increase in the electron density would be expected to accelerate the rate of reaction.

Treatment of the data given by Hudson and Klopman[21] for the rate of reaction of substituted thiophenols with benzyl bromide gives a ρ of -0.64. A comparison of the magnitude of ρ obtained for the reactions of the free mercaptan and the coordinated mercaptan show that in the latter case a more pronounced substituent effect is observed. ρ obtained for the coordinated 8-mercaptoquinoline series indicates that a stronger electron demand is being made by the sulfur atom in the transition state. A strong electron demand would be required if the alkyl halide possessed an appreciable positive charge prior to reaching the transition state.

The data in hand are consistent with the mechanism proposed by Busch and coworkers[1] and subsequently supported by steric hindrance studies[2] and solvent-dependence studies.[22] Coordination of the alkyl halide through the halogen bond is indicated since it has been possible to force the reaction to deviate from the normal pseudo-first-order dependence at high concentrations of alkyl halide for *N*-alkyl-2-aminoethanethiol nickel complexes.[2,16] The steric constraints imposed by the *N*-alkyl groups impede the coordination of the halogen of the incoming group. Distances of closest approach in the transition state estimated from the dielectric

dependence for bis(8-mercaptoquinoline)nickel(II) reactions with methyl iodide are in agreement with this postulate.[22]

Furthermore, a highly polarized carbon-halogen bond, as evidenced by the large negative value of ρ, in the vicinity of a nucleophile such as the coordinated sulfur atom on the nickel, strongly intimates a four-centered transition state; *i.e.*, the nickel is simultaneously polarizing the alkyl halide and acting as a template to hold the reactive centers in close proximity. Such a transition state would call for large negative entropies of activation and a relatively fast reaction in the case of the 7-methyl derivative, since the incoming group approaches the sulfur away from its shielded side. Both of these demands of the postulate are met.

(21) A. Hudson and G. Klopman, *J. Chem. Soc.*, 672 (1962).
(22) J. A. Burke and S. E. Campbell, *J. Inorg. Nucl. Chem.*, 33, 1163 (1971).

Metal-Exchange Reaction between Ethylenediaminediacetatonickelate(II) and Copper(II)

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The reaction between copper(II) and ethylenediaminediacetatonickelate(II) was studied between pH 3.2 and 5.0 over a 70-fold variation in copper concentration at an ionic strength of 1.25 and a temperature of 25°. The reaction order in ethylenediaminediacetatonickelate(II) is first while that for copper varied from first to zero and then back to first as the copper concentration increased. At low copper concentration, the first-order rate constant is pH independent and represents the attack of copper on the nickel complex through a pathway in which EDDA is half unwrapped before reaction with copper. Evidence is given for a stepwise unwrapping mechanism followed by copper attack to give a dinuclear intermediate. The zero-order rate is pH dependent. At high copper concentrations, the shift back to another first-order copper dependence is due to the formation of a weak copper-ethylenediaminediacetatonickelate complex which then goes through the dinuclear intermediate to give products. A general mechanism is presented which is consistent with all the kinetic data.

Introduction

Multidentate ligand transfer between two metal ions, as represented by eq 1, has been subject of extensive study for

$$M + M'L \rightleftarrows M' + ML \qquad (1)$$

a variety of metal ion combinations and aminocarboxylate ligands under many different conditions, using many different methods.[1-11] Detailed studies have shown the mechanism

of these reactions to follow the successive breaking of a series of coordinate bonds from the metal-ligand complex, fol-

(1) T. J. Bydalek and D. W. Margerum, *J. Amer. Chem. Soc.*, 83, 4326 (1961).
(2) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, 1, 852 (1962).
(3) T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, 2, 678 (1963).
(4) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, 2, 683 (1963).
(5) T. J. Bydalek and M. L. Blomster, *Inorg. Chem.*, 3, 667 (1964).
(6) T. J. Bydalek and H. Constant, *Inorg. Chem.*, 4, 833 (1965).

(7) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Amer. Chem. Soc.*, 87, 4464 (1965).
(8) D. W. Margerum, B. A. Zabin, and D. L. Janes, *Inorg. Chem.*, 5, 250 (1966).
(9) D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, 6, 283 (1967).
(10) G. F. Smith and D. W. Margerum, *Inorg. Chem.*, 8, 135 (1969).
(11) See the following papers and references contained therein:
(a) N. Tanaka, H. Osawa, and M. Kamoda, *Bull. Chem. Soc. Jap.*, 36, 530 (1963); (b) G. A. Rechnitz and Z. F. Lin, *Anal. Chem.*, 39, 1406 (1967); (c) B. Bosnich, F. P. Dwyer, and A. M. Sargeson, *Aust. J. Chem.*, 19, 2213 (1966); (d) S. S. Krishnan and R. E. Jervis, *J. Inorg. Nucl. Chem.*, 28, 1973 (1967); (e) N. Tanaka and M. Kimura, *Bull. Chem. Soc. Jap.*, 40, 2100 (1967); (f) J. R. Kuempel and W. B. Schapp, *Inorg. Chem.*, 7, 2435 (1968); (g) B. Wiseall and C. Balcombe, *J. Inorg. Nucl. Chem.*, 32, 1751 (1970); (h) M. Kimura, *Bull. Chem. Soc. Jap.*, 43, 1594 (1970); (i) R. R. Dias, T. R. Bhat, and J. Shankor, *Indian J. Chem.*, 8, 997 (1970).

