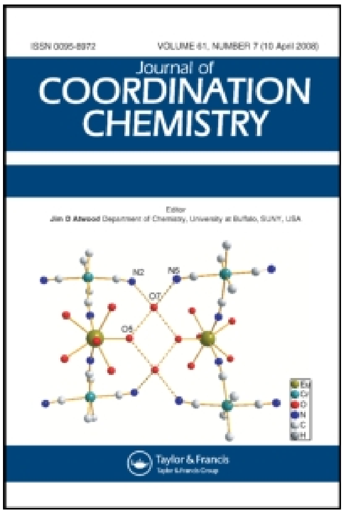

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The metal exchange reaction between NiMIDA and copper(II)

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The metal exchange reaction between copper(II) and N-methyliminodiacetatonickelate(II) (NiMIDA) was studied at 25.0°C and ionic strength of 1.25 within the pH range 3.5 to 4.8. The copper(II) to NiMIDA concentration ratio was varied over a two-hundred-fold range. The reaction is first-order in NiMIDA, copper(II) and hydrogen ion. The rate constant for the addition of copper(II) to NiMIDA is $k_{\mathrm{Cu}}^{\mathrm{NiMIDA}} = 5.10 \times 10^{-3}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The rate constants for both the hydrogen ion dependent- and independent- dissociations of NiMIDA are, respectively, $k_{\mathrm{H}}^{\mathrm{NiMIDA}} = 0.400\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k^{\mathrm{NiMIDA}} = 7.76 \times 10^{-5}\,\mathrm{s}^{-1}$. A mechanisim is presented which shows that MIDA does not prevent formation of a dinuclear intermediate and that MIDA partly unwraps from nickel before reacting with copper(II).

Keywords: Metal exchange; Copper(II); N-methyliminodiacetic acid; Kinetics; Multidentate ligands; N-methyliminodiacetatonickelate(II)

1. Introduction

Copper(II) exchange reactions have been reported with a variety of simple nickel(II) complexes including NiNTA [1], Ni(IDA) [2] and Ni(IDA)2 [3]. In this article, the copper(II) exchange reaction with NiMIDA (MIDA = N-methyliminodiacetic acid) is reported:

$$\mathrm{NiMIDA} + \mathrm{Cu}^{2+} \rightarrow \mathrm{CuMIDA} + \mathrm{Ni}^{2+} \tag{1}$$

Bydalek and Margerum [1, 2] found that many metal exchange reactions involve a dinuclear intermediate with both nickel and copper bound to the multidentate ligand. This manuscript reports the effect of coordinated ligand MIDA on the rate law, the formation of dinuclear intermediates, and the reaction mechanism.

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2. Experimental

The procedures employed in this study have been discussed by Bydalek [1, 2] and Steinhaus [3]. High purity reagents were used (> 99%). All reactions were carried out at 25.0°C, with an ionic strength of 1.25 M and within the pH range 3.5 to 4.8 without the addition of buffer. The final solution pH was adjusted with sodium hydroxide or perchloric acid while the ionic strength of all reaction mixtures was set using sodium perchlorate. Excess nickel (ten times the NiMIDA concentration) was added to all reaction mixtures. Calculations using the conditional stability constant for the formation of NiMIDA show that excess nickel(II) prevents dissociation of NiMIDA. A Fisher Scientific Accumet pH meter with glass and reference electrodes was used. The pH of each reaction mixture, measured at the start and end of each reaction, was constant.

