

# Kinetics and mechanism of the metal exchange reaction between N,N'-bis( $\beta$ -carbamoylethyl) ethylenediamine nickel(II) and copper(II)

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## Abstract

The kinetics of the  $[\text{Ni N,N}'\text{-bis}(\beta\text{-carbamoylethyl) ethylenediamine}]^{2+}/\text{Cu}^{2+}$ ,  $\text{Ni}(\text{bcen})^{2+}/\text{Cu}^{2+}$  metal exchange reaction in aqueous solution has been studied using spectrophotometry to follow  $\text{Cu}(\text{bcen})^{2+}$  formation at 640 nm (bcen is N,N'-bis( $\beta$ -carbamoylethyl) ethylenediamine). The reaction was studied at pH 6.9, ionic strength 0.5 M and in the temperature range 15 to 35 °C. The kinetics was studied under pseudo-order conditions with  $[\text{Ni}(\text{bcen})^{2+}] \gg [\text{Cu}^{2+}]$ . The reaction this under the condition has been found to be a two-step process mechanism is proposed involving: (1) partially dissociation of the  $\text{Ni}(\text{bcen})^{2+}$  complex, following with formation of a dinuclear intermediate and (2) metal exchange. Step 1 is rapid and depends on  $[\text{Ni}(\text{bcen})^{2+}]$  while step 2 is rate determining and independent of  $[\text{Ni}(\text{bcen})^{2+}]$ . The rate constants  $k_1$  (step 1) and  $k_2$  (step 2) are  $4.40 + 0.14 \text{ M}^{-1}\text{s}^{-1}$  and  $(11.25 + 0.94) \times 10^{-2} \text{ s}^{-1}$  respectively at 25 °C. Activation parameters are also reported.

**Keyword:** Kinetics, Mechanism, Metal exchange, Diamine diamide ligand, Biphasic reaction

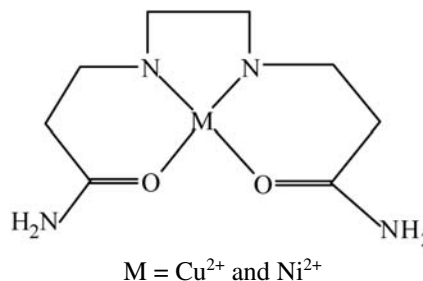
## 1. Introduction

Metal exchange reactions of complexes with multidentate ligands as represented by equation 1 have been the subject of very extensive studies for a variety of metal ions and ligands under different conditions using various methods.<sup>1-7</sup>



Metal exchange reactions have also been used for analytical measurement of the concentration of metal ions.<sup>8</sup> Metal exchange reactions have been shown to proceed through two general pathways differentiated by the nature of the intermediate species involved. The mechanism involves dissociation of the initial multidentate ligand-metal, followed by reaction of the entering metal with the free ligand. The other mechanism is a direct attack of the entering metal on the complex to form a binuclear intermediate species, in which the multidentate ligand is partially cleaved from the initial metal ion complex and partially bound to the entering metal ion. These two reac-

tion pathways may be influenced by the nature of both the metal and the ligand. Although many metal exchange reactions proceed predominantly by forming binuclear intermediates,<sup>1-3, 9, 10</sup> the mechanism of metal exchange reaction reported by Hay et al<sup>11</sup> proceeds via the first pathway while the mechanism of metal exchange reaction reported by Rorabacher et al<sup>4</sup> and Mentasti et al<sup>12</sup> proceeds via both pathways. From the thermodynamic point of view, one would expect that there is a driving force for replacing the initial metal ion with the incoming metal ion to form more stable complexes.



**Scheme 1.** Structural of complexes in the present study.

In this investigation, we have studied the kinetics of the metal exchange reaction between N,N'-bis( $\beta$ -carbamoylethyl) ethylenediamine nickel(II) nitrate complex,  $[\text{Ni}(\text{bcen})](\text{NO}_3)_2$  and copper(II), scheme 1.

