

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA**Multidentate Ligand Kinetics. IV. Copper(II) and N-Hydroxyethylethylenediaminetriacetatonicelate(II)**BY T. J. BYDALEK AND D. W. MARGERUM¹

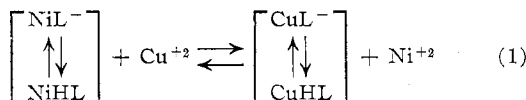
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The kinetic expression, the rate constants, and the activation energy for the copper(II) reaction with the N-hydroxyethyl-ethylenediaminetriacetate (HEEDTA) complex of nickel(II) are nearly identical with the corresponding terms for the copper(II) reaction with the ethylenediaminetetraacetate (EDTA) complex of nickel(II) despite the difference in the coordination of HEEDTA and EDTA. This kinetic behavior is consistent with previously proposed dinuclear reaction intermediates where the multidentate ligand is partially unwrapped from the nickel ion and an iminodiacetate segment is coordinated to the attacking copper ion prior to the rate-determining step. The cleavage of the nickel-nitrogen bond of the last chelate (a glycinate group) is the probable rate-determining step.

Introduction

Studies of the copper(II) reaction with nickel-EDTA² and the zinc(II) reaction with nickel-EDTA³ have indicated that the relative stability of dinuclear EDTA reaction intermediates can be related to these reaction rates. Reaction intermediates were proposed with a significant portion of EDTA unwrapped from nickel ion and with an iminodiacetate segment coordinated to the attacking metal ions before or during the rate determining step. The present study investigates the kinetic effect that the removal of one of the coordinating groups in EDTA has on this type of reaction. Replacing an acetate group on EDTA by a hydroxyethyl group gives the ligand, N-hydroxyethyl-ethylenediaminetriacetate (HEEDTA or L⁻³), and the copper attack of its nickel complex, NiL⁻, is studied. The lack of one acetate group in HEEDTA could cause a reaction rate which is much faster, much slower, or unchanged compared to EDTA and therefore the kinetic result helps to identify the most probable reaction path for this type of multidentate substitution reaction.

The system studied is



where the acid forms of the complexes are in rapid equilibrium compared to the rate of exchange of the metal ions. The rate of formation of the copper complex is

$$\frac{d[\text{CuLT}]}{dt} = k_{\text{CuNiLT}}[\text{Cu}^{+2}][\text{NiLT}] \quad (2)$$

where [CuLT] and [NiLT] refer to the sum of the concentrations of the protonated and unprotonated HEEDTA complexes at any time.

Experimental

The experimental procedures were similar to those reported previously.² A constant ionic strength of 1.25 was maintained

with NaClO₄ in order to make comparisons with the earlier kinetic results. The reactions were studied in the absence of buffers to avoid other complexing ligands, but the pH was constant during each run. The acid form of HEEDTA (L. Light and Co., Ltd.) was recrystallized twice from water before use. Solutions of NiHL and NaCuL were prepared by adding excess metal perchlorate to HEEDTA and precipitating the excess as the metal hydroxide before adjusting the solutions to pH 5.5. Solutions of NiL⁻ were standardized spectrophotometrically (285 mμ) after reaction with cyanide ion to form the tetracyanonickelate(II) complex. The molar absorptivity of CuL⁻ was determined by allowing a known amount of NiL⁻ to react with excess Cu⁺². Solutions of NaCuL were standardized spectrophotometrically at the 735 mμ absorption band of CuL⁻.

The reaction in eq. 1 was followed spectrophotometrically at 735 mμ using the molar absorptivity values given in Table I and the expressions

$$[\text{CuLT}] = \frac{A - A_i}{b(\epsilon_{\text{CuLT}} + \epsilon_{\text{Ni}} - \epsilon_{\text{Cu}} - \epsilon_{\text{NiLT}})} \quad (3)$$

and

$$A_i = b(\epsilon_{\text{NiLT}}[\text{NiLT}]_i + \epsilon_{\text{Cu}}[\text{Cu}^{+2}]_i) \quad (4)$$

where the cell length, *b*, is 2 or 5 cm., *A* is the observed absorbance, and the *i* subscript terms refer to initial conditions (zero time of reaction). There was no evidence of any stable mixed NiLCu complex. The reactions were first order in [NiLT] and first order in [Cu⁺²], giving rate constants reproducible to 8% or better. Conditions were such that the reverse reaction in eq. 1 was not appreciable in any of the runs. The possible indirect formation of CuLT which might be caused by an acid dissociation of NiLT followed by a rapid reaction between Cu⁺² and LT was negligible in all runs.