A Perkin-Elmer Lambda 20 uv/vis spectrophotometer was used for all spectral and kinetic measurements. The product CuMIDA was followed at 715.6 nm using a thermostated 10 cm cell; this wavelength showed the greatest change in molar absorptivity between reactants and products. At this wavelength, the values of the molar absorptivities ($M^{-1}\,cm^{-1}$) are as follows: $\varepsilon(\mathrm{CuMIDA}) = 71.7$, $\varepsilon(\mathrm{NiMIDA}) = 2.2$, $\varepsilon(\mathrm{Cu(ClO_4)_2}) = 7.7$ and $\varepsilon(\mathrm{Ni(ClO_4)_2}) = 2.3$. These values did not show a functional dependence on pH. Equation (2) was used to calculate the product concentration at any time t:

$$[\mathrm{Cu(MIDA)}] = \frac{A_t - A_i}{b(\varepsilon_{\mathrm{CuMIDA}} + \varepsilon_{\mathrm{Ni}} - \varepsilon_{\mathrm{NiMIDA}} - \varepsilon_{\mathrm{Cu}})} \tag{2}$$

In equation (2), A_i and A_t represent absorbance values of CuMIDA initially and at time t whereas b is the pathlength. Values of the initial absorbance extrapolated to time zero correspond to calculated values, indicating that no mixed complexes are present. Duplicate kinetic runs were made at each pH value.

3. Results

Pseudo-first-order conditions were used with excess copper(II) in the range 1.00×10^{-3} to 2.00×10^{-2} M and Ni(MIDA) at 1.00×10^{-4} M, as summarized in table 1. All reactions were followed to at least 90% completion. An example plot of NiMIDA concentration versus time is shown in figure 1.

If the reaction is first-order in NiMIDA, then at constant pH, the following rate equation is derived using the fact that $[\mathrm{Cu^{2+}}] \gg [\mathrm{NiMIDA}]$:

$$-\frac{\mathrm{d[NiMIDA]}}{\mathrm{d}t} = \frac{\mathrm{d[CuMIDA]}}{\mathrm{d}t} = k_0[\mathrm{NiMIDA}] \tag{3}$$

where k_0 is the pseudo-first-order rate constant. When equation (3) is integrated, a plot of log [NiMIDA] versus time gives a straight-line of slope k_0. All such plots, such as the one shown in figure 2, gave straight lines establishing the reactant order in NiMIDA to be one.

Table 1. First-order rate constant data at 25.0°C, $\mu = 1.25$, with $[\text{NiMIDA}] = 1.00 \times 10^{-4}$ M and $[\text{Ni}^{2+}] = 1.00 \times 10^{-3}$ M.

pH	10^3 $[\text{Cu}^{2+}]$ M	$10^4 k_0\,\text{s}^{-1}$
3.50	1.00	2.13
3.51	5.00	2.34
3.49	10.00	2.58
3.50	15.00	2.81
3.81	1.00	1.38
3.80	5.00	1.51
3.82	10.0	1.85
3.80	15.0	2.10
3.81	20.0	2.30
4.15	1.00	1.06
4.15	5.00	1.31
4.15	10.0	1.67
4.15	15.0	1.86
4.15	20.0	2.09
4.45	1.00	0.93
4.46	4.00	1.22
4.43	6.00	1.46
4.45	10.0	1.66
4.45	20.0	1.96
4.80	1.00	0.98
4.80	5.00	1.15
4.80	10.0	1.32
4.81	15.0	1.55
4.80	20.0	1.91