lowed by a stepwise coordination to the attacking metal.[1-3,5-8] This process leads to the formation of a dinuclear intermediate found in all cases where sterically possible,[4,9,10] followed by breakup to form products. The position of the rate-determining step is a function of pH, attacking metal concentration,[7] the relative stability of the intermediate metal segments,[3] and the relative rates of water loss of the metals involved.[8] In some cases, the ratio of rate constants of two systems can be approximated by the ratio of relative stability constants for the dinuclear intermediates involved.[3] In one case, a change in attacking metal concentration and hydrogen ion concentration caused several shifts in the rate-determining step.[7]

In this investigation, the reaction studied is given by eq 1 where M is copper(II) and M'L is ethylenediaminediacetato-nickelate(II) ($NiEDDA^{2+}$). The study was undertaken to investigate the effect of dentate number and the generality of the unusual kinetic dependence of reaction order upon metal ion concentration thus far seen only in the reaction of copper(II) and ethylenediaminetetraacetonickelate(II) ($NiEDTA^{2+}$).[7] Further, since ethylenediaminediacetate (EDDA) has only one acetate group per nitrogen compared to two for EDTA, it was of interest to see if a weakly bonded NiEDDACu species involving only an acetate bond to copper was present as is the case with the NiEDTA-copper system at high copper concentrations. Due to the similarity of the ligands, it is not surprising that the results of the present study fit the mechanism of the NiEDTA-copper system. Interesting differences are found between the two systems at high copper concentrations involving the weakly bonded NiEDDACu species.

Experimental Section

Reagents. EDDA was obtained from K and K Laboratories and purified twice by recrystallization from a hot basic solution by adding perchloric acid and cooling. It was standardized by a mole ratio plot against standard copper(II) at 670 nm and pH 5.0. Solutions of $Cu(ClO_4)_2$ and $Ni(ClO_4)_2$ were prepared from G. F. Smith metal salt hexahydrates and standardized by titration with EDTA.

Solutions of CuEDDA and NiEDDA were prepared by adding a 5% molar excess of copper or nickel perchlorate to a standard solution of EDDA followed by the addition of NaOH to pH 10.5. The excess metal hydroxide was filtered and the pH of the solution was adjusted to 7. The NiEDDA solution was standardized spectrophotometrically both by the determination of the nickel content, using NaCN to form $Ni(CN_4)^{2-}$, and by comparison to a standard solution of NiEDDA prepared from standard $Ni(ClO_4)_2$ and an excess of EDDA.The CuEDDA solutions were standardized spectrophotometrically by comparison to a standard CuEDDA solution prepared from standard $Cu(ClO_4)_2$ and an excess of EDDA.

All other chemicals were reagent grade and used without further purification. All solutions were prepared with deionized distilled water. The ionic strength was maintained at 1.25 in all measurements using $NaClO_4$.

Equilibrium and Kinetic Measurements. All pH measurements were made on a Beckman Model 110 Research pH meter with a NaCl reference electrode. All spectrophotometric measurements were made on a Cary Model 14 spectrophotometer.

A spectral study of all reactants and products showed the greatest change in molar absorptivity between reactants and products to be at 670 nm. All kinetic measurements were made at this wavelength. The molar absorptivities of reactants and products at 670 nm, μ = 1.25 M, and 25° are as follows: $Ni(ClO_4)_2$, 2.16; $Cu(ClO_4)_2$, 4.38; NiEDDA, 3.64; CuEDDA, 111.

The rate of reaction of eq 1 was studied by following the increase in absorbance due to the formation of CuEDDA. No buffer was used since there was no net change in the number of protons in the reaction. This was demonstrated by mixing reactants and monitoring pH as the reaction proceeded. The copper concentration was varied from 2.88 × 10^{-4} to 2.19 × 10^{-1} M while NiEDDA varied from 2.99 × 10^{-4} to 1.54 × 10^{-3} M. The reaction was studied over the pH range of 3.2–5.0. All data were obtained at 25.0 ± 0.1° and μ = 1.25 M.
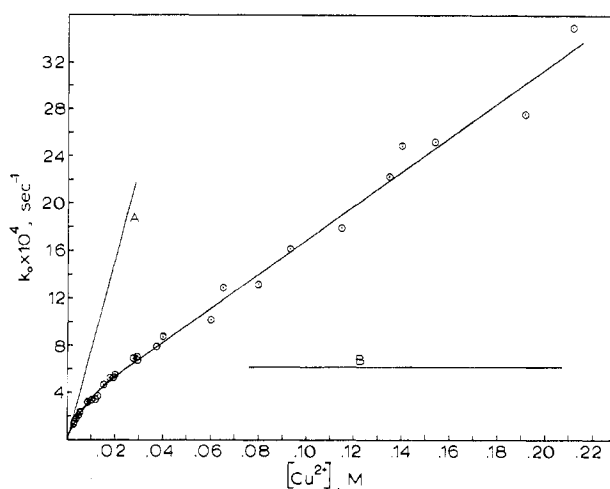

Figure 1. Effect of copper concentration upon k_0 at pH 3.7 (μ = 1.25 M, 25°). Line A represents eq 4; line B represents complete zero-order behavior in copper.