An important aspect of chemistry of these complexes is the ability of the amide groups coordinate to metal through oxygen or nitrogen. We have chosen, therefore, to investigate the rate and mechanisms of metal exchange reaction involving such as ligands are interest to study.

## 2. Experimental

### 2.1. Syntheses

The diamine diamide ligand N,N'-bis( $\beta$ -carbamoylethyl) ethylenediamine (bcen) was prepared as described by Chung<sup>13</sup> from ethylenediamine and acrylamide in acetonitrile by heating the mixture under reflux. The white powder re-crystallized from  $\text{CHCl}_3$ .

The metal complexes (scheme 1) were prepared as described by Hay<sup>14</sup> using the reaction between a solution of metal nitrate salt in EtOH and a solution of the bcen ligand in  $\text{H}_2\text{O}$  (1:1 ratio). The blue solution was heated with constant stirring for 1 h. The hot solution was then filtered and the filtrate allowed standing overnight.

**$[\text{Ni}(\text{bcen})](\text{NO}_3)_2$ :** Yield 57%. Anal. Calculated for  $\text{C}_8\text{H}_{18}\text{NiN}_6\text{O}_8$ : C, 24.96; H, 4.71; N, 21.83. Found: C, 25.09; H, 4.63; N, 21.66.  $\lambda_{\text{max}}$  / nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ) in  $\text{H}_2\text{O}$ , 910 (22), 600 (8), 363 (15).

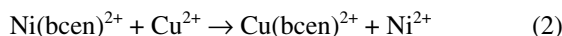
**$[\text{Cu}(\text{bcen})](\text{NO}_3)_2$ :** Yield 72%. Anal. Calculated for  $\text{C}_8\text{H}_{18}\text{CuN}_6\text{O}_8$ : C, 24.65; H, 4.65; N, 21.56. Found: C, 24.52; H, 4.53; N, 21.61.  $\lambda_{\text{max}}$  / nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ) in  $\text{H}_2\text{O}$ , 654 (154).

### 2.2. Reagents

All chemical reagents and solvents used in this study were obtained from Merck and Fluka and used without further purification. The twice distilled water was used in the preparation of all the solutions.

### 2.3. Kinetic Measurements

The metal exchange reaction of  $[\text{Ni}(\text{bcen})]^{2+}$  is demonstrated by reaction 2:



To measure reaction rate, visible spectra of reaction mixtures were recorded as a function of time using a Cintra 101 spectrophotometer. The greatest changes in molar absorptivity, due to formation of  $\text{Cu}(\text{bcen})^{2+}$ , were observed at 640 nm, and therefore all kinetic measurements of absorbance versus time were made at this wavelength. All runs were made at pH 6.9 and ionic strength 0.50 M (adjusted with  $\text{NaNO}_3$ ). No buffer was used since no protons

were involved in the reaction. The Cu(II) concentration was held constant at  $2.5 \times 10^{-3}$  M while  $[\text{Ni}(\text{bcen})^{2+}]$  varied up 30 times that of  $[\text{Cu}^{2+}]$  so that pseudo-first-order kinetic behavior was exhibited. The reaction was studied in the temperature range (15–35) + 0.1 °C.

To initiate reaction, equal volumes of  $\text{Cu}(\text{NO}_3)_2^{2+}$  and  $\text{Ni}(\text{bcen})^{2+}$  were mixed and the absorbance of product  $\text{Cu}(\text{bcen})^{2+}$  at 640 nm was followed as a function of time. At least three runs at each concentration and each temperature were recorded. The absorbance versus time data were computer fitted by sigmaplot 9.0 software with equations 3 (irreversible first-order reaction), 4 (biphasic reaction), and 5 (triphasic reaction) to find the best fit and  $k_{\text{obs}}$ <sup>15</sup>:

$$A = a_1 \exp[-k_{\text{obs}}(1)t] \quad (3)$$

$$A = a_1 \exp[-k_{\text{obs}}(1)t] + a_2 \exp[-k_{\text{obs}}(2)t] + A_{\infty} \quad (4)$$

$$A = a_1 \exp[-k_{\text{obs}}(1)t] + a_2 \exp[-k_{\text{obs}}(2)t] + a_3 \exp[-k_{\text{obs}}(3)t] + A_{\infty} \quad (5)$$