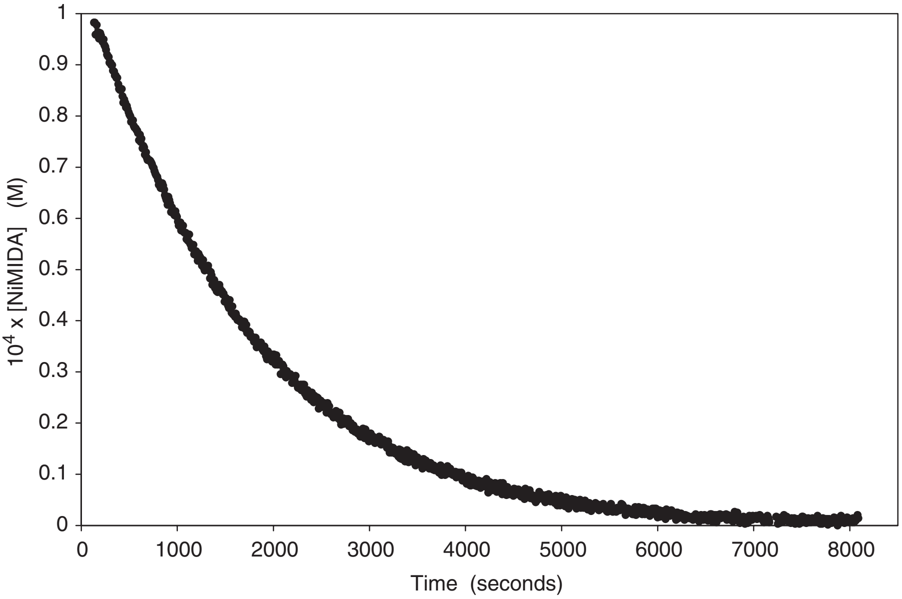


Figure 1. Plot of [NiMIDA] *vs*. time at pH 4.80 for $[\text{Cu}^{2+}] = 5.00 \times 10^{-3}$ M, $[\text{NiMIDA}] = 1.00 \times 10^{-4}$ M and $[\text{Ni}^{2+}] = 1.00 \times 10^{-3}$ M.

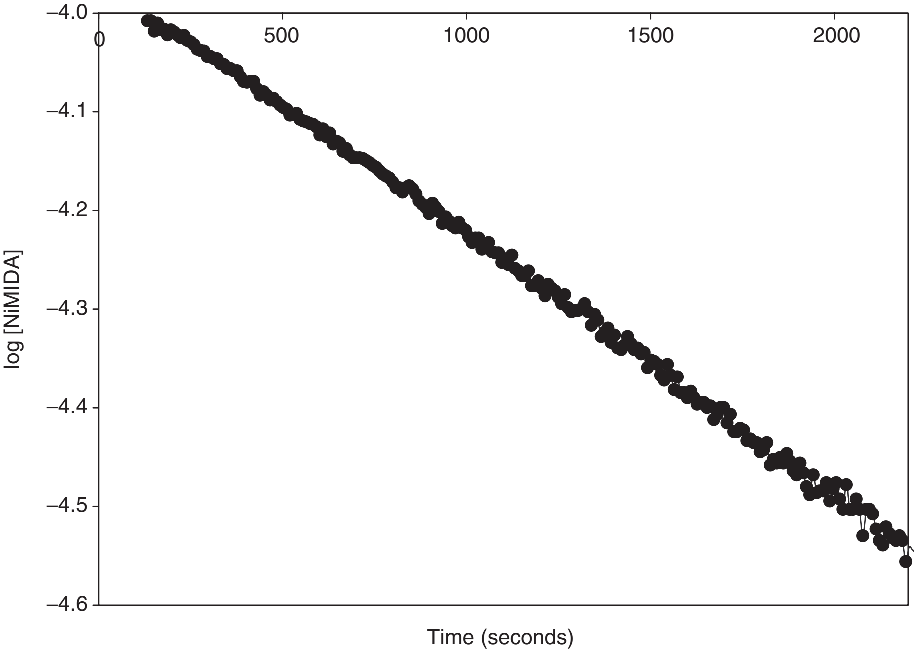


Figure 2. Plot of log [NiMIDA] *vs.* time at pH 4.80 for $[Cu^{2+}] = 5.00 \times 10^{-3}$ M, $[NiMIDA] = 1.00 \times 10^{-4}$ M and $[Ni^{2+}] = 1.00 \times 10^{-3}$ M.