TABLE I
MOLAR ABSORPTIVITIES AT 735 mμ, μ = 1.25, 25.0°

Species	Molar absorptivity
NiL ⁻	ε _{NiL} = 2.3
NiHL	ε _{NiHL} = 1.3
CuL ⁻	ε _{CuL} = 101
CuHL	ε _{CuHL} = 48.6
Cu ⁺²	ε _{Cu} = 9.7
Ni ⁺²	ε _{Ni} = 2.1

Results

Protonation of NiL⁻ and CuL⁻.—The metal complexes of HEEDTA add a proton at low pH in a manner analogous to the EDTA complexes and it was necessary to

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(2) T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961).

(3) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).

determine the acid dissociation constants of these complexes. Figures 1 and 2 show plots of the absorbance of the Ni-HEEDTA and Cu-HEEDTA complexes as a function of pH. The nickel complex was studied at 790 $m\mu$ rather than at 735 $m\mu$, where the absorbance change is small. The concentration of NiL_T was $1.87 \times 10^{-2} M$ and below pH 2.5 excess Ni^{+2} , $1.57 \times 10^{-3} M$, was added to ensure complete complexation. The absorbance was corrected for the excess Ni^{+2} . The acid dissociation constant was evaluated from the inflection point.⁴

$$K_{NiHL} = \frac{[NiL^-][H^+]}{[NiHL]} = 2.9 \times 10^{-3} \text{ (1.25 } \mu, 25.0^\circ)$$

The effect of pH on the copper complex was studied at the same wave length used for the kinetic runs. The concentration of CuL_T was $1.87 \times 10^{-3} M$ and below pH 2.5 excess Cu^{+2} , $2.20 \times 10^{-3} M$, was present. The copper complex of HEEDTA does not protonate quite as readily as the nickel complex and both are more acidic than the corresponding EDTA complexes.

$$K_{CuHL} = \frac{[CuL^-][H^+]}{[CuHL]} = 4.8 \times 10^{-3} \text{ (1.25 } \mu, 25.0^\circ)$$

The molar absorptivities for NiHL and CuHL in Table I were calculated from these constants.

Only one proton adds to the HEEDTA complexes of copper and nickel while in the same pH range two protons add to the corresponding EDTA complexes.² This is consistent with proton addition to the acetate groups of the ligand which are either free or somewhat strained in their coordination. EDTA has two such acetate groups at opposite ends of the ligand while HEEDTA has only one.

Kinetics.—The reaction was followed with excess copper(II) at low pH to measure any contribution from the rate of acid dissociation of Ni-HEEDTA. Figure 3 shows the effect that varying the $[Cu^{+2}]$ in three runs (each in duplicate) has on the observed first-order rate constant, k_0 , where k_0 can be expressed as $k_d^{NiL_T} + k_{Cu}^{NiL_T}[Cu^{+2}]$. The reactions gave excellent plots with a first-order dependence in $[NiL_T]$ and the straight line in Fig. 3 indicates a first-order dependence in $[Cu^{+2}]$. The fact that the intercept is zero means that $k_d^{NiL_T}$ can be neglected under these conditions. The rate of acid dissociation also was negligible for all the other runs since this was the lowest pH used.

Table II summarizes the values found for the second-order rate constant, $k_{Cu}^{NiL_T}$, at a variety of pH values and of concentration ratios. The value of $k_{Cu}^{NiL_T}$ ($0.015 M^{-1} \text{ sec.}^{-1}$) is the same as that found in Fig. 3 and it is independent of $[H^+]$ from pH 2.5 to 5.0.

The rate also can be expressed as

$$\frac{d[CuL_T]}{dt} = k_{Cu}^{NiL}[Cu^{+2}][NiL^-] + k_{Cu}^{NiHL}[Cu^{+2}][NiHL]$$

but as before² we find that k_{Cu}^{NiL} and k_{Cu}^{NiHL} must essentially be identical and equal to $k_{Cu}^{NiL_T}$.