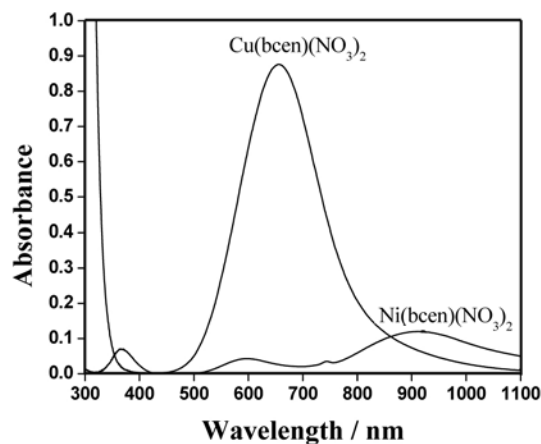
where  $a_1$  and  $a_2$  are comprised of rate constants and molar absorptivities.

## 3. Results and Discussions

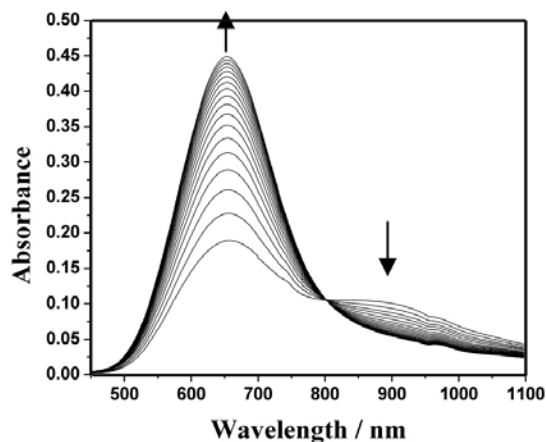
### 3.1. Absorption Spectra

As shown in Fig. 1, the visible absorption spectra of copper and nickel complexes in  $\text{H}_2\text{O}$  show maximum absorption due to a d-d transition at 650, 913, 597 and 365 nm. The spectra indicate that  $\text{Cu}(\text{bcen})^{2+}$  and  $\text{Ni}(\text{bcen})^{2+}$  complexes exist in solution, and that there are no deprotonated species of these complexes (i.e.  $\text{Cu}(\text{H}_1\text{bcen})^+$ ,  $\text{Cu}(\text{H}_2\text{bcen})$ ,  $\text{Ni}(\text{H}_1\text{bcen})^+$  and  $\text{Ni}(\text{H}_2\text{bcen})$ ).<sup>13, 16–18</sup> It is clear from the visible spectrum of the complexes that the metal exchange reaction can be followed spectrophotometrically. Figure 2 shows a set of spectra recorded in  $\text{H}_2\text{O}$  for the  $\text{Ni}(\text{bcen})^{2+}/\text{Cu}^{2+}$  system at  $25 \pm 0.1^\circ\text{C}$  and is representative of an increasing observed shift, with respect to the  $\text{Ni}(\text{bcen})^{2+}$  spectrum. The spectrum produced by mixing corresponding amounts of the  $\text{Cu}(\text{bcen})^{2+}$  complex and  $\text{Ni}^{2+}$  ions in  $\text{H}_2\text{O}$  is similar to the latter spectrum shown in Fig. 2. These observations indicate that the  $\text{Ni}(\text{bcen})^{2+}$  complex has been converted to the  $\text{Cu}(\text{bcen})^{2+}$  complex (reaction 2).

