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## The Kinetics of the Metal Exchange Reaction between N-(2-Hydroxyethyl) Iminodiacetonickelate (II) and Copper(II)

Craig R. Weed

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THE KINETICS OF THE METAL EXCHANGE REACTION BETWEEN  
N-(2-HYDROXYETHYL)IMINODIACETATO-  
NICKELATE(II) AND COPPER(II)

by

Craig R. Weed

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Arts  
Department of Chemistry

Western Michigan University  
Kalamazoo, Michigan  
December 1984

THE KINETICS OF THE METAL EXCHANGE REACTION BETWEEN  
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Craig R. Weed, M.A.

Western Michigan University, 1984

The reaction between copper(II) and N-(2-hydroxyethyl)iminodiacetato-nickelate(II) (NiHEIDA) was studied between pH 4.0 and 5.6 over a 70 fold variation in copper concentration at an ionic strength of 1.25 and a temperature of 25° C. The reaction order in both NiHEIDA and Cu(II) is first. The reaction rate is pH sensitive and a hydrogen dependent pathway as well as copper dependent and copper and hydrogen independent pathways were found.

Evidence is given for a stepwise mechanism for the unwrapping of HEIDA from its nickel complex, followed by copper attack to give a dinuclear intermediate, which then breaks up to products. The first-order copper rate constant can be predicted from the stability of the dinuclear intermediate. No pronounced effect could be assigned to the hydroxyethyl segment of HEIDA reacting with either the incoming copper ion or the leaving nickel ion.

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Craig R. Weed

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WESTERN MICHIGAN UNIVERSITY

M.A. 1984

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## TABLE OF CONTENTS

ACKNOWLEDGEMENTS .....	ii
LIST OF TABLES .....	iv
LIST OF FIGURES .....	v
INTRODUCTION .....	1
APPARATUS AND REAGENTS .....	5
Apparatus .....	5
Reagents .....	5
EXPERIMENTAL .....	8
Spectrophometric Study of Reactants and Products .....	8
Reaction Rates and Conditions .....	8
RESULTS .....	11
Kinetic Expression for Reaction .....	11
Resolution of Rate Constants .....	19
DISCUSSION .....	22
APPENDIX Concentration - Absorbance Relationship.....	32
REFERENCES .....	33

## LIST OF TABLES

1. Ligand Structures and Abbreviations .....	3
2. Molar Absorptivities at 735nm pH = 4.00 $\mu = 1.25\text{M}$ .....	9
3. Experimental Conditions .....	9
4. Values of $k_0$ at Constant Hydrogen Ion Concentration .....	14
5. Values of $k_0$ at Constant Copper Concentration .....	17
6. Resolved Rate Constants .....	21
7. Comparison of NiHEIDA-Cu and NiL-Cu Reaction Intermediates .....	25
8. Calculated Rate Constants for the NiHEIDA-Cu System .....	31

## LIST OF FIGURES

1. Typical first-order plot of $k_0$ at constant copper concentration.....	13
2. Effect of copper concentration on $k_0$ at constant hydrogen ion concentration .....	16
3. Effect of Hydrogen ion concentration on $k_0$ at constant copper(II) concentration.....	18
4. Mechanism for transfer of HEIDA from nickel to copper .....	27

## INTRODUCTION

Multidentate ligand transfer between two metal ions, as represented by equation 1, has been the focus of considerable study for a variety of combinations of metal ion and ligands (1-12).



The mechanism of these metal exchange reactions has been shown to follow the successive breaking of coordinate covalent bonds from the metal-ligand complex, followed by a stepwise coordination to the attacking metal (1-3, 5-8,11). When the attacking metal coordinates to the ligand before it is completely unwrapped, the process results in the formation of a dinuclear intermediate which greatly speed up the rate of the reaction relative to complete dissociation of the ligand.

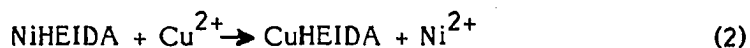
There are many factors which affect the rate and mechanism of metal exchange reactions. Those studied include dependence of the rate determining step upon complexed metal (7, 13-19), dependence of shift in reaction order upon attacking metal concentration (7,11,20), dependence of rate upon pH and hydrolyzed forms of the attacking metal (7, 11, 20-23), dependence of dinuclear intermediate structure upon dentate site of the complexed ligand (22), dependence of exchange rate upon anions (8, 23-26), dependence of exchange rate upon coordinated ligands (20), and dependence of mechanism and exchange rate upon steric effects caused by substituents on the complexed ligand (27).

Hydroxide dentate sites have received very little attention although alcoholic oxygen donor atoms do function as weak dentate sites. The forma-

tion of nickel(II) and cobalt(II) complexes with the poly(amino alcohol) ligands TKED and THPED proceeds through a mechanism in which first bond formation involves an alcoholic oxygen donor atom (28). Table 1 illustrates the structure of these and other ligands pertinent to this study.

The log stability constant of N-(2-hydroxyethyl)iminodiacetatonickelate (II) is 9.33 while that of iminodiacetatonickelate(II) is only 8.13, indicating a certain degree of added stability due to the hydroxyethyl group. On the other hand, the metal exchange reaction of N-hydroxyethylethylenediaminetriacetatonickelate(II) and copper(II) proceeds through the same mechanism and with almost identical rate constants as the metal exchange reaction of ethylenediaminetetraacetatonickelate(II) and copper(II) (3).

This study was undertaken to establish the effect of the hydroxyethyl group on the metal exchange reaction involving N-(2-hydroxyethyl)iminodiacetatonickelate(II), NiHEIDA, and copper(II), shown in equation 2.



The study demonstrates that the reaction shown in equation 2 has three pathways: a copper dependent pathway, a hydrogen dependent pathway, and a copper and hydrogen independent pathway, that the copper dependent pathway proceeds through a dinuclear intermediate, NiHEIDACu, and that the structure of the intermediates could be estimated from the relative stability constants of the coordinated segments involved.

Although the rate of exchange between copper(II) and NiHEIDA was slightly depressed compared to that of NiIDA, no pronounced effect could be assigned to interaction between the incoming copper ion and the hydroxyethyl ligand segment, or to interaction between the hydroxyethyl segment and nickel as the ligand unwrapped from nickel.

Table 1

## Ligand Structures and Abbreviations

Ligand	Structure	Abbreviation
iminodiacetic acid	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{CH}_2 - \text{C} - \text{OH} \\  \diagup \\  \text{HN} \\  \diagdown \\  \text{CH}_2 - \text{C} - \text{OH} \\  \parallel \\  \text{O}  \end{array}  $	IDA
N-(hydroxyethyl)ethylene diaminetriacetic acid	$  \begin{array}{c}  \text{HO} - \text{CH}_2 - \text{CH}_2 \diagdown \\  \text{HO} - \text{C} - \text{CH}_2 \diagup \\  \parallel \\  \text{O}  \end{array}  \text{N} - \text{CH}_2 - \text{CH}_2 - \text{N} \begin{array}{c} \diagup \text{CH}_2 - \text{C} - \text{OH} \\ \diagdown \text{CH}_2 - \text{C} - \text{OH} \\ \parallel \\ \text{O} \end{array}  $	HEIDA
ethylenediaminetetracetic acid	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{HO} - \text{C} - \text{H}_2\text{C} \diagdown \\  \text{HO} - \text{C} - \text{H}_2\text{C} \diagup \\  \parallel \\  \text{O}  \end{array}  \text{N} - \text{CH}_2 - \text{CH}_2 - \text{N} \begin{array}{c} \diagup \text{CH}_2 - \text{C} - \text{OH} \\ \diagdown \text{CH}_2 - \text{C} - \text{OH} \\ \parallel \\ \text{O} \end{array}  $	EDTA
2-hydroxyethylglycine	$  \text{HO} - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{C} - \text{OH} \\  \parallel \\  \text{O}  $	HEG

Table 1 (Continued)