The temperature dependence of k_{Cu}^{NiL} was measured at pH 5.0, where the protonation of NiL^- can be

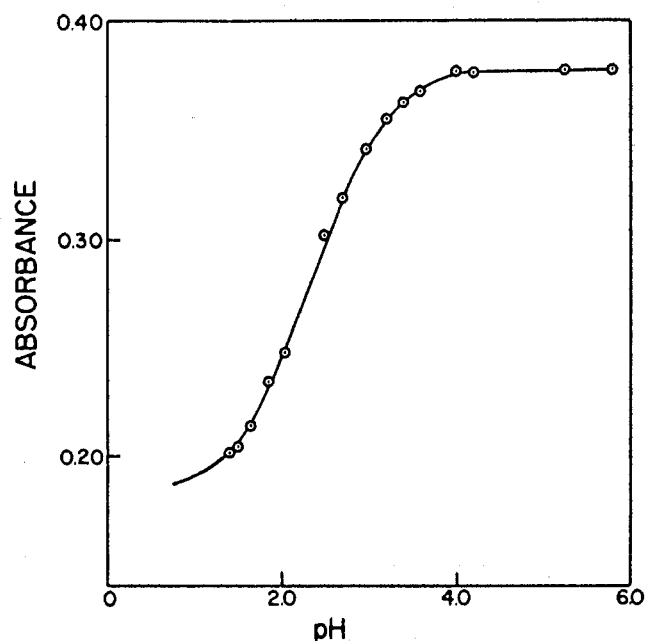


Fig. 1.—Protonation of the Ni-HEEDTA complex causes its absorbance (corrected for other species) to decrease at 790 $m\mu$. The pK_{NiHL} value from these data is 2.54: $[NiL_T] = 1.87 \times 10^{-2} M$, Ni^{+2} added at low pH, 5-cm. cell, 25.0° , $\mu = 1.25$.

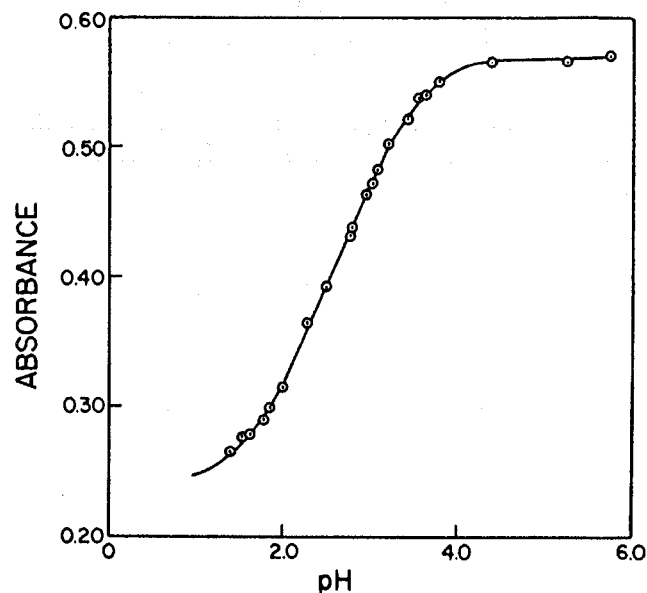


Fig. 2.—Protonation of the Cu-HEEDTA complex causes its absorbance (corrected for other species) to decrease at 735 $m\mu$. The pK_{CuHL} value from these data is 2.32: $[CuL_T] = 1.87 \times 10^{-3} M$, Cu^{+2} added at low pH, 2-cm. cell, 25.0° , $\mu = 1.25$.