In fact, the observed changes in the visible spectrum due to the conversion of  $\text{Ni}(\text{bcen})^{2+}$  to  $\text{Cu}(\text{bcen})^{2+}$  indicates that the  $\text{Cu}(\text{bcen})^{2+}$  is thermodynamically more stable than the  $\text{Ni}(\text{bcen})^{2+}$  complex. To confirm this conclusion, the conversion of  $\text{Cu}(\text{bcen})^{2+}$  to the  $\text{Ni}(\text{bcen})^{2+}$  complex has been examined. It has been found that the opposite direction to reaction 2 does not take place. Therefore, under the studied conditions, the  $\text{Ni}(\text{bcen})^{2+}$  complex can be only converted to the  $\text{Cu}(\text{bcen})^{2+}$  complex irreversibly. This



**Figure 1.** UV-Visible spectra of  $[\text{Ni}(\text{bcen})](\text{NO}_3)_2$ , ( $5.0 \times 10^{-3}$  M) and  $[\text{Cu}(\text{bcen})](\text{NO}_3)_2$ , ( $5.0 \times 10^{-3}$  M) complexes in  $\text{H}_2\text{O}$



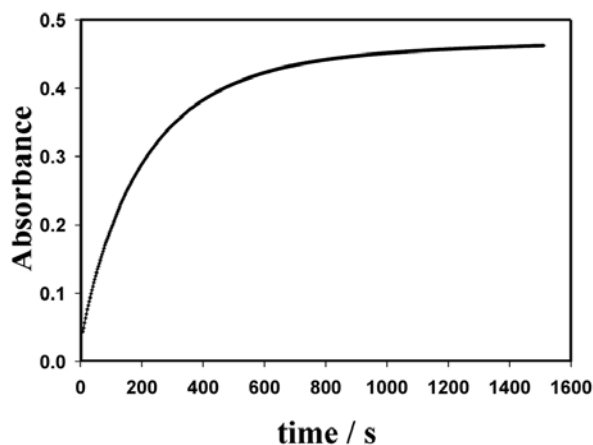
**Figure 2.** Changes in the absorption spectrum of a  $[\text{Ni}(\text{bcen})](\text{NO}_3)_2$ , ( $2.5 \times 10^{-3}$  M) with increasing  $\text{Cu}(\text{NO}_3)_2$ , ( $2.5 \times 10^{-3}$  M) in  $\text{H}_2\text{O}$  within 20 min at  $25 \pm 0.1$  °C

observation is in agreement with a common feature of the greater stability of copper complexes over nickel complexes. The formation constant values ( $\log K_f$ ) for  $\text{Cu}(\text{bcen})^{2+}$  and  $\text{Ni}(\text{bcen})^{2+}$  in aqueous solution at 25 °C of  $12.58 \pm 0.07$  and  $7.90 \pm 0.06$ , respectively,<sup>17, 18</sup> are in agreement with this conclusion.

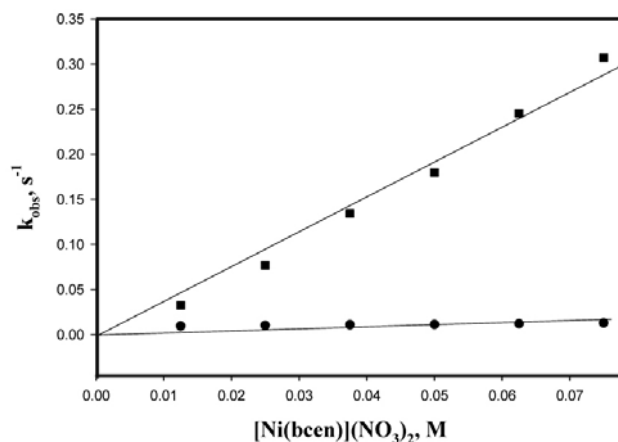
### 3. 2. Kinetic Study

The study of the metal exchange reaction of the  $\text{Ni}(\text{bcen})^{2+}/\text{Cu}^{2+}$  system is only possible at pH = 6.8–7.0 at which the predominant form of Ni(II) is the  $\text{Ni}(\text{bcen})^{2+}$  complex. On the one hand, as in the reaction solution pH is raised, the protons of the amide group in the  $\text{Ni}(\text{bcen})^{2+}$  complex are ionized, and the Ni-O bond is rearranged to form a Ni-N bond. On the other hand, with a decrease in the pH of the reaction solution mixture, the predominant form of the reactant species becomes  $\text{Ni}^{2+}$ .<sup>17</sup> All the experiments in this work were therefore carried out at pH = 6.9. Under these conditions, nickel exists only as the  $\text{Ni}(\text{bcen})^{2+}$  complex.