Ligand	Structure	Abbreviations
ethylenediamine-diacetic acid	$\begin{array}{c} \text{O} & & \text{O} \\    & &    \\ \text{HO}-\text{C}-\text{CH}_2 & \text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2 & \text{C}-\text{OH} \end{array}$	EDDA
N-(2-hydroxyethyl)-iminodiacetic acid	$\begin{array}{c} & & \text{O} \\ & &    \\ & & \text{CH}_2-\text{C}-\text{OH} \\ & \nearrow & \\ \text{HO}-\text{CH}_2-\text{CH}_2-\text{N} & & \\ & \searrow & \\ & & \text{CH}_2-\text{C}-\text{OH} \\ & &    \\ & & \text{O} \end{array}$	HEIDA
N, N, N', N' -tetrakis (2-hydroxyethyl)ethylenediamine	$\begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}_2 & & \text{CH}_2-\text{CH}_2-\text{OH} \\ & \searrow & \nearrow \\ & \text{N}-\text{CH}_2-\text{CH}_2-\text{N} & \\ & \nearrow & \searrow \\ \text{HO}-\text{CH}_2-\text{CH}_2 & & \text{CH}_2-\text{CH}_2-\text{OH} \end{array}$	TKED
N, N, N', N' -tetrakis (2-hydroxypropyl)ethylenediamine	$\begin{array}{c} \text{OH} & & \text{OH} \\   & &   \\ \text{CH}_3-\text{CH}-\text{CH}_2 & & \text{CH}_2-\text{CH}-\text{CH}_3 \\ & \searrow & \nearrow \\ & \text{N}-\text{CH}_2-\text{CH}_2-\text{N} & \\ & \nearrow & \searrow \\ \text{CH}_3-\text{CH}-\text{CH}_2 & & \text{CH}_2-\text{CH}-\text{CH}_3 \\   & &   \\ \text{OH} & & \text{OH} \end{array}$	THPED
Nitrilotriacetic acid	$\begin{array}{c} \text{O} & & \text{O} \\    & &    \\ \text{HO}-\text{C}-\text{CH}_2 & & \text{N}-\text{CH}_2-\text{C}-\text{OH} \\ & \nearrow & \\ & & \\ \text{HO}-\text{C}-\text{CH}_2 & & \\    & & \\ \text{O} & & \end{array}$	NTA

## APPARATUS AND REAGENTS

### Apparatus

All spectra were taken on a Cary Model 14 recording spectrophotometer. All kinetic measurements were made in five or ten centimeter cells on a Beckman DU spectrophotometer with a Gilford 2000 multiple sample Absorbance Recorder and a Gilford Auxilliary Offset Control. The spectrophotometric cells were maintained at  $25 \pm 0.1^{\circ}\text{C}$  in the spectrophotometer with water jacketed cell holders.

The spectrophotometer settings for all measurements were as follows: wavelength 735nm, slit width varied between 0.2 - 0.3mm, source tungsten, and chart speed 5 inches per hour.

All pH measurements were made with a Beckman Research Model 110 pH meter. A glass-calomel electrode pair was used. In the reference electrode sodium chloride was substituted for potassium chloride to avoid any interference due to precipitation of potassium perchlorate. Beckman standard buffer solutions (pH 4.01 and 6.86) were used to standardize the pH meter.

### Reagents

All solutions were prepared from deionized water that had been treated by passing distilled water through a deionizing column of Amberlite MB-3 mixed bed resin.

#### N-(2-hydroxyethyl)iminodiacetic acid (HEIDA)

N-(2-hydroxyethyl)iminodiacetic acid was obtained from Sigma Chemi-



cals and was further purified by two successive recrystallizations from hot deionized water. The HEIDA solution was standardized by potentiometric titration against a carbonate free standard sodium hydroxide solution.

#### Ethylenediaminetetracetic acid (EDTA)

Standard EDTA was obtained from Anachemia Chemical Ltd. as an Acculute standard volumetric solution and was prepared with deionized water according to the instructions provided.

#### Copper(II) perchlorate, nickel(II) perchlorate

Copper(II) and nickel(II) perchlorate were obtained from the G. Frederick Smith Chemical Company as hexahydrates. The copper(II) perchlorate and nickel(II) perchlorate were standardized by titration against a standard EDTA solution using NAS as the indicator (29).

#### CuHEIDA

The CuHEIDA solution was prepared by combining equimolar volumes of standard copper(II) perchlorate with standard HEIDA followed by adjustment of the pH with solid sodium hydroxide to pH 6.5.

#### NiHEIDA

The NiHEIDA solution was prepared by adding a measured excess of standard nickel(II) perchlorate to a standard solution of HEIDA, to suppress the formation of  $\text{Ni(HEIDA)}_2$ . A computer program, GENDIS, was used to calculate the amount of nickel in excess over HEIDA which was necessary to suppress the formation of  $\text{Ni(HEIDA)}_2$  to the point where  $\text{NiHEIDA}/\text{Ni(HEIDA)}_2$  was 1.25 X

$10^4$ . For a  $3.80 \times 10^{-2}$  M solution of NiHEIDA this amounted to an excess nickel concentration of  $2.03 \times 10^{-2}$  M. The solution was then adjusted to pH 6.5 with solid sodium hydroxide.

All other chemicals were ACS grade and used without further purification.

## EXPERIMENTAL

### Spectrophotometric Study of Reactants and Products

The absorption spectra of all reactants and products were obtained from 400nm to 800nm. To follow the course of the reaction, and wavelength of 735nm was chosen. This corresponds to an absorption maximum for CuHEIDA with minimal contribution from the other species.

The molar absorptivities of all species were determined at 735nm and are listed in Table 2. The ionic strength of all solutions was adjusted to 1.25 M with sodium perchlorate so that rate constants in this study could be compared to those obtained in previous work.

### Reaction Rates and Conditions

All rates of reaction of equation 2 were studied by measuring the increase in absorbance due to the formation of CuHEIDA. Since there is no net change in the number of protons in the reaction (see equation 2), no buffer was necessary. The pH of the reactants was adjusted using hydrochloric acid and sodium hydroxide. The pH remained constant throughout the entire course of the reaction as demonstrated by monitoring the pH as the reaction proceeded. A ten to approximately 100 fold excess of copper over NiHEIDA was present in all cases. The experimental conditions used in all reaction rate studies are given in Table 3.

To initiate the reactions, a volume of stock copper perchlorate was introduced into a 100-ml volumetric flask with a buret. Enough stock sodium perchlorate was added to give an ionic strength of 1.25 M upon dilution to

TABLE 2

Molar Absorptivities at 735 nm pH = 4.00 $\mu = 1.25 \text{ M}$	
<u>SPECIES</u>	<u><math>\epsilon_{735\text{nm}}</math></u>
CuHEIDA	65.4
NiHEIDA	2.65
$\text{Cu}^{2+}$	8.97
$\text{Ni}^{2+}$	1.56

TABLE 3

Experimental Conditions			
<u>Constant pH</u>			
Copper (II)	$6.67 \times 10^{-2} \text{ M}$	$9.53 \times 10^{-4} \text{ M}$	
NiHEIDA	$7.46 \times 10^{-4} \text{ M}$	$9.24 \times 10^{-5} \text{ M}$	
Hydrogen ion	$1.00 \times 10^{-4} \text{ M}$		
<u>Constant Copper(II)</u>			
Copper (II)	$3.77 \times 10^{-3} \text{ M}$		
NiHEIDA	$3.73 \times 10^{-4} \text{ M}$	$3.46 \times 10^{-4} \text{ M}$	
Hydrogen ion	$9.89 \times 10^{-5} \text{ M}$	$2.50 \times 10^{-6} \text{ M}$	
Temperature = $25.0 \pm .1^\circ\text{C}$ and $\mu = 1.25 \text{ M}$ for all reaction mixtures.			

the final volume. The flask was filled to the mark with deionized water. The copper and stock NiHEIDA were placed in a constant temperature bath at 25.0°C and allowed to equilibrate. At the time of the experiment the copper solution was poured into a 150-ml beaker which was placed on a magnetic stirrer. An aliquot of stock NiHEIDA was injected into the stirred copper solution with a syringe. The recorder to the spectrophotometer was turned on at the same time that the NiHEIDA was injected. The pH was then adjusted with hydrochloric acid and sodium hydroxide. The reaction mixture was stirred continuously during this process before being transferred to a 5 or 10-cm spectrophotometric cell.