TABLE II
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF Cu^{+2}
AND NiL_T AT 25.0° , $\mu = 1.25$

pH	$[NiL_T]_i$ $\times 10^3$	$[Cu^{+2}]_i$ $\times 10^3$	$k_{Cu}^{NiL_T}$, $M^{-1} \text{ sec.}^{-1}$
5.05	0.468	6.60	0.0147
4.41	.468	6.60	.0143
3.90	.468	6.60	.0152
3.75	.468	6.60	.0148
3.50	.936	6.60	.0152
2.85	.468	6.60	.0152
3.70	2.81	11.0	.0143
3.25	4.68	11.0	.0145
3.30	2.81	2.20	.0142

Av. .015

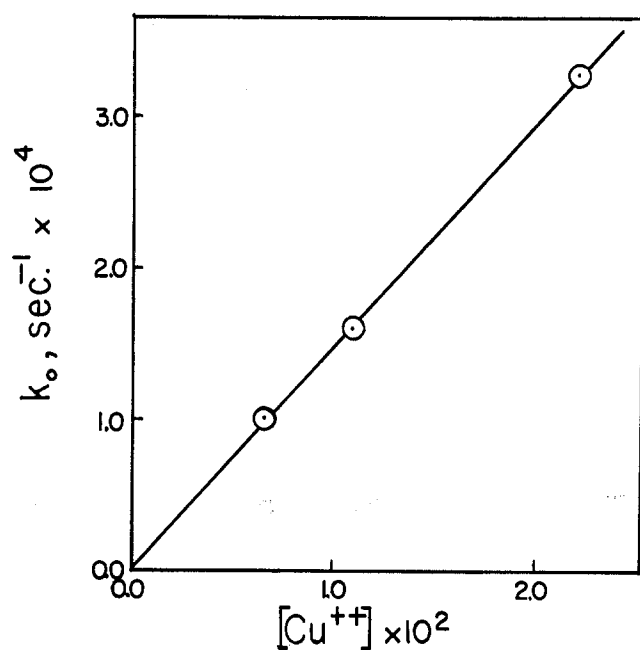


Fig. 3.—Variation of excess copper ion concentration in its reaction with nickel-HEEDTA shows the linear dependence of the observed first-order rate constant with $[Cu^{+2}]$. The intercept indicates a negligible copper-free rate path under these conditions and the over-all reaction is first order in $[NiL_T]$ and in $[Cu^{+2}]$: pH 2.55, $\mu = 1.25$, 25.0° , $[NiL_T] = 4.68 \times 10^{-4} M$, and 14 to 47-fold excess of $[Cu^{+2}]$.

neglected. The results given in Table III follow the Arrhenius expression and give an E_a value of 17.4 kcal./mole.

TABLE III
TEMPERATURE DEPENDENCE

Temp.	$k_{Cu^{NiL}}$, $M^{-1} \text{ sec.}^{-1}$
12.0°	0.0035
25.0°	.015
35.0°	.033
Kinetic Parameters	
E_a , kcal.	17.4
A , $M^{-1} \text{ sec.}^{-1}$	7.5×10^{10}

Equilibrium Constant.—The equilibrium constant, $K = [CuL^-][Ni^{+2}]/[NiL^-][Cu^{+2}]$, determined spectrophotometrically for solutions ranging from pH 4.2 to 5.2, gave an average value of 2.0 (25.0° , $\mu = 1.25$). This is in good agreement with the known stability constants of NiL^- and CuL^- , $10^{17.0}$ and $10^{17.4}$, respectively, measured at 29.6° in 0.1 M KCl.⁵

Discussion

The general kinetic expressions for the reaction of copper with nickel-HEEDTA and the reaction of copper with nickel-EDTA are the same. Neither reaction shows an appreciable pH effect. The rate constant for the HEEDTA reaction is $0.015 M^{-1} \text{ sec.}^{-1}$, while it is $0.016 M^{-1} \text{ sec.}^{-1}$ for the EDTA reaction. The activation energies are 17.4 and 18.0 kcal./mole, re-