Under  $[\text{Ni}(\text{bcen})^{2+}] \gg [\text{Cu}^{2+}]$  conditions, the conversion of  $\text{Ni}(\text{bcen})^{2+}$  to  $\text{Cu}(\text{bcen})^{2+}$  according to equation 2, turned out to be described best as a biphasic reaction. Also, the reactions at different temperatures were found to be a two-step process, biphasic (Fig. 3). Therefore, two rate constants  $k_{\text{obs}}(1)$  and  $k_{\text{obs}}(2)$  were obtained by fitting the absorbance versus time data to equation 4 (Table 1). The first-step reaction was fast while the subsequent step reaction was slow (i.e.  $k_{\text{obs}}(1) > k_{\text{obs}}(2)$ ). The dependence of the rate constants on the excess concentration of the  $\text{Ni}(\text{bcen})^{2+}$  complex has also been studied. Fig. 4 shows the effect of changes in  $[\text{Ni}(\text{bcen})^{2+}]$  on the rate constants  $k_{\text{obs}}(1)$  and  $k_{\text{obs}}(2)$ . This figure indicates that  $k_{\text{obs}}(1)$  is dependent on the concentration of the  $\text{Ni}(\text{bcen})^{2+}$  complex, while  $k_{\text{obs}}(2)$  is independent of the concentration of the  $\text{Ni}(\text{bcen})^{2+}$  complex.



**Figure 3.** Plot of absorbance vs. time for reaction of  $[\text{Ni}(\text{bcen})](\text{NO}_3)_2$ , ( $2.5 \times 10^{-3}$  M) with  $\text{Cu}(\text{NO}_3)_2$ , ( $2.5 \times 10^{-3}$  M) in  $\text{H}_2\text{O}$  at  $25 \pm 0.1$  °C



**Figure 4.** Plot of the rate constants  $k_{\text{obs}}(1)$ ,  $\blacksquare$  and  $k_{\text{obs}}(2)$ ,  $\bullet$  vs.  $[\text{Ni}(\text{bcen})(\text{ClO}_4)_2]$  for reaction 2 ( $[\text{Cu}^{2+}] = 2.5 \times 10^{-3}$  M,  $I = 0.5$  M  $\text{NaNO}_3$  and  $25 \pm 0.1$  °C)

The value of  $k_{\text{obs}}(1)$  varies linearly as a function of  $[\text{Ni}(\text{bcen})^{2+}]$  with a proportionality constant  $k_1$ . Therefore, it can be written

$$k_{\text{obs}}(1) = k_1 [\text{Ni}(\text{bcen})^{2+}] \quad (6)$$

where  $k_1 = 4.40 \pm 0.14 \text{ M}^{-1} \text{ s}^{-1}$  at  $25 \pm 0.1 \text{ }^\circ\text{C}$ . The rate constant of the second-step reaction can be expressed as

$$k_{\text{obs}}(2) = k_2 \quad (7)$$

which is  $\sim (11.3 \pm 0.94) \cdot 10^{-2} \text{ s}^{-1}$  at  $25 \pm 0.1 \text{ }^\circ\text{C}$ . Table 1 gives a summary of the rate constants at different temperatures.