The reactions were monitored for at least three half lives or approximately three hours, although some reactions were monitored for more than twenty half lives to check for reversibility. No evidence of a significant reverse reaction was found in these cases.

## RESULTS

### Kinetic Expression for Reaction

In order to correctly interpret the kinetic data it is necessary to determine if the reaction being studied is going to completion. Two studies were undertaken to test for completion of the reaction. The first involved obtaining the change in absorbance for a reaction mixture allowed to react in excess of twenty half lives. The second involved calculating the change in absorbance for a solution of the same composition based on the reaction going to completion, using the experimentally obtained molar absorptivities. A comparison of the two values showed excellent correlation, and establishes that the reaction shown in equation 2 proceeds completely to the formation of products.

The rate expression tested was the simple first-order expression shown in equation 3.

$$\frac{-d[\text{NiHEIDA}]}{dt} = k_0[\text{NiHEIDA}] \quad (3)$$

where

$$k_0 = k_{\text{Cu}}^{\text{NiL}}[\text{Cu}^{2+}] \quad (4)$$

The integrated form of this expression is shown in equation 5.

$$\ln[\text{NiHEIDA}]_t = \ln[\text{NiHEIDA}]_0 - k_0 t \quad (5)$$

where the subscripts  $t$  and  $0$  refer to time  $t$  and zero respectively.

The loss of NiHEIDA is equal and opposite to the gain of CuHEIDA and can be obtained from the change in absorbance as time passes. Equation 6 can be derived, see appendix, which relates the concentration of NiHEIDA

at any time to the final absorbance,  $A_f$ , the absorbance at any time,  $A_t$ , the molar absorptivities of reactants and products, and the cell path length,  $b$ .

$$[\text{NiHEIDA}] = \frac{A_t - A_f}{b(\epsilon_{\text{NiHEIDA}} + \epsilon_{\text{Cu}} - \epsilon_{\text{CuHEIDA}} - \epsilon_{\text{Ni}})} \quad (6)$$

Plots of  $-\ln(A_f - A_t)$  versus time, see Figure 1, were linear over three half lives and demonstrated that the reaction followed equation 5 and was first order in NiHEIDA. Consequently a curve fitting program was used for each determination to obtain optimum values of the observed pseudo-first-order rate constant,  $k_0$ ,  $A_f$ , and the change in absorbance that the reaction experienced,  $A_1$ . The program gave the best least squares fit to equation 7.

$$A_t = A_1 e^{-k_0 t} + A_f \quad (7)$$

The order in copper was obtained by monitoring reactions at constant pH in which the copper concentration was varied between a ten and ninety fold molar excess relative to NiHEIDA. The excess copper causes the copper concentration to be essentially constant. Table 4 lists the data. Figure 2 demonstrates the linearity of the plot obtained from the data in Table 4, establishing a first-order dependence in copper.

The dependence upon hydrogen ion was established by measuring reactions at a constant ten fold excess copper(II) concentration and varying the pH from 4.0 to 5.6, Table V lists the data. A plot of  $k_0$  corrected for copper dependent pathway versus hydrogen ion concentration, shown in Figure 3, is linear thus demonstrating first-order behavior in hydrogen ion.

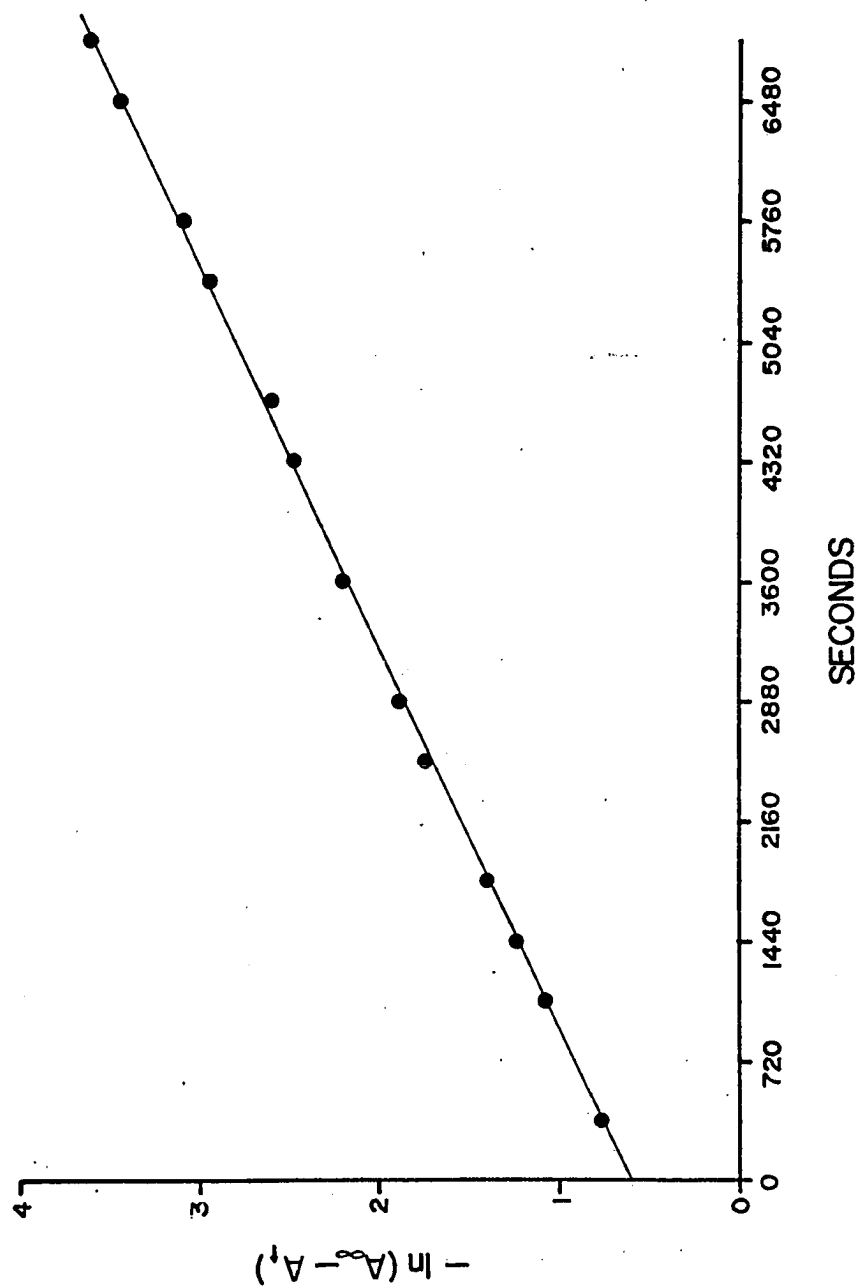


Figure 1. Typical first-order plot of  $k_0$  at constant copper concentration.