Results

The reaction was shown to be first order in NiEDDA but varied in order from first to zero in copper. All reactions followed the rate expression

$$\frac{-d[NiEDDA]}{dt} = \frac{d[CuEDDA]}{dt} = k_0[NiEDDA] \qquad (2)$$

At copper concentrations of 10-fold excess or greater

$$rate = k_0[NiEDDA] \qquad (3)$$

where the variation of k_0 with excess copper depended upon the copper concentration. The effect of copper concentration upon the rate is shown in Figure 1. Table I lists the data. Figure 2 has expanded a small portion of Figure 1 and shows that as the copper concentration increases, the copper dependence upon the rate decreases. This becomes more significant at higher pH values than at low ones. The straight line marked A in Figures 1 and 2 represents eq 4, which is

$$k_0 = k_{Cu}^{NiEDDA}[Cu^{2+}] \qquad (4)$$

approached at low copper concentrations in the range of 0.002–0.0002 M. Figure 1 shows that a complete shift to zero-order dependence in copper, given by line B, is never fully realized; rather another first-order dependence appears. As the copper concentration is further increased, a linear dependence in copper remains up through 0.22 M at pH 3.7.

Equation 5[7] can be used to show that the curvature shown

$$k_0 = \frac{ab[Cu^{2+}]}{a + b[Cu^{2+}]} \qquad (5)$$

in Figure 2 is the result of a shift from first- to zero-order dependence in copper. Here, $a > b[Cu^{2+}]$ at 10^{-3} M copper, but $b[Cu^{2+}] > a$ at 10^{-2} M copper. Equation 5 can be rearranged to eq 6 and plotted as shown in Figure 3 for each

$$\frac{[Cu^{2+}]}{k_0} = \frac{1}{b} + \frac{[Cu^{2+}]}{a} \qquad (6)$$

pH of Figure 2. The linear relationship found is in agreement with a transition from first-order to zero-order copper dependence. The intercepts of eq 6 as shown in Figure 3 are essentially constant and, thus, pH independent. Analogous to the NiEDTA-Cu system,[7] the term $1/b$ represents $1/k_{Cu}^{NiEDDA}$. The slopes of each plot are copper independent but vary with pH and again, by analogy, represent

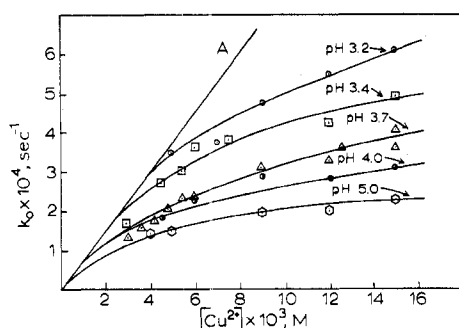**Figure 2.** Effect of varying pH and copper concentration at low copper concentrations upon k_0 ($\mu = 1.25\,M$, 25°). Line A represents eq 4.
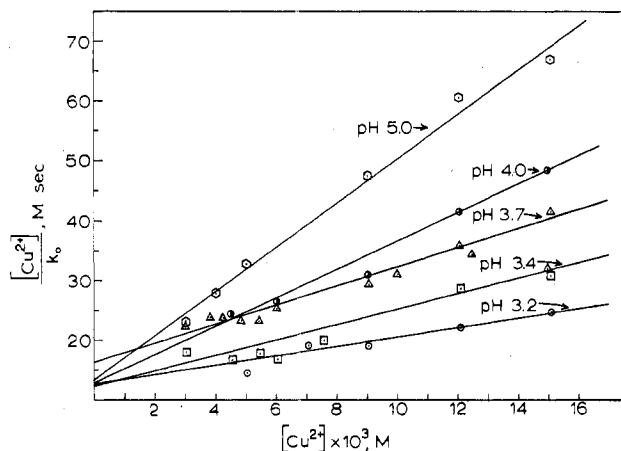

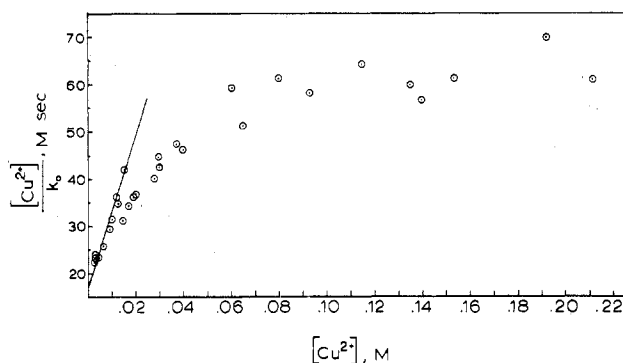**Figure 3.** Resolution of k_0 into terms a and b of eq 6 at varying pH values.

Figure 4. Deviation of experimental data from eq 6 at high copper concentrations at pH 3.7.