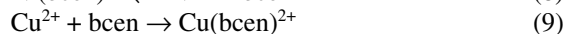
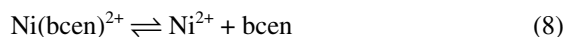
**Table 1.** Rate constants and activation parameters for the metal exchange reaction  $[\text{Ni}(\text{bcen})]^{2+}$  with  $\text{Cu}^{2+}$

$t \text{ }^\circ\text{C}$	$K_1, \text{M}^{-1} \text{s}^{-1}$	$10^2 k_2, \text{s}^{-1}$	$\Delta H_1^\ddagger, \text{kJ mol}^{-1}$	$\Delta S_1^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$	$\Delta H_2^\ddagger, \text{kJ mol}^{-1}$	$\Delta S_2^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$
15	$2.91 \pm 0.13$	$5.83 \pm 0.66$				
20	$3.36 \pm 0.18$	$9.89 \pm 0.94$				
25	$4.40 \pm 0.14$	$11.25 \pm 0.94$	$35.4 \pm 3.8$	$-113.8 \pm 1.29$	$42.1 \pm 4.5$	$-121.7 \pm 24.3$
30	$5.56 \pm 0.43$	$15.09 \pm 1.47$				
35	$8.20 \pm 0.55$	$21.37 \pm 2.55$				

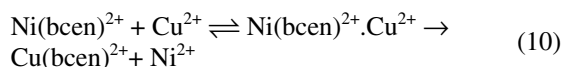
### 3. 3. Proposed Mechanism

The metal exchange reaction in the  $\text{Ni}(\text{bcen})^{2+}/\text{Cu}^{2+}$  system can be carried out via two different pathways:

- (1) Dissociation of the  $\text{Ni}(\text{bcen})^{2+}$  complex followed by an attack of copper on the dissociated bcen ligand



- (2) Attack by copper on partially dissociated  $\text{Ni}(\text{bcen})^{2+}$  to form a binuclear intermediate.



As mentioned earlier, the metal exchange of copper with nickel in  $\text{Ni}(\text{bcen})^{2+}$  has been found to be a two-step process (biphasic reaction) involving two rate constants  $k_{\text{obs}}(1)$  and  $k_{\text{obs}}(2)$ . The rate constant of the first step reaction depends on the concentration of  $\text{Ni}(\text{bcen})^{2+}$ . These results show that the mechanism of this metal exchange reaction proceeds predominantly through a binuclear intermediate pathway (the second pathway, reaction 10).

Previous studies of metal exchange reactions have shown that the entry of the incoming metal depends on the reaction rate and proceeds through a binuclear intermediate species.<sup>1–3, 9, 10</sup>

The activation parameters for the metal exchange reaction are shown in table 1. The  $\Delta H^\ddagger$  values for the reac-

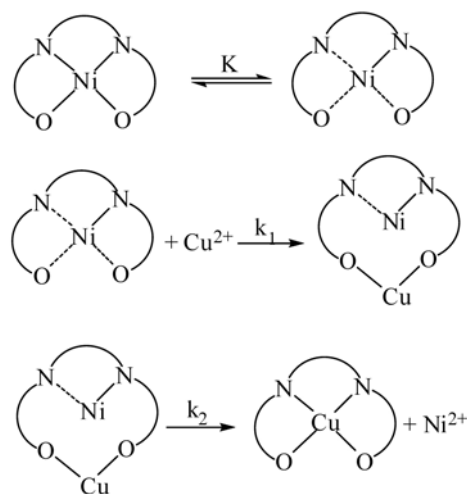
tions are in agreement with this conclusion in which the second-step is rate determining. The entropies of activation will be markedly affected by specific solvation effect, both for metal ion and complex, the precise origin of these values is difficult to define. However, the negative values of  $\Delta S^\ddagger$  support associative mechanism (formation of binuclear intermediate) presented in scheme 2.

Chung et al.<sup>18</sup> in a kinetic study of the formation and dissociation of the  $\text{Ni}(\text{bcen})^{2+}$  complex, reported that dissociation involves firstly the fast pre-equilibration of an intermediately bonded species, and finally, second nickel-nitrogen bond breakage, the latter being the rate-determining step. Chung et al.,<sup>19</sup> in an additional kinetic study of the formation and dissociation of the  $\text{Cu}(\text{bcen})^{2+}$  complex,

indicated that the formation of the first copper(II)-nitrogen bond was the rate determining step while the formation of subsequent bonds was rapid.