Table 4

Values of  $k_0$  as a Function of Copper(II) Concentration at  
Constant Hydrogen Ion Concentration

$T = 25.0\text{ }^\circ\text{C}$ ,  $\mu = 1.25\text{ M}$ ,  $[\text{H}^+] = 1.00(10)^{-4}\text{ M}$

$[\text{Cu}^{2+}], \text{M}$	$[\text{NiL}], \text{M}$	$k_0 \times (10)^4, \text{s}^{-1}$
$6.67(10)^{-2}$	$7.46(10)^{-4}$	$6.97 \pm .04$
$5.72(10)^{-2}$	$7.46(10)^{-4}$	$5.92 \pm .09$
$5.72(10)^{-2}$	$7.46(10)^{-4}$	$6.32 \pm .07$
$4.77(10)^{-2}$	$7.46(10)^{-4}$	$5.93 \pm .06$
$4.77(10)^{-2}$	$7.46(10)^{-4}$	$4.92 \pm .09$
$4.20(10)^{-2}$	$7.46(10)^{-4}$	$5.46 \pm .09$
$3.76(10)^{-2}$	$7.46(10)^{-4}$	$4.86 \pm .09$
$3.43(10)^{-2}$	$7.46(10)^{-4}$	$4.37 \pm .02$
$3.05(10)^{-2}$	$7.46(10)^{-4}$	$5.34 \pm .09$
$3.00(10)^{-2}$	$7.46(10)^{-4}$	$4.36 \pm .06$
$2.86(10)^{-2}$	$7.46(10)^{-4}$	$4.16 \pm .03$
$2.67(10)^{-2}$	$7.46(10)^{-4}$	$4.59 \pm .05$
$2.63(10)^{-2}$	$7.46(10)^{-4}$	$4.98 \pm .01$
$2.29(10)^{-2}$	$7.46(10)^{-4}$	$3.56 \pm .01$
$2.25(10)^{-2}$	$7.46(10)^{-4}$	$4.37 \pm .04$
$1.88(10)^{-2}$	$7.46(10)^{-4}$	$3.91 \pm .03$
$1.50(10)^{-2}$	$7.46(10)^{-4}$	$3.62 \pm .03$
$1.13(10)^{-2}$	$7.46(10)^{-4}$	$2.98 \pm .03$
$7.51(10)^{-3}$	$7.46(10)^{-4}$	$2.92 \pm .02$

Table 4 (Continued)

$[\text{Cu}^{2+}]_{\text{M}}$	$[\text{NiL}]_{\text{M}}$	$k_0 \times (10)^4, \text{s}^{-1}$
$3.76(10)^{-3}$	$7.11(10)^{-4}$	$2.52 \pm .02$
$2.86(10)^{-3}$	$7.11(10)^{-4}$	$2.27 \pm .02$
$1.91(10)^{-3}$	$9.24(10)^{-5}$	$2.03 \pm .02$
$1.72(10)^{-3}$	$9.24(10)^{-5}$	$2.27 \pm .03$
$1.53(10)^{-3}$	$9.24(10)^{-5}$	$2.27 \pm .02$
$1.43(10)^{-3}$	$9.24(10)^{-5}$	$2.04 \pm .02$
$1.14(10)^{-3}$	$9.24(10)^{-5}$	$2.44 \pm .01$
$9.53(10)^{-4}$	$9.24(10)^{-5}$	$2.48 \pm .04$

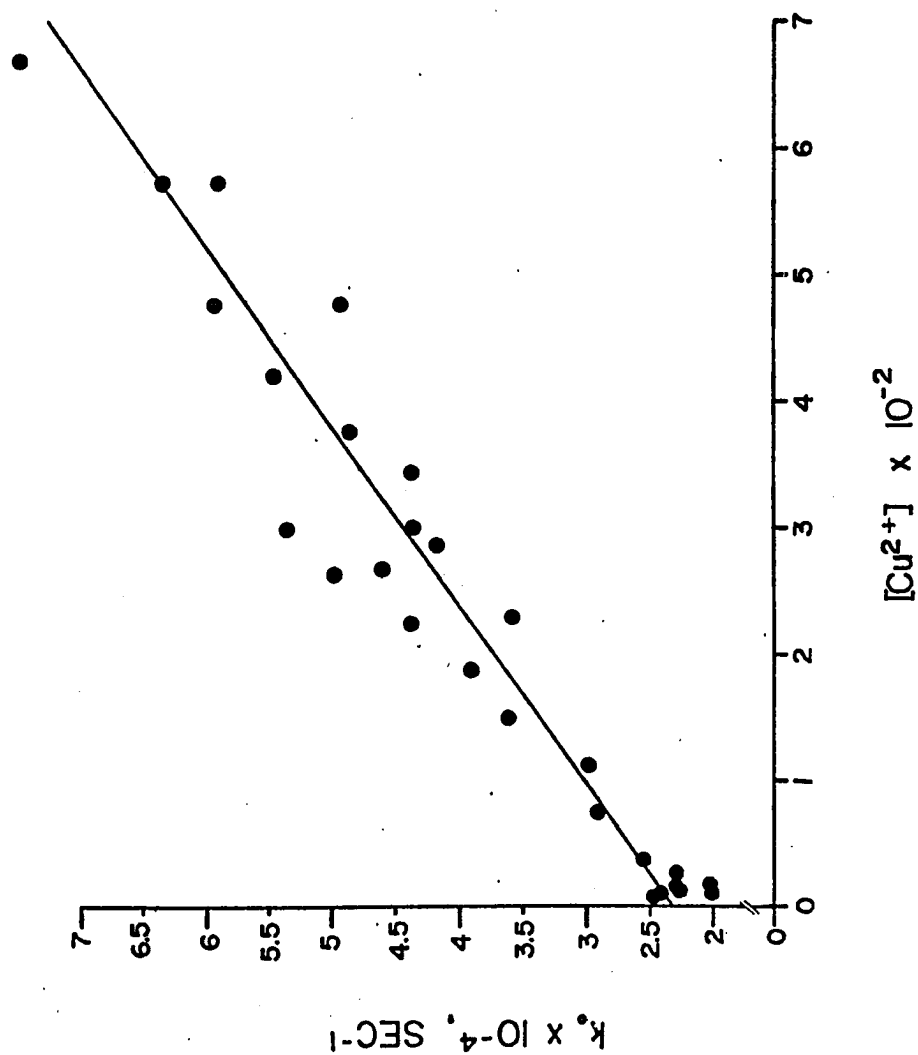


Figure 2. Effect of copper concentration on  $k_0$  at constant hydrogen ion concentration.

Table 5

Values of  $k_0$  as a Function of Hydrogen Ion Concentration  
at Constant Copper(II) Concentration

$T = 25.0\text{ }^{\circ}\text{C}$ ,  $\mu = 1.25\text{ M}$ ,  $\text{Cu}^{2+} = 3.77(10)^{-3}\text{ M}$

$[\text{NiL}] \times 10^4, \text{M}$	$[\text{H}^+], \text{M}$	$k_0 \times (10)^4, \text{s}^{-1}$
$3.46(10)^{-4}$	$2.50(10)^{-6}$	$1.07 \pm .01$
$3.46(10)^{-4}$	$3.19(10)^{-6}$	$1.18 \pm .01$
$3.46(10)^{-4}$	$4.01(10)^{-6}$	$1.15 \pm .006$
$3.46(10)^{-4}$	$5.15(10)^{-6}$	$1.19 \pm .005$
$3.46(10)^{-4}$	$7.57(10)^{-6}$	$1.23 \pm .02$
$3.46(10)^{-4}$	$8.83(10)^{-6}$	$1.15 \pm .02$
$3.46(10)^{-4}$	$1.05(10)^{-5}$	$1.26 \pm .01$
$3.46(10)^{-4}$	$1.23(10)^{-5}$	$1.22 \pm .01$
$3.73(10)^{-4}$	$1.56(10)^{-5}$	$1.23 \pm .01$
$3.73(10)^{-4}$	$1.71(10)^{-5}$	$1.25 \pm .02$
$3.73(10)^{-4}$	$1.98(10)^{-5}$	$1.27 \pm .01$
$3.73(10)^{-4}$	$2.42(10)^{-5}$	$1.32 \pm .006$
$3.73(10)^{-4}$	$3.06(10)^{-5}$	$1.53 \pm .01$
$3.73(10)^{-4}$	$3.95(10)^{-5}$	$1.68 \pm .01$
$3.73(10)^{-4}$	$5.00(10)^{-5}$	$1.73 \pm .07$
$3.73(10)^{-4}$	$6.00(10)^{-5}$	$1.88 \pm .01$
$3.73(10)^{-4}$	$7.80(10)^{-5}$	$1.84 \pm .006$
$3.73(10)^{-4}$	$8.91(10)^{-5}$	$1.94 \pm .01$
$3.73(10)^{-4}$	$9.89(10)^{-5}$	$2.30 \pm .02$