spectively. Thus, despite the lack of one acetate group in HEEDTA it behaves in a nearly identical manner with EDTA in the nickel to copper exchange. In the zinc and copper ion attack of nickel-EDTA complexes it has been proposed that reaction intermediates exist with the attacking metal ion bonded to an iminodiacetate segment.^{2,3} In a subsequent paper we will show that the copper ion reaction with 1,2-diaminocyclohexanetetraacetatonickelate(II) is zero order in copper concentration.⁶ The complete lack of copper attack in this case is attributed to the cyclohexane ring, which prevents the formation of a dinuclear iminodiacetate type intermediate. Thus, there is strong support for this portion of the mechanism. In the present comparison of HEEDTA and EDTA the form of the dinuclear intermediate close to the transition state can be considered. Table IV indicates the structures of some possible reaction intermediates which have been chosen on the basis that: (1) five-membered chelate rings are most stable; (2) the large kinetic effect of copper ion cannot be explained by coordination only to an acetate group and, therefore, at least one nitrogen atom must break from nickel before the transition state; (3) since copper forms bonds rapidly compared to the breaking of nickel bonds, copper will coordinate to an entire iminodiacetate segment of EDTA after the first nickel nitrogen bond is broken; (4) any possible bonding stability in the alcoholic group of HEEDTA is not significant compared to the other groups⁷; and (5) comparison between the EDTA and HEEDTA structures is possible because the rate step involved in breaking bonds to nickel will be the same for these very similar complexes.

The experimental rate constants can be written as the product of the stability constant of a reaction intermediate, K_{NiYC_u} , and the rate constant for breaking nickel ion away from this intermediate, k^{NiYC_u} .

$$k_{Cu^{NiY}} = K_{NiYC_u} k^{NiYC_u} \quad (5)$$

$$k_{Cu^{NiL}} = K_{NiLC_u} k^{NiLC_u} \quad (6)$$

The structures of reaction intermediates in Table IV are grouped so the bonding to nickel is the same and, therefore, the dissociation rate constants k^{NiYC_u} and k^{NiLC_u} are equal. Equations 5 and 6 then indicate that the ratio of the experimental rate constants are directly proportional to the ratio of the intermediate stability constants as given in eq. 7.

$$\frac{k_{Cu^{NiY}}/k_{Cu^{NiL}}}{\left(\frac{\text{Rate constant ratio}}{\text{Intermediate stability constant ratio}}\right)} = \frac{K_{NiYC_u}}{K_{NiLC_u}} \quad (7)$$

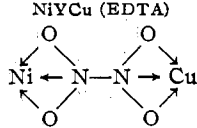
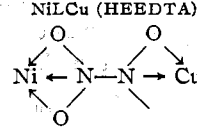
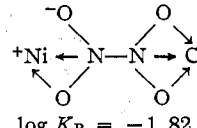
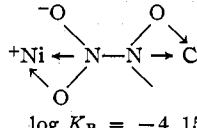
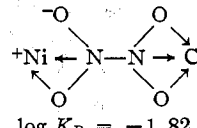
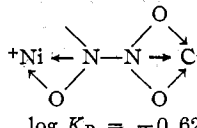
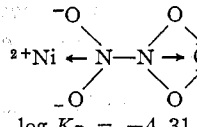
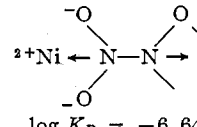
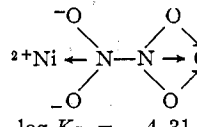
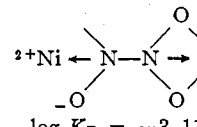
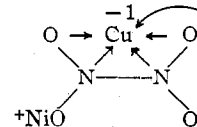
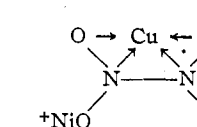
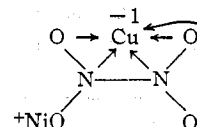
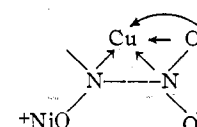
The restriction in the use of eq. 7 is that the bonding to nickel must be the same and thus it cannot be used to compare a structure in group II to one in group III. It is possible to estimate the actual values of K_{NiYC_u} and

(6) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).

(5) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

(7) $Ni(en)^{+2}$ is more stable than the Ni^{+2} complex of N,N,N',N' -tetraakis-(2-hydroxyethyl)-ethylenediamine: K. H. Pearson and K. H. Gayer, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, p. 26N. Similarly, the 1:1 copper triethanolamine complex is no more stable than the copper amine (ref. 5).

