order reaction was observed. Figure 1 shows the electronic spectrum of NiL and CuL complexes. It is possible to check the reaction of the metal exchange by using the UV-Vis method. The changes of the absorption were measured at a wavelength of 650 nm (the wavelength that had the greatest absorption change during the reaction) to investigate the metal displacement reaction.

By comparing the electron spectrum of complexes with the electron spectra obtained from the NiL reaction with  $Cu(NO_3)_2$  (Figure 2), it was found that the Ni-exchange reaction was carried out with  $Cu^{2+}$  ion and the CuL complex. The metal exchange reaction was also investigated. Due to the lack of change in the electron spectrum (Figure 3) resulting from the reaction of CuL with  $Ni^{2+}$  ions even after 24 hours, it is a one-side reaction. The reason is that the CuL complex is stable in comparison with NiL. The stability of the CuL complex compared to NiL can be explained according to the Irving-Williams series. Copper (II) and nickel (II) are in a special group and they are neither hard nor soft. The stability of this type of complexes based on the Irving-Williams series is  $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$  [13]. According to Irving-Williams series, the copper (II) complex is more stable than nickel (II).

The reaction rate was studied in quasi-first-order conditions, with the concentration of the NiL complex

exceeding the stoichiometric value of NiL [ $\gg$   $[\text{Cu}(\text{NO}_3)_2]$ ). Due to the high concentration of NiL, the changes of its concentration are low. The reaction rate is independent of NiL concentration, and it only depends on the concentration of  $\text{Cu}(\text{NO}_3)_2$ . Thus the metal exchange reaction is converted to the quasi-first degree in terms of  $\text{Cu}(\text{NO}_3)_2$ . The reaction was followed at a temperature of 25°C and a constant ionic strength of electrolyte K ( $\text{NO}_3$ ) (0.1M) at different concentrations of NiL by using the UV-Vis spectrum. The application of electrolyte at high concentrations caused the reaction to be carried out in constant ionic strength. If the ion is formed during the reaction, the reaction rate is not affected.

The time-dependent absorption data have to be placed in the three, five and seven-parameter equations [14] given as follows:

$$y = y_0 + ae^{-bx} \quad (5)$$

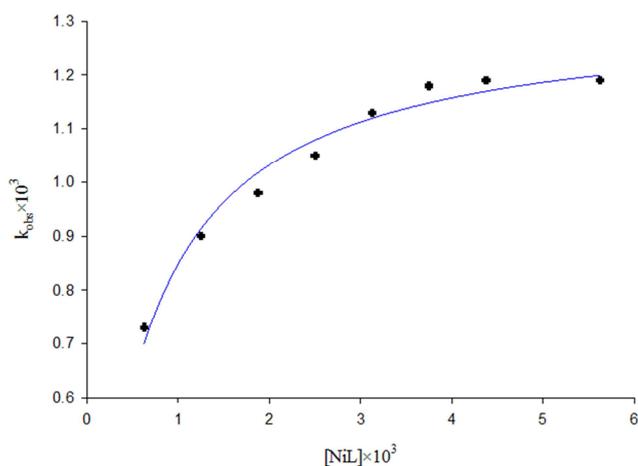
$$y = y_0 + ae^{-bx} + ce^{-dx} \quad (6)$$

$$y = y_0 + ae^{-bx} + ce^{-dx} + ge^{-ex} \quad (7)$$

It is found that only three-parameter equation had good results. Therefore, Eq. (3) is compared with the following equation.

$$A_t = A_\infty + ae^{-k_{obs}t} \quad (8)$$

As a result, the values of  $k_{obs}$  (the constant of pseudo first order reaction, which is equal to b) were obtained. Each experiment was repeated at least three times and the average of  $k_{obs}$  values were computed. Table 4 and Figure 10 show the reaction constant in terms of concentration.



**Figure 10.** The  $k_{obs}$  diagram in terms of the NiL concentration for the Ni metal exchange reaction with Cu

**Table 4.** The constant of pseudo first order of the Ni-exchange reaction with Cu (reaction 1) at a constant temperature of 25 °C and a fixed ionic strength of  $[\text{KNO}_3]=0.1 \text{ M}$  in DMF solvent plus 10-20 drops of distilled water as an electrolyte solvent.

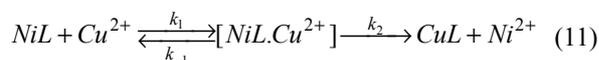
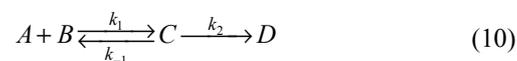
[NiL] × 10 <sup>3</sup> (M)	k <sub>obs</sub> × 10 <sup>3</sup> (S <sup>-1</sup> )
0.62	0.73

[NiL] × 10 <sup>3</sup> (M)	k <sub>obs</sub> × 10 <sup>3</sup> (S <sup>-1</sup> )
1.25	0.90
1.87	0.98
2.5	1.05
3.12	1.13
3.75	1.18
4.37	1.19
5.62	1.19

By using the experimental data and putting them in Eq. (9), the values of  $a$  and  $b$  were obtained.

$$y = \frac{ax}{1+bx} \quad (9)$$

The saturated kinetics indicates that a rate limiting factor exists at NiL concentration due to NiL. Cu species [14]. According to these evidences, Eq. (3) can be written for the reaction of metal exchange.