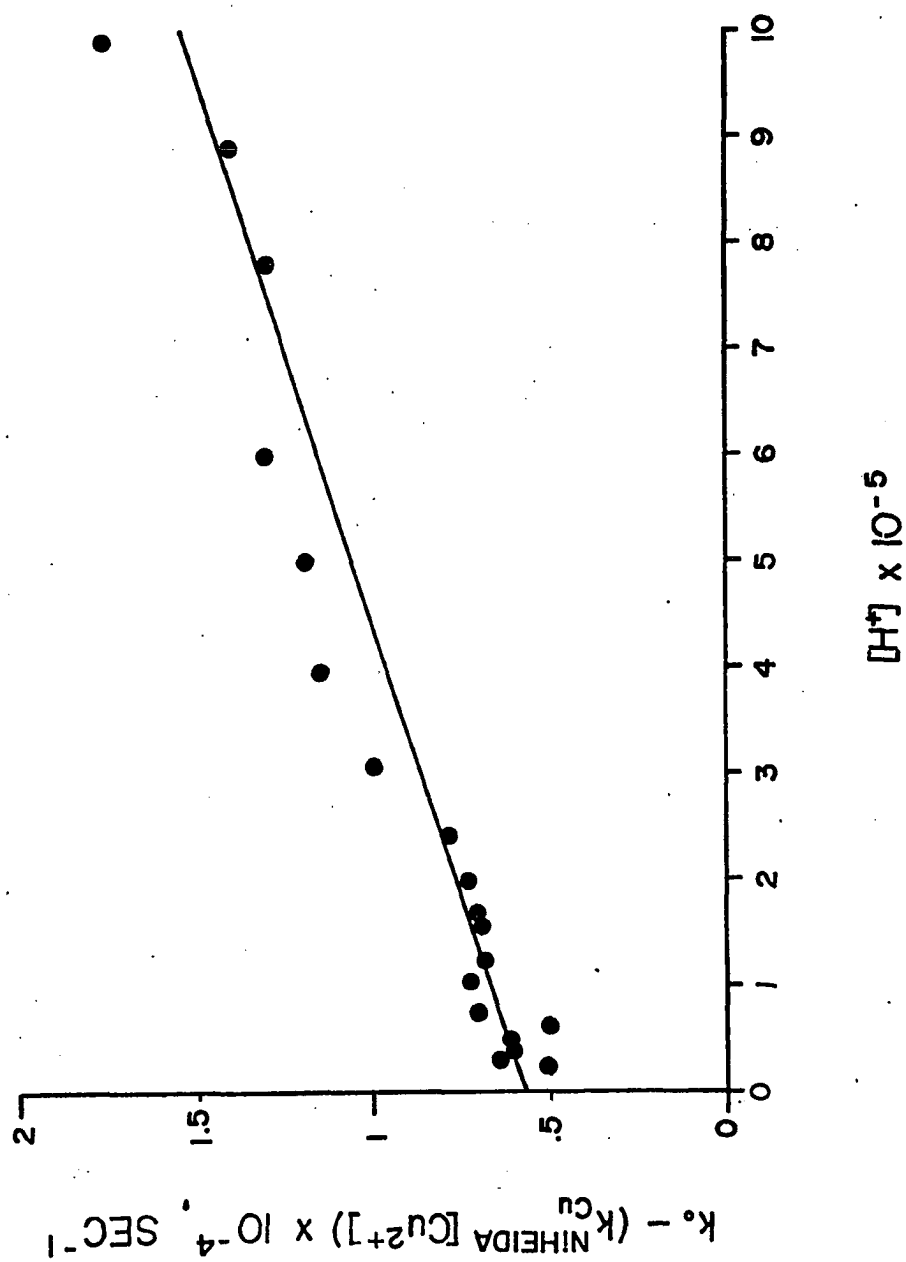


Figure 3. Effect of hydrogen ion concentration on  $k_o$  at constant copper(II) concentration

### Resolution of Rate Constants

Figures 2 and 3 show that  $k_0$  varies directly with both hydrogen and copper(II) ion concentration suggesting a copper dependent pathway and a hydrogen dependent pathway.

Figure 2, the plot of  $k_0$  versus copper(II) concentration at constant pH has a non-zero intercept suggesting either a hydrogen dependent dissociation of NiHEIDA or a hydrogen independent dissociation of NiHEIDA or both. The non-zero intercept of Figure 3, the plot of  $k_0 - (k_{\text{Cu}}^{\text{NiHEIDA}} [\text{Cu}^{2+}])$  versus hydrogen ion concentration at constant copper concentration, suggests either a copper dependent pathway or a hydrogen independent pathway or both.

The copper dependent term,  $k_{\text{Cu}}^{\text{NiHEIDA}}$ , is obtained from the slope of Figure 2. The value of  $k_{\text{Cu}}^{\text{NiHEIDA}}$ , obtained from a linear least squares analysis of the data, is  $(7.06 \pm .37) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ .

Values of  $k_0$  at a constant copper concentration, shown in Table 5, were corrected for the copper ion dependence by subtracting out the term  $k_{\text{Cu}}^{\text{NiHEIDA}} [\text{Cu}^{2+}]$ . A plot of these corrected values versus hydrogen ion concentration, shown in Figure 3 was linear. The slope of this line represents the hydrogen dependent term,  $k_{\text{H}}^{\text{NiHEIDA}}$ , and the intercept a copper and hydrogen independent dissociation term,  $k^{\text{NiHEIDA}}$ . The values obtained from linear least squares analysis are  $k_{\text{H}}^{\text{NiHEIDA}} = (1.11 \pm .06) \text{ M}^{-1} \text{ s}^{-1}$  and  $k^{\text{NiHEIDA}} = (5.71 \pm .27) \times 10^{-5} \text{ s}^{-1}$ .

The overall rate expression, as shown in equation 3 may be expressed as

$$-\frac{d(\text{NiHEIDA})}{dt} = (k_{\text{Cu}}^{\text{NiHEIDA}} [\text{Cu}^{2+}] + k_{\text{H}}^{\text{NiHEIDA}} [\text{H}^+] + k^{\text{NiHEIDA}}) [\text{NiHEIDA}] \quad (8)$$

where

$$k_0 = k_{\text{Cu}}^{\text{NiHEIDA}} [\text{Cu}^{2+}] + k_{\text{H}}^{\text{NiHEIDA}} [\text{H}^+] + k^{\text{NiHEIDA}} \quad (9)$$

Some metal exchange systems involving the copper attack on nickel complexes show a  $\text{CuOH}^+$  term which is revealed by an inverse dependence in hydrogen ion at constant copper concentration or an increase in observed rate as pH increases (30). This system did not display those characteristics, nevertheless the possible presence of a  $\text{CuOH}^+$  term was tested for by running multiple linear regression analysis of the data in Table 4 using equation 10.

$$k_0 = k^{\text{NiHEIDA}} + k_{\text{Cu}}^{\text{NiHEIDA}} [\text{Cu}^{2+}] + k_{\text{H}}^{\text{NiHEIDA}} [\text{H}^+] + k_{\text{CuOH}}^{\text{NiHEIDA}} K^{\text{CuOH}} K_w \frac{[\text{Cu}^{2+}]}{[\text{H}^+]} \quad (10)$$

where

$$[\text{CuOH}^+] = \frac{K^{\text{CuOH}} K_w [\text{Cu}^{2+}]}{[\text{H}^+]} \quad (11)$$

and

$$K^{\text{CuOH}} = \frac{[\text{CuOH}^+]}{[\text{Cu}^{2+}][\text{OH}^-]} = 2.0 \times 10^6 \quad (12)$$

A very small negative value resulted for the  $k_{\text{CuOH}}^{\text{NiHEIDA}}$  term showing it to be insignificant.