TABLE IV
POSSIBLE STRUCTURES AND RELATIVE STABILITIES OF NiYCu AND NiLCu REACTION INTERMEDIATES^a

Structure	Ni bonding in intermediate before transition state	NiYCu (EDTA)	NiLCu (HEEDTA)	Intermediate stability constant ratio K_{NiYCu}/K_{NiLCu}
I	Iminodiacetate	 $\log K_R = 1.62$	 $\log K_R = -0.71$	430
		statistical factor of 2		
II	Glycinate	 $\log K_R = -1.82$	 $\log K_R = -4.15$	430
		statistical factor of 2		
	B	 $\log K_R = -1.82$	 $\log K_R = -0.62$	0.8
		$\log K_{el} = +0.5$, statistical factor of 4		
III	Amine	 $\log K_R = -4.31$	 $\log K_R = -6.64$	430
		statistical factor of 2		
	B	 $\log K_R = -4.31$	 $\log K_R = -3.11$	0.4
		$\log K_{el} = +0.5$, statistical factor of 2		
IV	A	 $\log K_R = -0.1$	 $\log K_R = -0.4$	10
		$\log K_{el} = +0.4$, statistical factor of 2		
	B	 $\log K_R = -0.1$	 $\log K_R = -0.1$	10
		$\log K_{el} = +0.4$, statistical factor of 4		

^a K_R values are based on the following stability constants which have been chosen from ref. 5 to match temperature and ionic strengths as nearly as possible

Complex	$\log K$
NiY ⁻²	18.2 ^b
NiL ⁻	17.0
CuY ⁻²	18.4 ^b
CuL ⁻	17.4
Intermediate metal segment	$\log K_M$ segment
Ni(iminodiacetate)	8.73 ^c
Cu(iminodiacetate)	11.09 ^c
Ni(glycinate) ⁺	5.29 ^d
Cu(glycinate) ⁺	7.56 ^d
Ni(NH ₃) ⁺²	2.8
Ni(acetate) ⁺	0.7
Cu(N,N-ethylenediamine-diacetate)	15.9
Cu(N,N'-ethylenediamine-diacetate)	16.2

^b These EDTA values are corrected to match the constants calculated for HEEDTA [S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955)]. They correspond to work which used the same experimental techniques [G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951)] and are corrected for the 10° temperature difference [R. G. Charles, *J. Am. Chem. Soc.*, **76**, 5854 (1954)]. ^c Values are based on methyliminodiacetate complexes. ^d Values are based on hydroxyethylethylaminoacetate as a model.

K_{NiLCu} but since their ratios are to be used it is more convenient to use relative values for these constants. The relative stability (K_R) of each structure can be defined in terms of the equilibrium stability constants of the copper and nickel segments compared to the equilibrium stability of the initial nickel complex.⁸

$$K_R = \frac{K_{\text{Cu segment}} K_{\text{Ni segment}}}{K_{\text{Ni complex}}} \quad (8)$$

The K_R values from eq. 8 are larger than the expected stability of the intermediate because some important electrostatic and entropy terms are not included. For the most part these terms are common to both the EDTA and the HEEDTA intermediates and cancel one another. For example a common electrostatic repulsion in the ${}^2+\text{Ni}-\text{N}-\text{C}-\text{C}-\text{N}-\text{Cu}^{+2}$ bond system exists for most structures. On the other hand, differences in the electrostatic attraction of the glycinate and iminodiacetate segments are incorporated in the values of $K_{\text{M segment}}$.

In some structure comparisons an electrostatic attraction helps to stabilize one structure relative to the other. In these cases the additional stability can be estimated using eq. 9.

$$\Delta E_{\text{electrostatic}} = \frac{Z_A Z_B e^2}{D r_{AB}} = 2.3RT \log K_{el} \quad (9)$$

Thus, for the IIB EDTA structure there is a net attraction of the unbound acetate group for the nickel glycinate group which does not exist in the IIB HEEDTA structure. A value of $\log K_{el} = 0.5$ is obtained for this case using an r_{AB} value estimated from the models as 6 Å. and the dielectric constant for water.

All the EDTA intermediate structures are favored statistically over the HEEDTA structures. In the IIB structures, for example, nickel and copper can form the EDTA intermediate in four equivalent ways but can form the HEEDTA intermediate in only one way. The right-hand column in Table IV gives the ratio of the stability constants of the intermediates calculated from the K_R , K_{el} , and statistical factors. The stability constants used to calculate the K_R values are summarized in Table IV. Substituted derivatives of iminodiacetic acid and glycine were chosen to give better models but the general conclusions discussed below hold for any consistent set picked for the metal-segment models.