$1/k_{dis}^{NiEDDA}$. These values are listed in Table II.

Above 0.01 M copper, another first-order dependence in copper appears. This is easily seen in Figure 1 where line B represents the zero-order dependence expected from Figure 3. It is also seen in Figure 4 which extends the plot of Figure 3 to 0.22 M copper at pH 3.7. Figure 1 shows an excellent linear relationship between k_0 and [Cu^{2+}] up to 0.22 M copper.

Discussion

General Mechanism. The NiEDDA-Cu system appears to behave kinetically in a fashion identical with that of the NiEDTA-Cu system.[7] Points of similarity are (1) pH dependence, both reactions having faster rates at lower pH values and slower rates at higher ones, (2) order with respect to copper at very low copper concentration, both being first order in copper at very low copper concentration and shifting

Table I. Variation of the Observed First-Order Rate Constant with Respect to pH and Excess Copper Ion Concentration ($\mu = 1.25\,M$, 25°)

pH	10^4[NiEDDA], M	10^2[Cu^{2+}], M	$10^4 k_0$, sec^{-1}
3.2	2.92	0.504	3.44
	2.92	0.706	3.69
	2.92	0.907	4.73
	2.92	1.21	5.46
	2.92	1.51	6.10
3.4	2.92	0.302	1.67
	2.92	0.454	2.68
	2.92	0.544	3.00
	2.92	0.605	3.58
	2.92	0.756	3.78
	2.92	1.21	4.22
	2.92	1.51	4.90
3.7	2.92	0.302	1.35
	2.92	0.383	1.61
	2.92	0.423	1.77
	2.92	0.484	2.07
	2.92	0.544	2.33
	2.92	0.605	2.37
	2.92	0.907	3.08
	3.07	1.00	3.21
	2.92	1.21	3.37
	3.07	1.25	3.63
	3.07	1.50	4.09
	2.92	1.51	3.62
	3.07	1.75	5.16
	2.99	1.87	5.21
	3.07	2.00	5.50
	2.99	2.80	6.98
	3.07	3.00	6.73
	2.99	3.74	7.93
	3.07	4.00	8.65
	3.07	6.00	10.1
	2.99	6.53	12.8
	3.07	8.00	13.1
	2.99	9.34	16.1
	15.4	11.5	17.9
	15.4	13.5	22.6
	2.99	14.0	24.8
	15.4	15.4	25.2
	15.4	19.2	27.6
	15.4	21.2	34.9
4.0	2.92	0.454	1.85
	2.92	0.605	2.29
	2.92	0.907	2.94
	2.92	1.21	2.86
	2.92	1.51	3.11
5.0	2.92	0.302	1.32
	2.92	0.403	1.44
	2.92	0.504	1.53
	2.92	0.907	1.91
	2.92	1.21	2.00
	2.92	1.57	2.26

Table II. Resolved Rate Constants at Low Copper Concentration as a Function of pH

pH	$10^4 k_{dis}^{NiEDDA}$, sec^{-1}	$10^2 k_{Cu}^{NiEDDA}$,[a] M^{-1} sec^{-1}
3.2	12.8	7.88
3.4	7.90	8.15
3.7	6.20	6.06
4.0	4.13	7.92
5.0	2.72	7.45

[a] Average $k_{Cu}^{NiEDDA} = 7.49 \times 10^{-2}\,M^{-1}$ sec^{-1}.

to a zero-order dependence at higher copper concentrations, and (3) order with respect to copper at high copper concentration, both showing a shift to a new first-order copper behavior before the zero order is fully realized.

Points of difference between the systems occurred at very high copper concentrations. The NiEDTA-Cu system showed a shift back to a second zero-order copper dependence at high copper concentrations and never gave a linear depen-

dence between k_0 and copper concentration whereas the NiEDDA–Cu system showed an excellent linear relationship between k_0 and copper concentration from 0.03 to 0.22 M copper and never showed a trend to a second zero-order dependence. The NiEDTA–Cu system showed initial absorbance jumps at high copper concentrations. These absorbance jumps along with the second first-order to zero-order shift in copper dependence were attributed to a weakly bonded NiEDTA–Cu complex. This complex is found only at high copper concentrations and is different from the dinuclear intermediate which occurs later on in the mechanism. This type of complex is also seen in the reaction of lead and copper with *trans*-1,2-diaminocyclohexanetetraacetatocadmate(II) (CdCyDTA).[10] In both cases, an acetate segment of CdCyDTA has unwrapped and is bonded to the attacking metal. Unlike the NiEDTACu complex, the CyDTA ones are unreactive due to the inability of CyDTA to unwrap and transfer from cadmium to the attacking metal. The NiEDDA–Cu system showed excellent agreement between the predicted initial absorbance values and the experimental ones up to 0.22 M copper. Nevertheless, the dependence of k_0 on copper concentration at higher copper concentrations provides kinetic evidence for a weakly bonded NiEDDACu complex and it is proposed that, like the NiEDTA–Cu system, this type of species does exist.