The resolved rate constants of equation 9, listed in Table 6, have been used to construct the solid lines of Figures 2 and 3. The reasonable fit of the experimental points to the lines lends confidence to the resolution of the rate constants.

Table 6

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Resolved Rate Constants

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$$k_{\text{Cu}}^{\text{NiHEIDA}} = (7.06 \pm .37) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{\text{H}}^{\text{NiHEIDA}} = 1.11 \pm .06 \text{ M}^{-1} \text{ s}^{-1}$$

$$k^{\text{NiHEIDA}} = (5.71 \pm .27) \times 10^{-5} \text{ s}^{-1}$$

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## DISCUSSION

The NiHEIDA - copper (II) reaction appears to proceed through three different pathways: (1) complete dissociation of NiHEIDA followed by attack of copper on dissociated HEIDA, the pathway represented by  $k^{\text{NiHEIDA}}$ ; (2) a proton-assisted dissociation of NiHEIDA followed by attack of copper, the pathway represented by  $k_{\text{H}}^{\text{NiHEIDA}}$ ; and (3) an attack by copper on partially dissociated NiHEIDA to yield a dinuclear intermediate, the pathway represented by  $k_{\text{Cu}}^{\text{NiHEIDA}}$ .

The structure of the dinuclear intermediate may be obtained using the same procedure followed for other similar systems (3-5). Previous work has established that the ratio of experimental rate constants for metal attack upon various nickel-ligand complexes is directly proportional to the ratio of the relative dinuclear intermediate stability constants immediately preceding the rate of determining step. Where the rate determining step for the two systems being compared involves cleavage of different ligand segments, the ration of nickel-ligand dissociation rate constants is used to account for the difference. Equation 13 illustrates the calculation.

$$\frac{k_{\text{Cu}}^{\text{NiHEIDA}}}{k_{\text{Cu}}^{\text{NiL}}} = \frac{K_{\text{r}}^{\text{NiHEIDACu}} \times k^{\text{NiHEIDA}}}{K_{\text{r}}^{\text{NiLCu}} \times k^{\text{NiL}}} \quad (13)$$

Proposed dinuclear intermediate structures for the system under study which are not correct yield relative dinuclear intermediate stability constants which, inserted in equation 13, do not give agreement with the rate constant ratio.

The relative stability constant,  $K_{\text{r}}^{\text{NiLCu}}$ , for each dinuclear intermedi-

ate is defined in terms of the CuHEIDA and the NiHEIDA segments of the intermediate structure compared to the stability constant of the initial complex, as in equation 14.

$$K^{\text{NiCu}} = \frac{K_{\text{Cu segment}} \times K_{\text{Ni segment}}}{K_{\text{Ni complex}}} \quad (14)$$

Dissociation rate constants for the various nickel species are either known ( $k^{\text{Ni(acetate)}} = 5 \times 10^3 \text{ s}^{-1}$ ) (32) or are calculated from formation rate constants (33) and stability constants (34) as shown in equations 14 and 15 for glycine and IDA respectively.

$$k^{\text{Ni(glycine)}} = \frac{k^{\text{glycine}}}{K_{\text{stability}}} = \frac{2.2 \times 10^4}{6.05 \times 10^5} = .036 \text{ s}^{-1} \quad (15)$$

$$k^{\text{NiIDA}} = \frac{k^{\text{IDA}}}{K_{\text{stability}}} = \frac{8.8 \times 10^4}{1.34 \times 10^8} = 6.6 \times 10^{-4} \text{ s}^{-1} \quad (16)$$

Electrostatic factors, arising when two different dinuclear intermediates have different charge separations, are calculated from equation 17

$$\log K_{\text{el}} = \frac{Z_A Z_B e^2}{2.3 \text{ RTDr}_{\text{AB}}} \quad (17)$$

where  $Z_A$  and  $Z_B$  are the charges,  $e$  is the charge on an electron,  $R$  is the gas constant,  $T$  the absolute temperature,  $D$  the dielectric constant of water, and  $r_{\text{AB}}$  the charge separation estimated from molecular models. Some dinuclear intermediates are favored statistically over others. Statistical and

electrostatic factors are included in the calculated ratio of relative stability constants.

The intermediate structures compared and their  $K_r$  values are presented in Table 7. Dinuclear intermediate structures having uncoordinated dentate sites were not tested since that is an unrealistic situation which has not been found in other systems. A comparison of the ratio of relative stability constants with the ratio of experimental rate constants demonstrates good agreement using structure II as the proposed dinuclear intermediate. Thus, the dinuclear intermediate which exists in the NiHEIDA - copper(II) system appears to involve an hydroxyethyl glycine segment bonded to nickel and an acetate segment bonded to copper. Nickel-nitrogen bond cleavage must be the rate-determining step since nickel-amine bonds cleave at  $6 \text{ s}^{-1}$  while nickel-acetate bonds cleave at  $5 \times 10^3 \text{ s}^{-1}$ . This is consistent with previous work involving copper(II) and nickel-aminocarboxylate complexes (3-6, 11, 20).

A mechanism which is consistent with the results obtained for the exchange reaction, as shown in equation 8, is presented in Figure 4. Protons are omitted from the mechanism for simplicity although step  $1 \rightarrow 2$  is proton dependent.

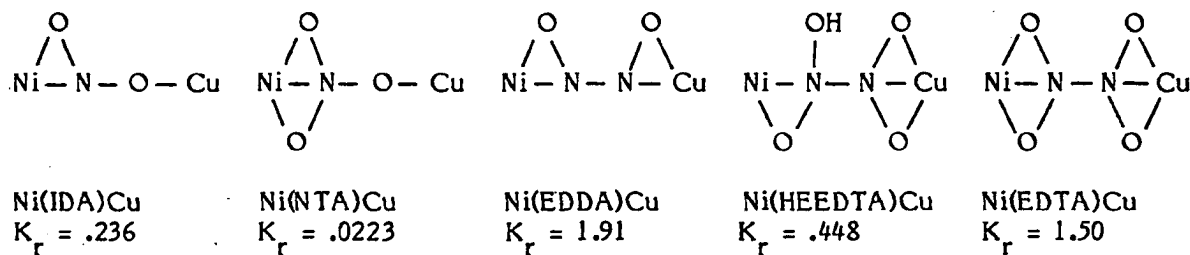
The dependence of the reaction with respect to copper will depend on the location of the rate-determining step. Steps  $2 \rightarrow 3$  and  $4 \rightarrow 5$  should not be rate-limiting as these involve formation reactions of the labile aquo-copper ion which has a rate of water loss of  $5 \times (10)^9 \text{ s}^{-1}$  (36). Step  $1 \rightarrow 2$  could not be rate limiting because it would result in zero-order behavior in copper for all pathways of the exchange. This leaves step  $3 \rightarrow 5$  as the rate-determining step for the copper dependent pathway  $k_{\text{Cu}}^{\text{NiHEIDA}}$  and step

Table 7

Comparison of NiHEIDA - Cu and NiL - Cu Reaction Intermediates<sup>a</sup>

## Part I

## Known Dinuclear Intermediates



Structures to be tested	$K_r$	$\frac{K^{Ni(HEIDA)Cu}}{K^{Ni(II)IDA}Cu}$	$\frac{K^{Ni(HEIDA)Cu}}{K^{Ni(II)NTA}Cu}$	$\frac{K^{Ni(HEIDA)Cu}}{K^{Ni(II)EDDA}Cu}$	$\frac{K^{Ni(HEIDA)Cu}}{K^{Ni(II)HEEDTA}Cu}$	$\frac{K^{Ni(HEIDA)Cu}}{K^{Ni(II)EDTA}Cu}$
I	.224	$1.33 \times 10^5$ b	$2.03 \times 10^7$ c,e,g	$1.64 \times 10^4$ b	$2.80^4$ b,g	$2.27 \times 10^5$ c,f,g
II	.037	.157	24.3 d,e,g	.0194	.0330 g	.271 d,f,g
<del><math>K^{NiHEIDA}</math> </del>		.485	5.17	.0957	.479	.49