The intermediate structure most representative of the reaction mechanism should have a $K_{\text{NiYCu}}/K_{\text{NiLCu}}$ value close to the experimental ratio of 1:1 for the rate constants in accordance with eq. 7. On this basis structures I, IIA, and IIIA can be eliminated and IVA and IVB are unlikely. Before considering the remaining structures an estimate of the relative rate constants for nickel-amine and nickel-acetate bond cleavage is helpful. According to Eigen⁹ the formation rates of nickel acetate and nickel amine depend on the outer

sphere association of the metal and the ligand and the rate of loss of coordinated water from nickel. The relative dissociation rates of the acetate complex and the amine complex can be estimated from their equilibrium stability constants and the relative outer sphere electrostatic attraction of acetate and amine for nickel. Without the electrostatic term it can be shown that the nickel-acetate cleavage is at least 130 times faster than the nickel-amine cleavage and when the electrostatic term is added this ratio is over 400. Using a value of 5.8 sec.⁻¹ for the Ni-N dissociation rate constant,¹⁰ the nickel acetate dissociation rate constant must be greater than 2.3×10^3 sec.⁻¹. This eliminates structures IVA, IVB, and an acetate cleavage in IIB because the k^{NiYCu} values would be so large that reasonable values could not be assigned to K_{NiYCu} (see eq. 5). Thus, structures IVA and IVB might follow but do not precede the transition state. Nitrogen-nickel cleavage in the IIB structures and in the IIIB structures are possible mechanisms. However, the value of 5.8 sec.⁻¹ for Ni-N cleavage gives a reasonable fit for IIB but not for IIIB, where the K_{NiYCu} value would have to be much greater than the K_R value in order to fit and this, of course, is not reasonable. Thus, the IIB structures fit the observed data best and are the preferred mechanism.

The conclusion is that copper attacks the nickel complex by coordinating to the released dentate groups until only a nickel-glycinate chelate remains and then the rate-determining step is the nickel-nitrogen bond cleavage. A most important factor in the rate of the reaction is the stability of the copper segment of the dinuclear intermediate. Thus, copper ties up the three-dentate end of HEEDTA rather than the two-dentate end. At first this appears anomalous because the two-dentate end should be more labile than the three-dentate end. However, the latter segment gives a more stable copper intermediate and copper ion is sufficiently rapid in its reactions compared to nickel to form the most stable intermediate prior to the breaking of the last nickel-chelate bond.

Another case which at first appears anomalous is the relative rate of nickel ion reaction with zinc-EDTA and copper-EDTA. These rate constants^{2,3} are compared in Table V. The first impression in comparing these reactions is that nickel should react faster with the less stable and more labile zinc-EDTA complex. Actually, nickel reacts 15.7 times faster with the copper-EDTA complex. The reason for this behavior becomes clear if again the stability of the intermediates is considered relative to the reactants. In this case the attacking metal ion is the more sluggish and the rate step should be the formation of the nickel-nitrogen bond. The zinc-EDTA or copper-EDTA must unwrap sufficiently to free a nitrogen that can coordinate to nickel. The intermediate stabilities that must be considered are based on the stability of the iminodiacetate segment of EDTA which remains bonded to copper or zinc rela-

(8) It is necessary to use the same reference states for all these comparisons and the unprotonated ligand and aquo metal ion are the reference states.

(9) M. Eigen, in S. Kirschner, Ed., "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N.Y., 1961, pp. 371-378.

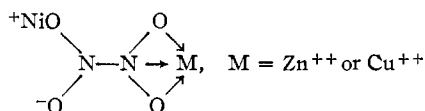
(10) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963)

tive to the initial complex. These are compared in Table V and give a predicted kinetic ratio of 14, in excellent agreement with the experimental ratio of 15.7. Copper-EDTA is more labile to nickel attack than zinc-EDTA because its iminodiacetate segment is much more stable than the iminodiacetate segment with zinc.