Despite the points of difference between the two systems, the same general mechanism is proposed to hold for both reactions. The mechanism is consistent with both systems on the points of similarity and the same type of weakly bonded NiEDTACu complex seen in the NiEDTA–Cu system is proposed for the NiEDDA–Cu system and is consistent with the kinetic data.

The mechanism is shown in Figure 5. Protons are omitted for simplicity although some of the steps are proton assisted. The dependence of the reaction order upon copper serves to locate the position of the rate-determining step. As with the NiEDTA–Cu system, steps **2–5** and **3–6** can be ruled out as rate determining due to the large value of the rate of water loss of copper.[12]

In the pH range of the present study, the reaction sequence **1-2-3-6** is not important. For this sequence, step **3–6** cannot be rate limiting as it involves the very labile aquocopper ion as compared to the sluggish dissociation of NiEDDA. The rate of path **1-2-3-6** would be simply the sluggish rate of dissociation of NiEDDA and, similar to NiEDTA dissociation,[7,13] would not be important above pH 3.[14] The reaction must proceed through pathway **1-2-5-6** or **1-4-5-6** or a combination of both. A general kinetic expression[7] for the remaining pathways, shown in eq 7, can be written by

$$k_0 =$$
$$\frac{\{k_{12}k_{25} + k_{45}K_{41}(k_{21} + k_{25}[Cu^{2+}])\}k_{56}[Cu^{2+}]}{\{k_{21}(k_{56} + k_{54} + k_{52}) + k_{25}(k_{56} + k_{54})[Cu^{2+}]\}(1 + K_{41}[Cu^{2+}])} \quad (7)$$

assuming the steady-state approximation for species **2** and **5**

(12) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).
(13) C. M. Cook, Jr., and F. A. Long, *J. Amer. Chem. Soc.*, **80**, 33 (1958).
(14) The value of k_H^{NiEDDA} can be estimated from Ni^{2+} + HEDDA$^-$ → NiEDDA + H$^+$, which has a stability constant of 10^4, and $k_{Ni}^{HEDDA} = 4 \times 10^2 \, M^{-1}$ sec^{-1}. The latter value is obtained using the method of D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969), which gives very good agreement between the experimental and predicted values for $k_{NiHEDTA}$ and k_{NiH_2EDTA}. Thus, $k_H^{NiEDDA} = (4 \times 10^2)/10^4 = 4 \times 10^{-2} \, M^{-1}$ sec^{-1}, and at pH 3.2, $k_H^{NiEDDA}[H^+]$ contributes less than 2% of the observed rate.
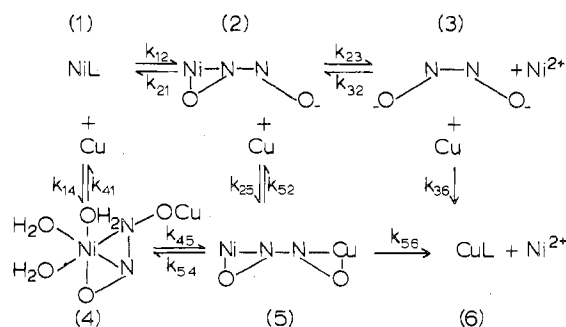

Figure 5. General mechanism for transfer of EDDA from nickel to copper. Protons and carbon atoms have been omitted for simplicity. L represents EDDA.
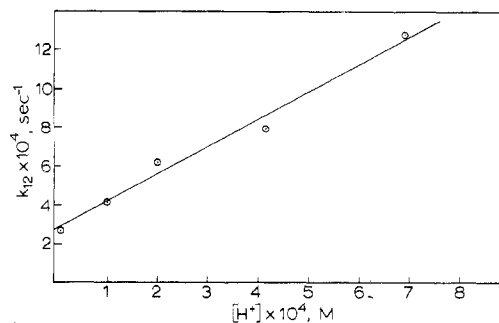

Figure 6. Resolution of k_{12} into proton-dependent and proton-independent terms.

and assuming a rapid equilibration between species **1** and **4**.

Kinetic Behavior at Low Copper Concentrations (<0.02 M). At low copper concentrations, <0.02 M, eq 7 is consistent with the behavior seen in Figures 2 and 3. Under these conditions, $1 \gg K_{41}[Cu^{2+}]$. Although K_{41} is not known, it certainly cannot be larger than the value for the NiEDTA–Cu system of 6.8 at $\mu = 1.25 \, M$.[7] Also, following the NiEDTA–Cu system, $k_{52} \gg k_{56} + k_{54}$ and $k_{56} \gg k_{54}$. Finally, after rearranging the numerator of the right-hand side of eq 7, $k_{12}k_{25}/k_{21} \gg k_{45}K_{41}$ and $k_{12}k_{25}/k_{21} \gg k_{25}k_{45}K_{41}[Cu^{2+}]/k_{21}$ because k_{25}/k_{21} involves a ratio of water loss rates $\simeq 10^3$ [12] $\gg K_{41}$ and k_{12} and k_{45} both involve nickel dissociation steps and must be on the same order of magnitude. The upper limit of $K_{41}[Cu^{2+}]$ at 0.02 M copper, assuming $K_{41} \approx 5$, would be 0.1. Thus, eq 7 becomes

$$k_0 = \frac{k_{12}k_{25}k_{56}[Cu^{2+}]}{k_{21}k_{52} + k_{25}k_{56}[Cu^{2+}]} \quad (8)$$

