

Metal-Exchange Reactions between Polyaminopolycarboxylatozincate(II) and Copper(II)

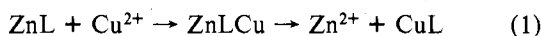
EDOARDO MENTASTI* and EZIO PELIZZETTI

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The kinetics of the metal-exchange reactions between polyaminopolycarboxylate complexes of Zn^{2+} and Cu^{2+} has been studied over the pH range of 4.25–5.75, at different copper concentrations, at ionic strength 0.10 M, and at different temperatures. The reaction is first order in the displaced complex, while the order with respect to copper ranges between one and zero, depending on the ligand nature and on pH. Individual reaction steps taking place for each system, with different copper concentration and pH dependence, are discussed. The experimental results indicate that the exchange reactions proceed through a dinuclear intermediate whose dissociation is the rate-determining step for the less coordinating ligands; increased chelating ability of the ligand shifts the rate-determining step to bond formation with the entering metal rather than bond breakage in the intermediate.

Introduction

For the metal-exchange reactions of metal chelates with multidentate ligands, it has been proposed that the substitution proceeds through a dinuclear intermediate species, in which the multidentate ligand is partially unwound from the initially complexed metal ion and partially bound to the entering metal ion



where the cleavage of the bonds between the ligand and the leaving metal ion is the rate-determining step.¹

In this research we measured the rates of complexation of copper ion in solutions of zinc polyaminopolycarboxylate complexes with a spectrophotometric stopped-flow technique. The ligands L were NTA, EDDA, HEEDTA, EGTA, CYDTA, and DTPA. The work was undertaken in order to clarify the effect of ZnL and ZnLCu stabilities on reactivity for a series of reactions. The different ligation capability of L plays a relevant role on precursor and intermediate complexes, so that detailed information can be achieved on the intermediate structure and reaction steps.

Experimental Section

Reagents. The ligands (namely, nitrilotriacetic acid, later referred to as NTA; ethylenediamine-*N,N'*-diacetic acid, EDDA; *N*-(2-hydroxyethyl)ethylenedinitrilo-*N,N',N'*-triacetic acid, HEEDTA; ethylenebis(oxyethylenenitrilo)tetraacetic acid, EGTA; *trans*-1,2-cyclohexylenedinitrilotetraacetic acid, CYDTA; diethylenetri-nitrilopentaacetic acid, DTPA) were reagent grade chemicals (Merck, Erba); EDDA was obtained from K & K and purified by successive recrystallization from a hot basic solution by adding perchloric acid and cooling. Their solutions were standardized by complexometric titrations with Cu^{2+} .

Zinc and copper perchlorates were obtained by dissolution of their carbonates in aqueous perchloric acid and recrystallization from water. Solutions of ZnL complexes were obtained by adding a 5% molar excess of zinc perchlorate to a standard solution of ligand, the solution pH was adjusted to 10, the excess metal ion was removed as the hydroxide, and the solution pH was lowered to 5. Other chemicals were reagent grade and were used without further purification.

Procedure. Reaction rates were followed by means of a Durham-Gibson stopped-flow spectrophotometer. The reaction progress was monitored at 700 nm (the absorption band of CuL) by following the product of the reaction. Kinetic runs were performed by mixing a ZnL solution (final concentration 4×10^{-4} M) with a Cu^{2+} solution (final concentration $(2.0-12) \times 10^{-3}$ M). All rate solutions contained excess Zn^{2+} ($(4-10) \times 10^{-4}$ M) to repress prior dissociation of ZnL. The concentration of Zn^{2+} in excess had no effect on the rate. The reactions were followed for at least 2 half-lives, and the rate constants were reproducible to $\pm 3\%$. The early part of reaction was followed for the lower Cu^{2+} concentrations. The pH range studied was 4.25–5.75. Both reactant solutions contained acetate buffer and sodium perchlorate in order to maintain 0.10 M ionic strength. The buffer

Table I. Stability Constants (log) Used Throughout the Work^a

ligand ^b	Zn ²⁺	Cu ²⁺	ligand ^b	Zn ²⁺	Cu ²⁺
Ac ⁻		1.8	EGTA ⁴⁻	12.8	17.7
Gly ⁻	5.0	7.6	HEEDTA ³⁻	14.6	17.6
IDA ²⁻	7.3	10.6	EDTA ⁴⁻	16.5	18.8
NTA ³⁻	10.7	13.0	DTPA ⁵⁻	18.4	21.5
EDDA ²⁻	11.2	16.2	OH ⁻		-8

^a The data have been taken from ref 2 to be as close to the investigated conditions as possible ($\mu = 0.10$ M, NaClO₄, 20.0 °C).