TABLE V
COMPARISON OF NICKEL ATTACK ON COPPER-EDTA AND ZINC-EDTA

$$\frac{k_{\text{Ni}}^{\text{CuY}}}{k_{\text{Ni}}^{\text{ZnY}}} = \frac{10.5 \times 10^{-3} M^{-1} \text{sec.}^{-1}}{0.67 \times 10^{-3} M^{-1} \text{sec.}^{-1}} = 15.7$$

Model



Kinetic ratio based on the relative stabilities of intermediates

$$\frac{K_{\text{CuYNi}}}{K_{\text{ZnYNi}}} = \frac{10^{11.09-13.79}}{10^{7.66-16.50}} = 10^{1.14} = 14$$

Similarly, for the reverse reaction to that studied here, the rate constant $k_{\text{Ni}}^{\text{CuL}}$ (calculated from the forward rate constant and the equilibrium constant for reaction 1) is $7.5 \times 10^{-4} M^{-1} \text{sec.}^{-1}$, which compared to $k_{\text{Ni}}^{\text{CuY}}$ gives a ratio of 0.71. On the basis of the proposed mechanism this ratio is 0.8. Copper-EDTA is more

$$\frac{k_{\text{Ni}}^{\text{CuL}}}{k_{\text{Ni}}^{\text{CuY}}} = \frac{\left(\frac{K_{\text{CuIMDA}K_{\text{NiOAc}}}}{K_{\text{CuL}}}\right)}{\left(\frac{K_{\text{CuIMDA}K_{\text{NiOAc}K_{\text{el}}}}}{K_{\text{CuY}}}\right)} = \frac{10^{18.4}}{4 \times 10^{17.4} \times 10^{0.5}} = 0.8 \quad (10)$$

stable thermodynamically but is less stable kinetically because of the greater stability of the nickel intermediate prior to the first nickel-nitrogen bond formation.

In conclusion, simple models of dinuclear reaction intermediates and their estimated relative stabilities give a satisfactory detailed analysis of several multidentate ligand kinetic systems. These models suggest that a labile metal ion attacking a sluggish EDTA type complex can be expected, in general, to form as strong an intermediate complex as possible short of breaking the last nitrogen bond of the ligand to the sluggish metal ion. When a sluggish metal ion attacks a labile complex the situation can be expected to be reversed so that the first nitrogen bond formation is rate determining and the labile complex must first unwrap sufficiently to provide a free nitrogen. Steric hindrance in the multidentate ligand can prevent some of the stronger intermediate complexes from forming and lead to a very sluggish exchange of the ligand between two metal ions.⁶

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Multidentate Ligand Kinetics. V. Copper(II) and Cyclohexylenediaminetetraacetatonickelate(II)

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The kinetics of the substitution reaction between the hydrated copper(II) ion and the cyclohexylenediaminetetraacetatonickelate(II) ion are studied from pH 1.5 to 3.5. In contrast to the dominant role of copper ion attack in the similar reaction with ethylenediaminetetraacetatonickelate(II), there is no copper ion attack of cyclohexylenediaminetetraacetatonickelate(II). The reaction is first order in the complex and independent of copper concentration but it is highly pH dependent. The acid dissociation rate constants are resolved. The absence of any copper dependence is attributed to the inability of the ion to form dinuclear iminodiacetate intermediates because of hindered rotation and steric blocking due to the hydrocarbon ring. The proposed mechanism indicates that nickel-nitrogen bond dissociation must be a rate-determining step in these multidentate ligand exchange reactions.

Introduction

In order to determine the steric requirements in the substitution reactions of metal ions with metal complexes of the EDTA type, the reaction of copper(II) with the nickel complex of *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CyDTA)^{1,2} is examined. Models show that the cyclohexane ring prevents the full rotation of the two iminodiacetate segments of the ligand and these segments cannot face in

opposite directions. With this restriction it is not possible to bond a different metal ion to each iminodiacetate segment of CyDTA although such reaction intermediates are possible with EDTA.^{3,4} In paper IV of this series⁵ a mechanism was presented suggesting that copper reaction with the nickel complex of EDTA (and HEEDTA) proceeds through a dinuclear intermediate with an iminodiacetate group bonded to copper and a glycinate group bonded to nickel. The rate-determining

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