Rearranging eq 8 gives

$$\frac{[Cu^{2+}]}{k_0} = \frac{k_{21}k_{52}}{k_{12}k_{25}k_{56}} + \frac{[Cu^{2+}]}{k_{12}} \quad (9)$$

which has the exact form of eq 6 and which is the form the data follow. The slopes of the lines of Figure 3 are $1/k_{12}$ and the intercept is $1/k_{Cu}^{NiEDDA}$. At low copper concentration, $k_{21}k_{52} > k_{25}k_{56}[Cu^{2+}]$ and eq 8 reduces to

$$k_0 = k_{Cu}^{NiEDDA}[Cu^{2+}] \quad (10)$$

which shows the observed first-order behavior in copper. Under these conditions, k_{56} is the rate-determining step. At higher copper concentrations, $k_{25}k_{56}[Cu^{2+}] \cong k_{12}k_{25}$ and a shift toward

$$k_0 = k_{12} \quad (11)$$

is seen. The value of k_{12} is pH dependent and was deter-

mined at five different pH values. Equation 12, plotted in

$$k_{12} = k_{dis}^{NiEDDA} + k_H^{NiEDDA}[H^+] \qquad (12)$$

Figure 6, shows the pH dependence of k_{12}. Values of $k_{dis}^{NiEDDA} = 2.7 \times 10^{-4}$ sec^{-1} and $k_H^{NiEDDA} = 1.4 M^{-1}$ sec^{-1} were obtained from Figure 6.

Structure of the Partially Unwrapped Intermediate. As with the NiEDTA–Cu system, the structure of the partially unwrapped NiEDDA, species 2, can be predicted by estimating the value of k_{dis}^{NiEDDA} based upon the extent to which EDDA has unwrapped. Assuming a glycine segment has unwrapped and approximating k_{21} as 1×10^5 sec^{-1} [15]

$$k_{12} = \frac{1}{2} k_{21} \frac{K_{Ni(gly)}}{K_{NiEDDA}} K_{el} \qquad (13)$$

where $K_{Ni(gly)}$ and K_{NiEDDA} are the stability constants of Ni(gly) and NiEDDA, respectively,[16] K_{el} is an electrostatic term to compensate for attraction of the negative charge of the unwrapped glycine segment of NiEDDA for the positive nickel,[3] and $\frac{1}{2}$ is a statistical factor which favors the dissociation. Thus, $k_{12} = 8.5 \times 10^{-4}$ sec^{-1} from eq 13 which is in good agreement with the observed value of 2.7×10^{-4} sec^{-1}. Either a larger or smaller extent of unwrapping would necessitate the use of a different stability constant in eq 13 and would cause severe disagreement between the predicted and experimental values.

Further evidence for a glycine segment being unwrapped from NiEDDA may be obtained by considering the structure of the dinuclear intermediate, species 5. Previous work has established that the ratio of experimental rate constants for metal attack upon various Ni-ligand complexes is directly proportional to the ratio of the dinuclear intermediate stability constants assuming the same rate-determining step to hold for both systems. The basis for this comparison may be found elsewhere.[1–3,5,6]

The relative stability constant, K_r, of each intermediate structure for each system is defined in terms of the stability of the Ni-ligand and Cu-ligand segments involved as compared to the stability of the initial Ni-ligand complex (eq 14).

$$K_r = \frac{K_{Ni-segment} K_{Cu-segment}}{K_{Ni-complex}} \qquad (14)$$

Electrostatic and statistical factors are included where appropriate. Table III lists structures and the predicted and experimental ratio of rate constants. The only intermediate shown for the NiEDDA–Cu system involves the unwrapping of a glycine segment from nickel and subsequent bonding to copper. Other possible intermediates with either more or less of the EDDA unwrapped gave K_r values which caused the predicted ratio of rate constants to be either very high or very low by powers of 10 compared to the experimental ratio. Thus, the intermediate which exists in the NiEDDA–Cu system involves a glycine segment bonded to nickel and a glycine segment bonded to copper. Evidence from both k_{12} and k_{Cu}^{NiEDDA} point to this.

The rate-determining step is k_{56} at low copper concentration. Two dentate sites remain bonded to nickel, an acetate and an amine. However, Ni-amine cleavage must be rate

(15) D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967). The value of $k_{NH_3}^{Ni(gly)} = 1.4 \times 10^4 M^{-1}$ sec^{-1} was corrected for $K_{os} = 0.1 M$ and a statistical factor of $^3/_4$ since NH$_3$ could attack at four sites but the partially bound EDDA could combine at only three. Thus, kNi(gly)–H$_2$O $= k_{21} = 1 \times 10^5$ sec^{-1}.