Having established first-order behavior with respect to NiMIDA, the dependence of k_0 on $[Cu^{2+}]$ was studied. A plot of k_0 versus $[Cu^{2+}]$ for five different pH values indicates a first-order dependence as shown in figure 3. The slope of the line represents the rate constant for addition of copper(II) to NiMIDA, given by $k_{Cu}^{NiMIDA} = 5.10 \times 10^{-3}\,M^{-1}\,s^{-1}$. If all of the lines had the same intercept, then the reaction would be independent of pH. However, since the intercepts are different, the intercept must be copper independent but hydrogen ion dependent. A plot of the Y intercepts versus $[H^+]$, as shown in figure 4, indicates a first-order dependence on hydrogen ion concentration. The slope of this line represents the hydrogen ion dependent dissociation of NiMIDA, given by $k_H^{NiMIDA} = 0.40\,M^{-1}\,s^{-1}$ while the intercept, given by k^{NiMIDA}, represents the hydrogen ion independent dissociation of NiMIDA given by $7.76 \times 10^{-5}\,s^{-1}$. These values are listed in table 2 along with corresponding values for the NiIDA-Cu^{2+} system [2, 3]. Using the three rate constants listed in table 2, an expression for k_0 can be expressed as

$$k_0 = \left(k_{Cu}^{NiMIDA}[Cu^{2+}] + k_H^{NiMIDA}[H^+] + k^{NiMIDA}\right) \tag{4}$$

which shows a first-order dependence on copper and hydrogen ion concentrations.

4. Discussion

According to equation (4), the Cu^{2+}-NiMIDA reaction is resolved into three pathways: (a) proton independent (b) proton dependent and (c) copper dependent. It is of interest

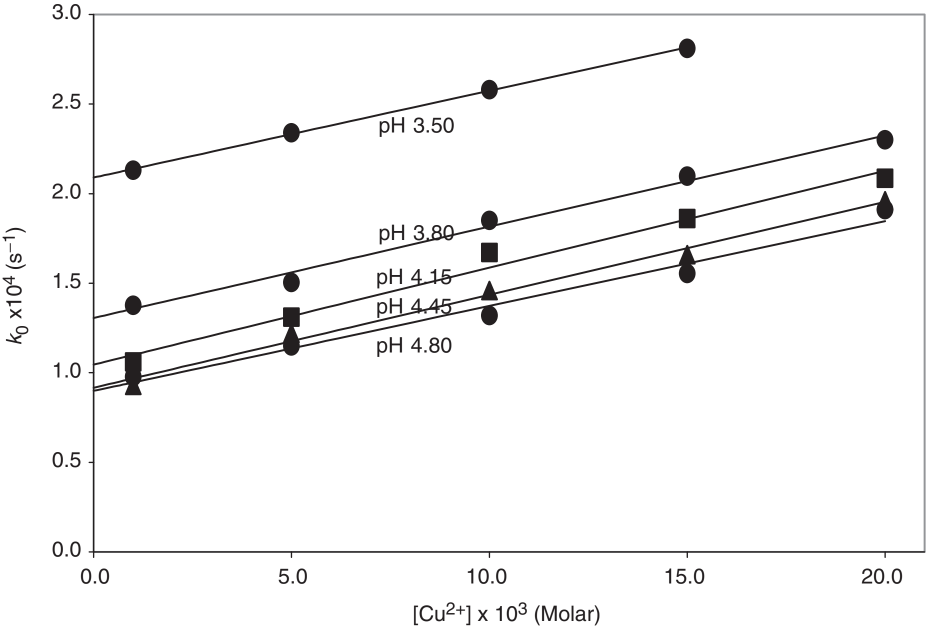


Figure 3. Effect of varying pH and copper concentration upon k_0.