^b Key: Ac⁻, acetate; Gly⁻, aminoacetate; IDA²⁻, iminodiacetate; for the other abbreviations, see the Experimental Section.

concentration was low with respect to Cu^{2+} (total concentration 2×10^{-3} M) in order to avoid acetate catalysis. All runs were performed at 20.0 and 8.0 or 37.0 °C (depending on the speed of the reaction) in order to obtain the activation parameters.

Results

The reactions were shown to be first order in ZnL but varied in order from first to zero in copper concentration, depending on the nature of L and on pH. All reactions followed the rate expression

$$d[CuL]/dt = -d[ZnL]/dt = k_{obsd}[ZnL] \quad (2)$$

Plots of $\ln(A_{eq}/(A_{eq} - A_t))$ vs. time (where A_{eq} and A_t represent the absorbances at equilibrium and at time t , respectively) were linear at least up to 2 half-lives, and from their slopes k_{obsd} values were obtained with a weighted linear-regression analysis. Under the conditions used, the back-reaction was negligible since $[Cu^{2+}]$ is in large excess with respect to $[ZnL]$ and since the equilibrium (1) is far displaced to the right (see Table I, where the stability constants used throughout the work have been collected; these constants have been chosen from literature to be as close to the present conditions as possible).²

Ligands NTA, EDDA, and HEEDTA. The variation of k_{obsd} with $[Cu^{2+}]$ was linear with significant intercept and slope. The straight-line dependence on $[Cu^{2+}]$ (see Figure 1, where, for example, some data for EDDA have been reported) indicates a term that is first order in Cu^{2+} , while the intercept indicates a term that gives the first-order dissociation of ZnL independent of $[Cu^{2+}]$. The overall rate can therefore be expressed as

$$d[CuL]/dt = k[ZnL] + k'[ZnL][Cu^{2+}] \quad (3)$$

where k and k' are functions of acidity, according to

$$k = k^{ZnL} + k_H^{ZnL}[H^+] \quad (4)$$

$$k' = k_{Cu}^{ZnL} + k'_{Cu}^{ZnL}[H^+]^{-1} \quad (5)$$

(see for example Figures 2 and 3); k' for HEEDTA was

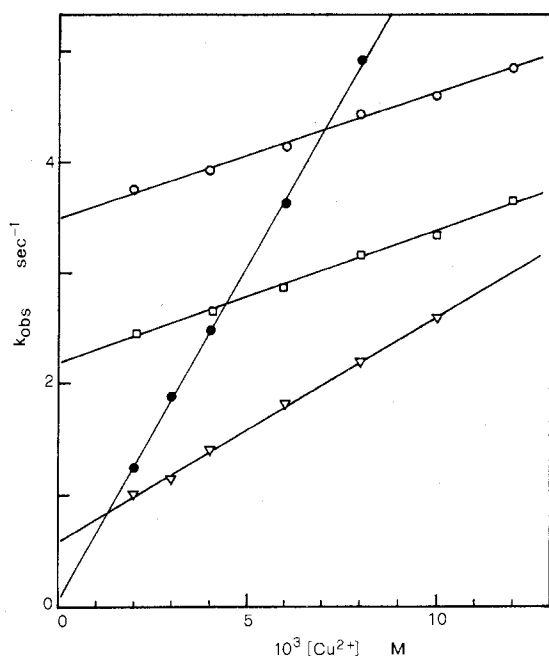


Figure 1. Variation of k_{obsd} as a function of $[\text{Cu}^{2+}]$ at different pHs and at 20.0 °C for the reaction of ZnEDDA. pH: (○) 4.25; (□) 4.50; (▽) 5.25; (●) 5.75.