The observed kinetic behavior of the studied complexes in the present work together with the results of the previous study of the dissociation of  $\text{Ni}(\text{bcen})^{2+}$  and formation of  $\text{Cu}(\text{bcen})^{2+}$  leads us to suggest the metal exchange reaction mechanism given by scheme 2.<sup>18, 19</sup>

The first-step of this metal exchange reaction is a fast pre-equilibration step (K) along with the rupture of two nickel-oxygen bonds and the formation of the first



**Scheme 2.** Reaction mechanism for metal exchange reaction of  $[\text{Ni}(\text{bcen})]^{2+}$  with  $\text{Cu}(\text{NO}_3)_2$ .

nickel-nitrogen bond.<sup>18</sup> This is followed by the coordination the unwrapping of oxygen of the bcen ligand to copper(II) with formation of binuclear intermediate (scheme 2). It is clear from the first-step reaction that the rate constant should increase linearly with the  $\text{Ni}(\text{bcen})^{2+}$  complex concentration. A kinetic expression for this process is shown in equation 6.

As indicated in scheme 2, the formation of the intermediate binuclear species is dependent on the concentration of both reactant species. The second-step of reaction is an intramolecular reaction and is independent on the  $[\text{Ni}(\text{bcen})^{2+}]$  concentration. The second step is the rupture of the second Ni-N bond and the formation of the first Cu-N bond simultaneously in binuclear intermediate. Since this step is slow compared with the first step, it controls the overall rate of reaction and can be regarded as rate determining step. This conclusion is in agreement with previous studies.<sup>18, 19</sup>

## 4. Conclusion

In this paper we studied the kinetics of metal exchange reaction in aqueous solution under pseudo-first-order conditions. Experimental data were computer-fitted to appropriate exponential functions using a non-linear least-square iterative method. It was found that the reaction rate was a two-step process, the step 1 was rapid and dependent on the concentration of  $\text{Ni}(\text{bcen})^{2+}$  complex and the step 2 was slow and independent of  $[\text{Ni}(\text{bcen})^{2+}]$ . The metal exchange reaction in the system  $\text{Ni}(\text{bcen})^{2+}/\text{Cu}^{2+}$  showed that a  $\text{Ni}(\text{bcen})^{2+}$  complex should be thermodynamically less stable than  $\text{Cu}(\text{bcen})^{2+}$  complex.

## 5. Acknowledgments

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## Povzetek

Proučevali smo kinetiko reakcije izmenjave  $\text{Ni}(\text{N,N}'\text{-bis}(\beta\text{-kارباموئيليل) \text{etilendiamin})^{2+}/\text{Cu}^{2+}$  ionov v vodni raztopini (okrajšano  $\text{Ni}(\text{bcen})^{2+}/\text{Cu}^{2+}$ ).

V temperaturnem območju med 15 in 35 °C smo zasledovali nastanek  $\text{Cu}(\text{bcen})^{2+}$  kompleksa spektrofotometrično pri pH 6.9 ter ionski moči 0.5 M. Pri pogoju  $[\text{Ni}(\text{bcen})^{2+}] \gg [\text{Cu}^{2+}]$  lahko kinetiko procesa opišemo kot reakcijo psevdoreda, kjer smo predpostavili mehanizem v dveh stopnjah: (1) delna disociacija  $\text{Ni}(\text{bcen})^{2+}$  kompleksa, ki ji sledi nastanek intermediata in (2) izmenjava kovinskih kationov. Prva stopnja je hitrejša in je odvisna od koncentracije  $\text{Ni}(\text{bcen})^{2+}$ , medtem ko druga, odločujoča stopnja, od koncentracije  $\text{Ni}(\text{bcen})^{2+}$ , ni odvisna. Za obe stopnji smo določili konstanti reakcijske hitrosti:  $k_1$  in  $k_2$  pri 25 °C znašata  $2.38 \pm 0.16 \text{ M}^{-1}\text{s}^{-1}$  in  $(11.25 \pm 0.94) \times 10^{-2} \text{ s}^{-1}$ .

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