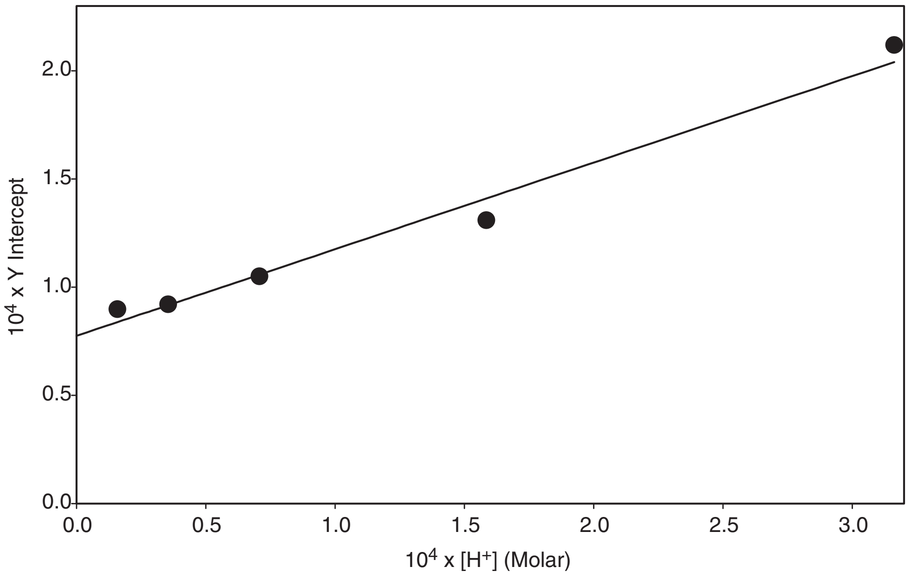


Figure 4. Resolution of hydrogen ion dependent- and independent-rate constants.

to find the rate-determining step (rds) of the dominant pathway. A possible mechanism is shown in figure 5.

If the reaction mechanism is solely dissociative, then it consists of the sequence: 1-2-3-5 as shown in figure 5, implying that NiMIDA must totally dissociate before

Table 2. Rate constant comparison for the reactions of Cu^{2+} with NiIDA and NiMIDA.

Rate constant	NiMIDA [This work]	IDA [2]	Ratio (IDA/MIDA)
k_{Cu}^{NiMIDA}	$(5.10 \pm 0.27) \times 10^{-3}\,M^{-1}\,s^{-1}$	$1.48 \times 10^{-2}\,M^{-1}\,s^{-1}$	2.9
k_{H}^{NiMIDA}	$(4.00 \pm 0.30) \times 10^{-1}\,M^{-1}\,s^{-1}$	$1.2\,M^{-1}\,s^{-1}$	3.0
k^{NiMIDA}	$(7.76 \pm 0.48) \times 10^{-5}\,s^{-1}$	$1.51 \times 10^{-4}\,s^{-1}$	1.9

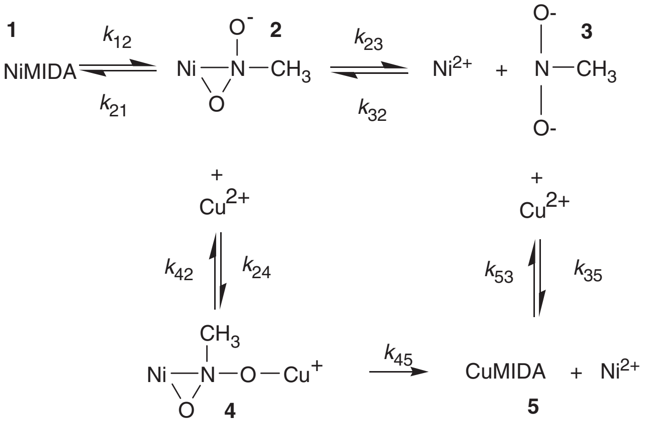


Figure 5. Mechanism for the NiMIDA–Cu^{2+} reaction.

combining with copper ion in step 3–5. For this path, the rds could not involve step 1–2 because this would result in zero-order dependence on copper. In addition, step 3–5 is ruled out as rate determining because copper ion is labile. Therefore, the rds could only involve step 2–3, and would be enhanced by the presence of hydrogen ions. The rate constant expression (4) would then exclude copper ion concentration and instead only contain proton dependent and proton independent terms.