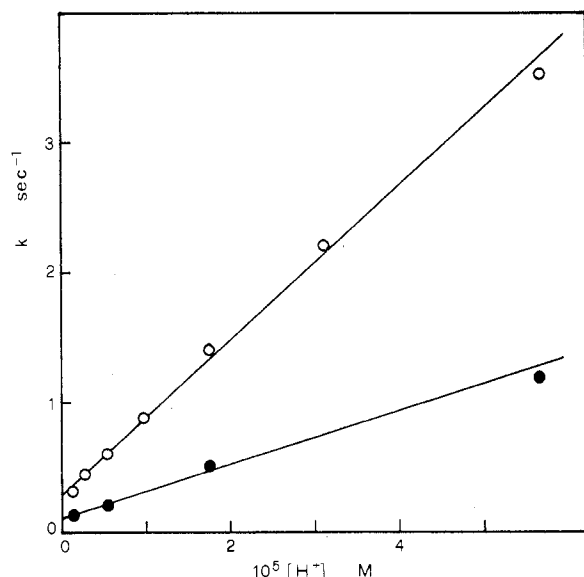


Figure 2. Variation of k (see eq 3 and 4) as a function of $[\text{H}^+]$ and temperature for the reaction of ZnEDDA: closed points, 8.0 °C; open points, 20.0 °C.

independent of acidity, so that the last term in eq 5 can be dropped.

Ligands EGTA and DTPA. Plots of k_{obsd} vs. $[\text{Cu}^{2+}]$ always deviated from linearity, and copper dependence upon the rate decreased reaching a saturation condition with a shift from first- to zero-order dependence. Equation 6 accounts for the

$$k_{\text{obsd}} = a[\text{Cu}^{2+}]/(1 + b[\text{Cu}^{2+}]) \quad (6)$$

experimental behavior which reduces to zero-order dependence when $1 \ll b[\text{Cu}^{2+}]$. The experimental data fitted with the linear functional form

$$[\text{Cu}^{2+}]/k_{\text{obsd}} = 1/a + (b/a)[\text{Cu}^{2+}] \quad (7)$$

(see for example Figure 4), and from slopes and intercepts the terms a and a/b could be obtained. In analogy with previous investigations,^{1d,3} the term a represents $k_{\text{Cu}}^{\text{ZnL}}$ and a/b rep-

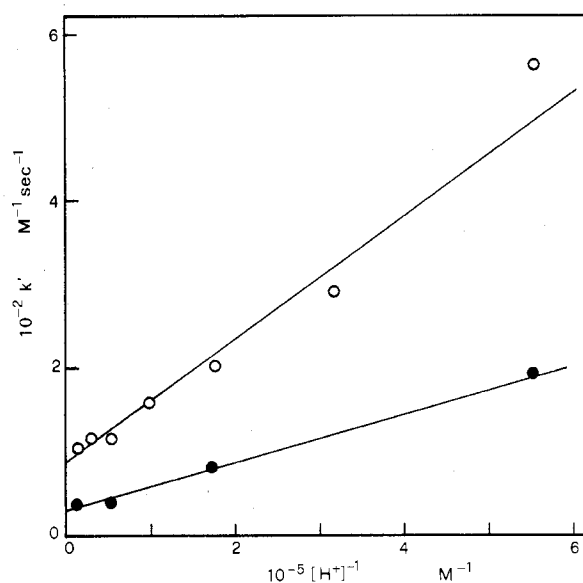


Figure 3. Variation of k' (see eq 3 and 5) as a function of $[\text{H}^+]^{-1}$ and temperature for the reaction of ZnEDDA: closed points, 8.0 °C; open points, 20.0 °C.

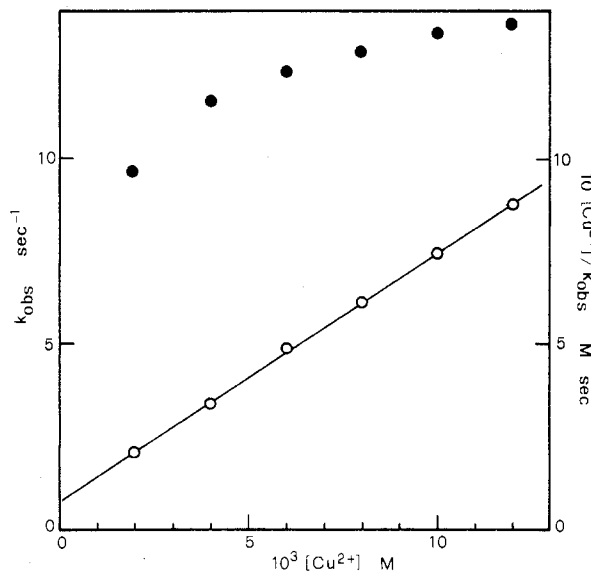
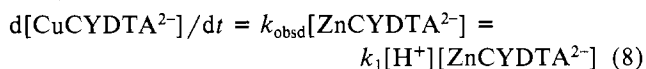