The theoretical rate is stated as follows:

$$\text{Rate} = \frac{d[\text{CuL}]}{dt} = k[\text{Cu}^{2+}][\text{NiL}] \quad (12)$$

$$\text{Rate} = \frac{d[\text{CuL}]}{dt} = k_{obs}[\text{Cu}^{2+}] \quad (13)$$

$$k_{obs} = k[\text{NiL}] \quad (14)$$

$$k_{obs} = \frac{kK[\text{NiL}]}{1+K[\text{NiL}]} = \frac{a[\text{NiL}]}{1+b[\text{NiL}]} \quad (15)$$

where

$$K = \frac{k_1}{k_{-1}} \quad (16)$$

Therefore, the following result is obtained for this mechanism.

$$b = K, a = kK, \frac{a}{b} = k_2 \quad (17)$$

in which  $a = 1.81 \times 10^{-3} \text{ M}^{-1}$  and  $b = 2.38 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$ .

### 3.4. Suggestion of the Reaction Mechanism

Copper ion attack the NiL complex. This leads to the formation of a dual-core intermediate (Eq. (7)). The process of exchanging copper-nickel metal in the NiL complex is carried out through a two-stage reaction. The constant of the first rate equation depends on the concentration of NiL. The dependence of the constant of the second reaction rate

equation on the concentration changes of the complex is very small. These results indicate that the mechanism of the metal exchange reaction proceeds through the formation of the two-core intermediate.

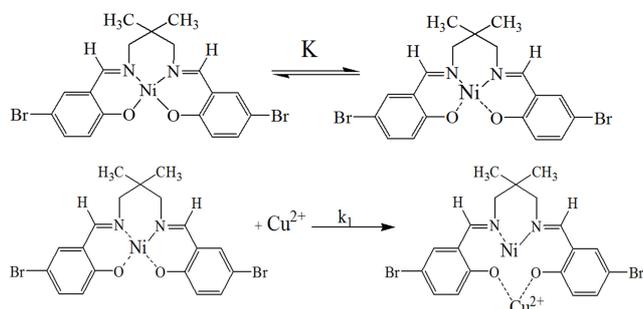


Figure 11. The first step of the suggested mechanism.

As shown in Figure 11, the first step of the metal-exchange reaction mechanism is a pre-equilibrium in which two nickel-

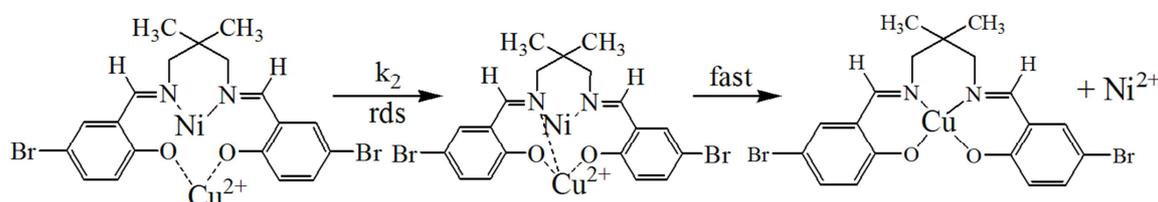


Figure 12. The second step of the suggested mechanism, copper substitution reaction in the NiL complex.

## 4. Conclusion

This study was dedicated to the electron spectrum in UV-Vis region to investigate about the kinetics of metal exchange reaction between ion  $\text{Cu}^{2+}$  and additional concentration of NiL complex that is soluble in dimethyl formamid solution with ionic strength of 0.1M  $\text{KNO}_3$ . The data of reaction product observed that the metal exchange reaction is a two-step reaction with an elementary reversibility. When the value of  $[\text{NiL}]$  is high, a pseudo first order reaction took place. A three-parameter equation,  $y = y_0 + ae^{-bx}$ , was used to obtain  $k_{\text{obs}}$  values at different concentration. When  $k_{\text{obs}}$  was plotted against  $[\text{NiL}]$ ,  $K_{\text{obs}} = a[\text{NiL}]/(1 + b[\text{NiL}])$  equation was obtain with  $b=1.81 \times 10^{-3} \text{ M}^{-1}$  and  $a=2.38 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$ . As a result, the first order constant ( $K_1=b$ ) and second order equivalence constant ( $k_2 = \frac{a}{b}$ ) were computed. These results led to suggestion of a mechanism for metal exchange reaction.

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