(16) L. Sillen and A. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

Table III. Comparison of NiEDDA–Cu and NiL–M Reaction Intermediates^a

Part I

Structures, K_r, and K_{el}		$K_{Cu}^{NiEDDA}/K_M^{NiL}$	
NiEDDA–Cu	NiL–M	Predicted	Exptl
$^+$Ni–N–N–Cu$^+$ \ / \ / O O $K_r = 2.24 \times 10^{-1}$	NiEDTA–Cu $^-$O O \ / \ $^+$Ni–N–N–Cu \ / \ / O O $K_r = 1.52 \times 10^{-2}$ $K_{el} = 3.16$ Statistical factor of 2	5.4	4.7
$K_r = 2.24 \times 10^{-1}$ Statistical factor of 2	NiHEEDTA–Cu O \ / \ $^+$Ni–N–N–Cu$^+$ \ / \ / O O $K_r = 2.4 \times 10^{-1}$	1.9	5.0
$K_r = 2.24 \times 10^{-1}$	NiEDTA–Zn $^-$O O \ / \ $^+$Ni–N–N–Zn$^+$ \ / \ / O O $K_r = 5.75 \times 10^{-7}$ $K_{el} = 3.16$ Statistical factor of 2	6.2×10^4	3.0×10^4

Part II

Complex	K_{stab}[16]	M	L	k_M^{Ni-L}, M^{-1} sec^{-1}
NiEDDA	3.16×10^{13}	Cu	EDDA	7.5×10^{-2} ^{b}
NiEDTA^{2-}	3.63×10^{18}	Cu	EDTA	1.6×10^{-2} ^{c}
NiHEEDTA$^-$	1.00×10^{17}	Cu	HEEDTA	1.5×10^{-2} ^{d}
Ni(gly)$^+$	1.95×10^5	Zn	EDTA	2.5×10^{-6} ^{e}
Cu(gly)$^+$	3.63×10^7			
Cu(IDA)	1.23×10^{11}			
Zn(IDA)	1.07×10^7			

^{a} K_r values are based on the stability constants given in part II of the 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 on the remaining values in part II, all at $25.0 \pm 0.1°$C and $\mu = 1.25 M$. Statistical and electrostatic factors follow those of reference 3. ^{b} This work. ^{c} Reference 1. ^{d} Reference 3. ^{e} Reference 2.

determining since Ni-acetate bonds cleave at $\sim 1 \times 10^4$ sec^{-1} [17] while Ni-amine bonds cleave at 5.8 sec^{-1}.[18] Further, the value of 1×10^4 sec^{-1} in conjunction with the K_r value of the NiEDDACu intermediate greatly exceeds the experimentally observed rate constant.

Kinetic Behavior at High Copper Concentrations (> 0.02 M). Above 0.02 M copper, the expected plateau of eq 11 does not materialize; rather as Figures 1 and 4 show, a new first-order behavior in copper appears. This is attributed to a weakly bonded NiEDDACu reactant which is in rapid equilibrium with reactants, NiEDDA and Cu^{2+}, and is different from the dinuclear intermediate of species 5. The structure would be similar to the NiEDTACu,[7] CdCyDTACu, and CdCyDTAPb[10] species and involve only an acetate bond to copper.

(17) M. A. Pancholy and T. K. Saksena, *Acustica*, **18**, 299 (1967).

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

Contrary to the NiEDTA-Cu system, no spectrophotometric evidence for its existence was found. The linearity of Figure 1 above 0.02 *M* copper shows that essentially just the sequence **1-4-5-6** is involved. Using the steady-state approximation for species **5** and assuming $[4] = K_{41}[Cu^{2+}]$, and as before with $k_{56} \gg k_{54}$, eq 15 results. The slope of the

$$k_0 = K_{41}k_{45}[Cu^{2+}] \tag{15}$$

pH 3.7 line in Figure 1, above 0.02 *M* copper, gives $K_{41}k_{45} = 1.45 \times 10^{-2} \ sec^{-1} \ M^{-1}$.

The general mechanism given in eq 7 also yields the same value of $K_{41}k_{45}$. Considering eq 7, at higher copper concentrations, again $k_{52} \gg k_{56} + k_{54}$ and $k_{56} \gg k_{54}$. Also $[Cu^{2+}] > k_{21}/k_{25}$ above 0.01 *M* copper and $1 > K_{41}[Cu^{2+}]$ assuming $K_{41} \approx 5$. Thus, eq 7 rearranges to

$$k_0 \left(\frac{k_{12} + k_{Cu}{}^{NiEDDA}[Cu^{2+}]}{k_{12}k_{Cu}{}^{NiEDDA}[Cu^{2+}]} \right) = 1 + \frac{k_{45}}{k_{41}}K_{41}[Cu^{2+}] \tag{16}$$

If the mechanism is correct and a weakly bonded NiEDDACu reactant is present, a plot of eq 16 predicts an intercept of 1 and a slope of $k_{45}K_{41}/k_{12}$ from which $k_{45}K_{41}$ may be calculated. Figure 7 shows a plot of eq 16 with an intercept of 0.75 and a slope which yields $k_{45}K_{41} = 1.41 \times 10^{-2} \ sec^{-1} \ M^{-1}$. The excellent agreement of the two values of $k_{45}K_{41}$ from Figures 1 and 6 lends confidence to the mechanism and shows it to be consistent with the data over the whole range of copper concentrations studied.