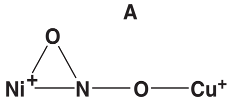
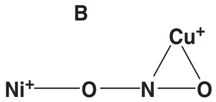
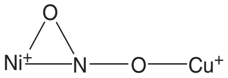
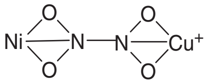
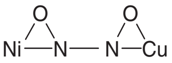
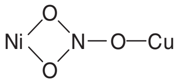
However, because the rate law involves a first-order copper dependence, the dissociative model can only be part of the mechanism. Figure 5 also shows an additional pathway dependent on copper ion, given by 1-2-4-5. In this path, for reasons previously discussed, both steps 1–2 and 2–4 can be ruled out as rate determining and therefore step 4–5 is the rds.

Since step 4–5 is the rds, the structure of intermediate **4** is of interest. To be consistent with other studies, its structure should have a five-membered ring, contain no uncoordinated sites and be dinuclear in nickel and copper [5]. Two possible intermediates, A and B, are shown in table 3.

The structure of the dinuclear intermediate formed before the rds, can be predicted using the method proposed by Bydalek and Margerum [1, 2] in which the measured ratio of the rate constants $k_{Cu}^{NiMIDA}/k_{Cu}^{NiL'}$ is matched to the ratio of relative stability constants of the dinuclear intermediate, corrected for a number of factors:

$$\frac{k_{Cu}^{NiMIDA}}{k_{Cu}^{NiL'}} = \frac{K_r^{NiMIDACu}}{K_r^{NiL'Cu}}\, x\, \frac{k^{NiMIDA}}{k^{NiL'}}\ x \text{ statistical } x \text{ electrostatic} \qquad (5)$$

Table 3. Comparison of NiMIDA–Cu and CuMIDA–Ni reaction intermediates as calculated from values in table 4.

	A  K_r =0.0355 $\frac{K_r^{\mathrm{Ni(MIDA)Cu}}}{K_r^{\mathrm{Ni(L')Cu}}}$	**B**  K_r = 1.02 $\frac{K_r^{\mathrm{Ni(MIDA)Cu}}}{K_r^{\mathrm{Ni(L')Cu}}}$	**Measured** $\frac{k_{\mathrm{Cu}}^{\mathrm{Ni\text{-}MIDA}}}{k_{\mathrm{Cu}}^{\mathrm{Ni\text{-}L'}}}$
L′ = IDA [2]  K_r = 5.78	6.0×10^{-2}	1.4×10^{3}	0.35
L′ = EDTA [4,5]  K_r = 1.50	$9.5\ \mathrm{x}10^{-3}$ [a]	56 [a]	0.33
L′ = EDDA [6]  K_r = 1.91	7.9×10^{-3}	180	7.0×10^{-2}
L′ =NTA [7]  K_r = 0.0222	0.43 [b]	1.0×10^{4} [b]	3.8

(a) Statistical factor of 1/2 (b) Statistical factor of 2/3

Equation (5) is known to hold true as long as the bonding to nickel is the same in each pair of intermediates compared.

On the right side of equation (5), is a series of terms used to predict the ratio given on the left side. The first set of terms involve K_r, a relative stability constant defined for each dinuclear intermediate by:

$$K_r = \frac{K_{\mathrm{Ni\text{-}segment}} K_{\mathrm{Cu\text{-}segment}}}{K_{\mathrm{NiL}}} \tag{6}$$

Table 4. Stability constants and rate constants used in the calculation of K_r values where N/A = not applicable. All values were chosen to be as close to 25°C and $\mu = 0.1$ as possible.