Table 7 (Continued)

Complex	Part II	
	$K_{\text{stability}}$	$k_{\text{NiL}}, \text{M}^{-1} \text{s}^{-1}$
NiHEIDA	$2.14 \times 10^9$	$7.06 \times 10^{-3} \text{ h}$
NiIDA	$1.34 \times 10^8$	$1.48 \times 10^{-2} \text{ i}$
NiNTA <sup>-</sup>	$3.16 \times 10^{11}$	$1.39 \times 10^{-3} \text{ j}$
NiEDDA	$4.46 \times 10^{13}$	$7.5 \times 10^{-2} \text{ k}$
NiHEEDTA <sup>-</sup>	$1.25 \times 10^{17}$	$1.5 \times 10^{-2} \text{ l}$
NiEDTA <sup>-2</sup>	$3.31 \times 10^{18}$	$1.6 \times 10^{-2} \text{ m}$
NiHEG <sup>+</sup>	$1.51 \times 10^6$	
Ni(glycine) <sup>+</sup>	$6.03 \times 10^5$	
Ni(acetate) <sup>+</sup>	5.5	
CuIDA	$3.71 \times 10^{10}$	
Cu(glycine) <sup>+</sup>	$1.41 \times 10^8$	
CuHEG	$8.71 \times 10^7$	
Cu(acetate) <sup>+</sup>	52.5	

a.  $K_{\text{f}}$  values are based on the stability constants given in Part II of this table and chosen to be as internally consistent as possible with respect to temperature and ionic strength. The experimental ratios of rate constants are based upon the rate constants given in Part II at 25°C and  $\mu = 1.25 \text{ M}$ . All stability constants are taken from references (33; 34).

b.  $k^{\text{NiOAc}}/k^{\text{Nigly}} = 1.4 \times 10^5$

h. This work

c.  $k^{\text{NiOAc}}/k^{\text{NiIDA}} = 7.6 \times 10^6$

i. Reference 20

d.  $k^{\text{Nigly}}/k^{\text{NiIDA}} = 5.5 \times 10^1$

j. Reference 5

e. Statistical factor of 1.5

k. Reference 11

f. Statistical factor of 2

l. Reference 3

g. Electrostatic factor of 2.5

m. Reference 1

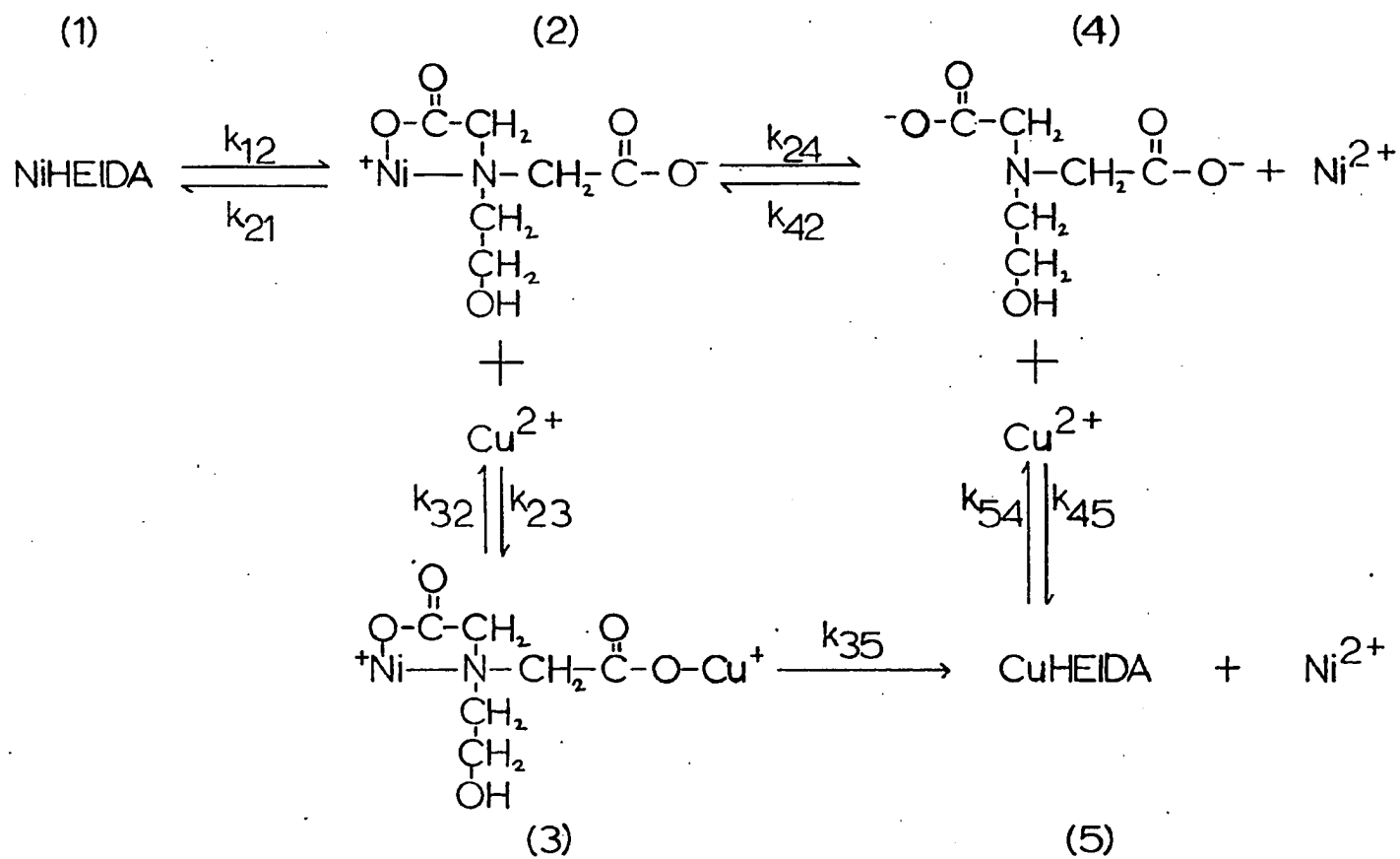


Figure 4. Mechanism for transfer of HEIDA from nickel to copper.

2  $\rightarrow$  4 as the rate determining step for the copper independent pathways  $k_{\text{H}}^{\text{NiHEIDA}}$  and  $k^{\text{NiHEIDA}}$ .

Reaction paths 1  $\rightarrow$  2  $\rightarrow$  4  $\rightarrow$  5 and 1  $\rightarrow$  2  $\rightarrow$  3  $\rightarrow$  5 both contribute to the formation of products. The former reaction path, however, is controlled by the rate of dissociation of NiHEIDA and is not dependent on copper or hydrogen ion concentration.