Comparison to Other Systems. The only other metal-exchange system studied with this great a variation in attacking metal ion is the NiEDTA-Cu system.[7] The experimental rate constants for both systems are summarized in Table IV. Points of similarity and difference are interesting.

First, NiEDTA is thought to exist as a five-coordinate species, which, along with the relative lability of Ni-acetate bonds, helps to explain the easy formation of the NiEDTA-Cu reactant. The fact that NiEDDA with only two acetate sites also forms such a species suggests either a three-coordinate reactant or else very labile Ni-acetate bonds. Since calculated relative stability constants show that a glycinate segment of EDTA and EDDA remains coordinated to nickel in the dinuclear intermediate despite the availability of another acetate group for EDTA, it is most likely that NiEDDA is four-coordinate.

Although the stability constant of the NiEDDACu species could not be measured, it must be no greater than that for NiEDTACu but probably a factor of 10 or more less because no linear portion of the k_0 vs. $[Cu^{2+}]$ plot for NiEDTA-Cu was seen at high copper concentrations. Rather, the EDTA system approached a second zero-order behavior in copper where all the reactants would be in the form of NiEDTACu. In the corresponding copper concentration range of the NiEDDA-Cu system, a linear behavior showing only first-order dependence in copper is seen and it can be concluded that k_0 approaches k_{45} only at much higher copper concentrations. This then places $K_{41}{}^{NiEDDACu} < K_{41}{}^{NiEDTACu}$.

Second, it is somewhat surprising that the loss of two dentate sites in going from EDTA to EDDA and corresponding to a decrease in stability of about 5.1 log *K* units is not reflected in the values of $k_{Cu}{}^{NiEDTA}$ and $k_{Cu}{}^{NiEDDA}$. The two values are about the same. The loss of stability in going from NiEDTA to NiEDDA is compensated for by the lower stability of Cu(gly) compared to CuIDA. This is easily seen
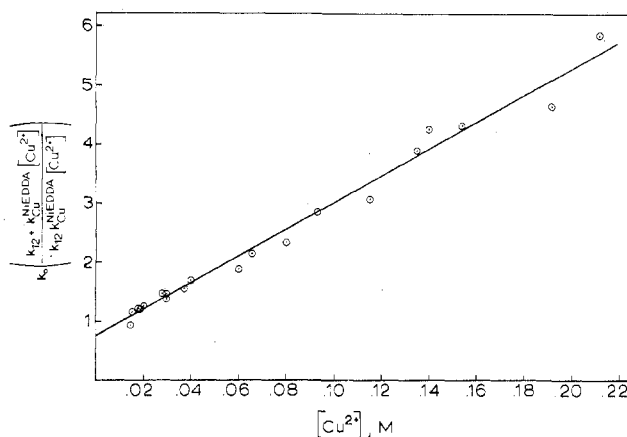
Table IV. Comparison of Rate Constants for NiEDDA-Cu and NiEDTA-Cu Systems ($\mu = 1.25 \ M$, 25°)

	NiEDDA-Cu	NiEDTA-Cu
$k_{Cu}{}^{NiL}$, $M^{-1} \ sec^{-1}$	7.5×10^{-2}	1.6×10^{-2}
$k_H{}^{NiL}$, $M^{-1} \ sec^{-1}$	1.4	2.2
$k_{dis}{}^{NiL}$, sec^{-1}	2.7×10^{-4}	1×10^{-4}
$K_{41}k_{45}$, $M^{-1} \ sec^{-1}$	2.3×10^{-3}	1.4×10^{-2}

in eq 17 which gives the ratio of the K_r values for NiEDDA

$$ratio = \frac{K_{Ni(gly)}K_{Cu(gly)}/K_{NiEDDA}}{K_{Ni(gly)}K_{CuIDA}/K_{NiEDTA}} = $$

$$\frac{(3.63 \times 10^7)(3.63 \times 10^{18})}{(1.23 \times 10^{11})(3.1 \times 10^{13})} \tag{17}$$

and NiEDTA. Thus, the decrease in reactant stability is compensated for by a decrease in stability of the dinuclear intermediate and the rate constants remain relatively unaffected.

The same type of arguments and equations can be written for the copper-independent dissociations and point out that the similarity of $k_{dis}{}^{NiEDDA}$ to $k_{dis}{}^{NiEDTA}$ and $k_H{}^{NiEDDA}$ to $k_H{}^{NiEDTA}$ is due to the loss in stability in going from NiEDDA to NiEDTA as compensated for by dissociation of Ni(gly) as opposed to that of NiIDA.

Finally, it is of interest to note that in reducing the number of dentate sites from six to four, the same shifts in rate-determining step in the mechanism occur and that the mechanism may be a general one for aminocarboxylate ligands regardless of their complexity. Other aminocarboxylate ligands possessing four[5] and three[6] dentate sites have been studied but not over as large a copper concentration range. However, the exchange of Ni(IDA)$_2$ and copper over a larger copper concentration range is presently under study in these laboratories.[19] Steric effects, of course, would alter the picture as would the relative stabilities of the metal intermediate segments and the relative rates of water loss of the two metals.

(19) R. K. Steinhaus and S. H. Erickson, to be submitted for publication.