Complex	K_{stab} [9]	Complex	K_{stab} [9]	$k_{\text{Cu}}^{\text{NiL}}$ $\text{M}^{-1}\,\text{s}^{-1}$
NiMIDA	4.68×10^8	CuMIDA	1.1×10^{11}	5.23×10^{-3} [this work]
NiIDA	1.34×10^8	CuIDA	3.71×10^{10}	1.48×10^{-2} [3]
NiEDTA^{2-}	3.31×10^{18}	CuEDTA^{2-}	N/A	1.6×10^{-2} [4, 5]
NiEDDA	4.46×10^{13}	CuEDDA	N/A	7.5×10^{-2} [6]
NiNTA^{-}	3.16×10^{11}	CuNTA^{-}	N/A	1.39×10^{-3} [1]
$\text{NiNH}_3{}^{2+}$	5.01×10^2	$\text{CuNH}_3{}^{2+}$	1.99×10^4	
Ni(ac)^+	5.5	Cu(ac)^+	5.25×10^1	
Ni(gly)^+	6.03×10^5	Cu(gly)^+	1.41×10^8	
Ni(sar)^+	3.16×10^5	Cu(sar)^+	8.71×10^7	

Equation (6) corresponds to the formation of the dinuclear intermediate just prior to the rds:

$$\text{NiMIDA} + \text{Cu}^{2+} \rightleftharpoons \text{NiMIDACu}^{2+} \tag{7}$$

According to equation (6), the K_r value for NiMIDACu^{2+} is computed using three factors; two in the numerator represent the ligand segments of the dinuclear intermediate bound separately to nickel and copper. The denominator gives the stability constant for NiMIDA.

The second ratio of terms in equation (5), the nickel-ligand dissociation rate constant ratio: $k^{\text{NiMIDA}}/k^{\text{NiL}'}$, is correct for the case when the two structures being compared have different types of bond breaking in the rds, for example Ni–O (intermediate B) versus Ni–N (intermediate A). The value of this ratio is 830 as calculated from the respective ratio of nickel–acetate ($5 \times 10^3\,\text{s}^{-1}$) and nickel–ammonia bond dissociations ($6\,\text{s}^{-1}$) [7].

The last two terms of equation (5) represent statistical and electrostatic factors, calculated as previously discussed [8]. The statistical factor takes into account the number of different ways a dinuclear intermediate can form while the electrostatic term arises from the attraction between nickel(II) and negative groups, such as acetate. The value calculated for K_{el} is 2.51 [3].

Table 3 provides a comparison between NiMIDACu dinuclear intermediates A and B where the K_r values are computed using stability constant and rate constant values provided in table 4. The last column of table 3 lists the measured rate constant ratio of NiMIDA to the reference nickel complex NiL′ listed in column one, i.e., NiIDA, NiEDTA, NiEDDA and NiNTA. Columns two and three of this table give predicted values of the rate constant ratio as calculated from equation (5) for two possible dinuclear intermediates A and B, both having five-membered rings. Structure B is corrected for the fact that its rds involves cleavage of a nickel-acetate bond whereas all of the structures to which it is compared (column one) involve a rds with nickel–nitrogen bond breakage. Comparison of the predicted rate constant ratios for intermediate A are generally within a factor of ten of the measured rate constant ratio while intermediate B's predicted values differ by a factors ranging from 1500 to 4000. Hence dinuclear intermediate A, with a sarcosinate segment bonded to nickel and an acetate bonded to the attacking copper ion, appears most plausible as the dinuclear intermediate.

Moreover, the rds must be step 4–5 involving the rupture of a Ni–N bond in intermediate A.

5. Conclusions

Mechanistic results for the NiMIDA–Cu(II) reaction indicate that several reaction paths occur simultaneously, a dominant copper dependent path given by 1-2-4-5 and a copper/hydrogen ion independent path given by 1-2-3-5, controlled by the rate of dissociation of NiMIDA.

The rate constant data listed in table 2 indicate that sarcosinate does not prevent formation of a dinuclear intermediate. Furthermore, an acetate segment must dissociate from NiMIDA before copper attacks and subsequently, nickel-nitrogen bond cleavage is the rds. In comparison to the NiIDA–Cu^{2+} system [2, 3], the results show that the methyl group may slow the metal exchange reaction by a factor of about three indicating a slight steric hindrance. These results show that the NiMIDA–copper(II) reaction is similar to the reported reactions of copper(II) with NiIDA and NiNTA.

Acknowledgements

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