The reaction sequence 1  $\rightarrow$  2  $\rightarrow$  3  $\rightarrow$  5 of Figure 4 is represented by  $k_{\text{Cu}}^{\text{NiHEIDA}}$  and  $k_{\text{H}}^{\text{NiHEIDA}}$  and a general kinetic rate expression can be derived for it, as shown in equation 18.

$$\frac{-d[\text{NiHEIDA}]}{dt} = \frac{d(\text{CuHEIDA})}{dt} = k_{\text{O}}[\text{NiHEIDA}] = k_{35}[3] \quad (18)$$

Application of steady state approximations to species 2 and 3 yields the following expressions where X refers to either copper ion or hydrogen ion.

$$[2] = \frac{k_{12}[1] + k_{32}[3]}{k_{21} + k_{23}[X]} \quad (19)$$

$$[3] = \frac{k_{23}[2][X]}{k_{32} + k_{35}} \quad (20)$$

Substituting equation 19 into equation 20 gives the following expression.

$$[3] = \frac{k_{12} k_{23} [1][X]}{k_{21} k_{35} + k_{21} k_{32} + k_{23} k_{35} [X]} \quad (21)$$

Substitution of this expression into the general rate expression yields

$$\frac{-d[\text{NiHEIDA}]}{dt} = \frac{k_{12} k_{23} k_{35} [X][1]}{k_{21} k_{35} + k_{21} k_{32} + k_{23} k_{35} [X]} \quad (22)$$

where

1

$$k_O = \frac{k_{12} k_{23} k_{35} [X]}{k_{21} k_{35} + k_{21} k_{32} + k_{23} k_{35} [X]} \quad (23)$$

A comparison of terms in the denominator of equation 23 allows some simplification of the expression. The term  $k_{23} k_{35} [X]$  is at least a factor of 10 greater than  $k_{21} k_{35}$  because  $k_{23}$  is about  $10^5$  greater than  $k_{21}$  due to the difference in the rate of water loss between copper and nickel and either copper or hydrogen is always at  $9 \times 10^{-4} \text{ M}$  or greater. Comparing  $k_{21} k_{32}$  with  $k_{23} k_{35} [X]$ ,  $k_{32}$  is about  $10^7$  greater than  $k_{35}$  whereas  $k_{23}$  is only about  $10^5$  greater than  $k_{21}$ . Thus,  $k_{21} k_{32}$  becomes larger than the other two terms and equation 23 reduces to

$$k_O = \frac{k_{12} k_{23} k_{35} [X]}{k_{21} k_{32}} \quad (24)$$

which demonstrates the observed first-order dependence in both copper and hydrogen. Equation 25 gives the second-order rate constant

$$k_X^{\text{NiHEIDA}} = \frac{k_{12} k_{23} k_{35}}{k_{21} k_{32}} \quad (25)$$

Where the rate-limiting step is  $k_{35}$ .

The first-order dependence in copper and hydrogen, described by equation 24, was found to hold over the entire range of copper and hydrogen concentrations studied.

Likewise, a kinetic expression may be derived for the pathway  $1 \rightarrow 2 \rightarrow 4 \rightarrow 5$  by assuming a steady state for species 2. The expression is given in equation 26



$$k^{NiL} = \frac{k_{12}k_{24}}{k_{21} + k_{24}} \quad (26)$$

In the denominator of equation 26,  $k_{21}$  which represents nickel-acetate bond formation is much greater than  $k_{24}$  which represents nickel-glycine dissociation. Thus, equation 26 simplifies to equation 27 with  $k_{24}$  as the rate determining step.

$$k^{NiL} = \frac{k_{12} k_{24}}{k_{21}} \quad (27)$$

Further evidence for the general mechanism as expressed by equation 24 and 27 is found by calculating values of  $k^{NiL}$ ,  $k_{Cu}^{NiL}$ , and  $k_H^{NiL}$  using relative stability constants calculated from equation 13 substituted into equations 24 and 27 for the ratios  $k_{12}/k_{21}$  and  $k_{12} k_{23}/k_{21} k_{32}$  and  $0.036 \text{ s}^{-1}$ , the rate of dissociation of nickel glycine as  $k_{24}$  or  $k_{35}$ . The value of  $0.036 \text{ s}^{-1}$  is obtained from the rate of formation of nickel glycine,  $2.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and the stability constant of nickel glycine,  $6.03 \times 10^5 \text{ M}^{-1}$ . The value of  $k_{12}/k_{21}$  is equal to the relative stability constant of species 2 in Figure 4,  $7.1 \times 10^4$  and the value of  $k_{12} k_{23}/k_{21} k_{32}$  is equal to the relative stability constant of species 3 in Figure 4 with either copper or hydrogen bound to the dissociated acetate arm. When copper is bound, the value is  $3.7 \times 10^{-2}$  and when hydrogen is bound, the value is  $4.0 \times 10^1$ . The calculated rate constants are shown in Table 8. As can be seen agreement between the calculated and experimental rate constants is excellent, indicating that the general kinetic expression is correct.

It is apparent that the 2-hydroxyethyl arm of HEIDA does not play a significant role in the exchange reaction. The stability constant of N-(2-hydroxyethyl) glycine reacting with nickel is greater than that of

Table 8

Calculated Rate Constants for the NiHEIDA - Cu System		
	<u>Calculated</u>	<u>Experimental</u>
$k^{\text{NiHEIDA}}$	$8.0 \times 10^{-5} \text{ s}^{-1}$	$(5.71 \pm .27)10^{-5} \text{ s}^{-1}$
$k^{\text{NiHEIDA}}$	$4.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	$(7.06 \pm .37)10^{-5} \text{ M}^{-1} \text{ s}^{-1}$
$k^{\text{NiHEIDA}}$	$4.48 \times \text{M}^{-1} \text{ s}^{-1}$	$1.11 \pm .06 \text{ M}^{-1} \text{ s}^{-1}$

glycine reacting with nickel; the same can be said for HEIDA compared with IDA. These differences are taken into account in calculating the relative stability constants which give excellent agreement with the various rate constant ratios. Since none of the relative stability constants include a term for interaction between copper and the 2-hydroxyethyl group, it can be concluded that that group does not affect the exchange kinetics and that there is no interaction as copper attacks. Apparently, the only affect which that group has is to enhance the basicity of the amine nitrogen which strengthens the nickel-nitrogen bond.

## APPENDIX

### Concentration - Absorbance Relationship

The relationship shown in equation 6 between NiHEIDA and the absorbance at any time,  $A_t$ , the final absorbance,  $A_f$ , and the molar absorptivities of reactants and products is derived as follows. Assuming no stable intermediate to be present, which was shown by spectral scans of the reaction, the absorbance at any time is equal to the absorbance of the reactants left and the products formed. The Beer-Lambert law is assumed to hold and the following equations can be written.

$$A_t = \epsilon_{\text{NiHEIDA}} b[\text{NiHEIDA}] + \epsilon_{\text{Cu}} b[\text{Cu}^{2+}] + \epsilon_{\text{Ni}} b[\text{Ni}^{2+}] + \epsilon_{\text{CuHEIDA}} b[\text{CuHEIDA}] \quad (28)$$

$$[\text{Cu}^{2+}] = [\text{Cu}^{2+}]_f + [\text{NiHEIDA}] \quad (29)$$

$$[\text{Ni}^{2+}] = [\text{Ni}^{2+}]_f - [\text{NiHEIDA}] \quad (30)$$

$$[\text{CuHEIDA}] = [\text{CuHEIDA}]_f - [\text{NiHEIDA}] \quad (31)$$

Where f represents final. Substitution of these expressions into equation 28 and rearranging gives equation 32.

$$A_t = [\text{NiHEIDA}] b(\epsilon_{\text{NiHEIDA}} + \epsilon_{\text{Cu}} - \epsilon_{\text{Ni}} - \epsilon_{\text{CuHEIDA}}) + b(\epsilon_{\text{Cu}} [\text{Cu}^{2+}]_f + \epsilon_{\text{Ni}} [\text{Ni}^{2+}]_f + \epsilon_{\text{CuHEIDA}} [\text{CuHEIDA}]_f) \quad (33)$$

since

$$A_f = \epsilon_{\text{CuHEIDA}} b[\text{CuHEIDA}]_f + \epsilon_{\text{Ni}} b[\text{Ni}^{2+}]_f + \epsilon_{\text{Cu}} b[\text{Cu}^{2+}]_f \quad (34)$$

substitution of equation 33 into equation 32 and rearranging, yields

$$[\text{NiHEIDA}] = \frac{A_t - A_f}{b(\epsilon_{\text{NiHEIDA}} + \epsilon_{\text{Cu}} - \epsilon_{\text{Ni}} - \epsilon_{\text{CuHEIDA}})} \quad (35)$$

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