Figure 4. Variation of k_{obsd} with $[\text{Cu}^{2+}]$ (closed points, left-hand scale) and of $[\text{Cu}^{2+}]/k_{\text{obsd}}$ with $[\text{Cu}^{2+}]$ (open points, right-hand scale) for the reaction of ZnEGTA²⁻ at 20.0 °C and pH 4.50.

resents $k_{\text{dis}}^{\text{ZnL}}$ (see later). For both ligands the term a is pH independent whereas the term a/b shows a linear dependence on $[\text{H}^+]$.

Ligand CYDTA. According to previous observations,⁴ no direct kinetic interaction between Cu^{2+} and ZnCYDTA^{2-} was observed. The reaction order on $[\text{Cu}^{2+}]$ was zero, whereas the reaction depended linearly on acidity (see Figure 5) according to



Tables II and III collect the experimental kinetic data for the investigated systems and the activation parameters for $k_{\text{H}}^{\text{ZnL}}$ and $k_{\text{Cu}}^{\text{ZnL}}$.

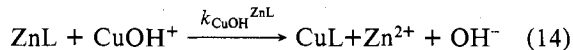
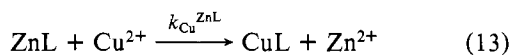
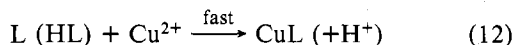
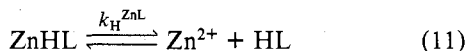
Discussion

The reactions between copper and ZnL complexes proceed by reaction paths that are similar to those reported in the displacement of metal ions in their polyaminopolycarboxylato

Table II. Values of k (s^{-1}), k' ($M^{-1} s^{-1}$) (eq 3), a/b (s^{-1}), a ($M^{-1} s^{-1}$) (eq 7), and k_{obsd} (s^{-1}) (eq 8) at Different Acidities and Temperatures, for the Investigated Reactions

ligand	parameter	pH						
		4.25	4.50	4.75	5.00	5.25	5.50	5.75
$T = 8.0^\circ\text{C}$								
EDDA	k	1.18		0.50		0.20		0.10
	$10^{-2}k'$	0.41		0.40		0.84		1.95
EGTA	a/b	7.4	6.6	5.7	5.7	5.5	5.6	5.0
	$10^{-3}a$	5.0	5.0	5.5	4.8	4.8	5.0	4.5
DTPA	a/b	16.2	13.8	12.8	12.0	11.0	11.0	11.0
	$10^{-3}a$	7.1	6.7	8.3	7.1	7.7	7.7	8.0
$T = 20.0^\circ\text{C}$								
NTA	$10k$	2.7	2.5	1.0	0.80	0.65	0.42	0.25
	k'	10.0	11.0	11.5	14.1	17.0	25	36
EDDA	k	3.5	2.2	1.43	0.90	0.60	0.45	0.30
	$10^{-2}k'$	1.00	1.10	1.15	1.62	2.1	2.9	5.7
HEEDTA	10^2k	11.0	6.0	4.0	3.0	2.0	1.0	1.0
	k'	19.5	17.5	18.0	17.5	19.0	18.0	19.0
EGTA	a/b	17.2	14.9	13.9	12.8	11.9	11.5	11.9
	$10^{-4}a$	1.25	1.25	1.20	1.25	1.25	1.10	0.90
DTPA	a/b	35	29	22	20	20	19	17
	$10^{-4}a$	1.7	1.8	2.0	2.0	2.0	2.2	2.0
CYDTA	10^2k_{obsd}	1.3	0.65	0.40	0.23	0.12		0.02
$T = 37.0^\circ\text{C}$								
NTA	k	0.65	0.34	0.23	0.18		0.15	0.10
	$10^{-2}k'$	0.65	0.60	0.58	0.72		1.28	2.10
HEEDTA	$10k$	2.0	1.30	0.60		0.30	0.20	0.2
	$10^{-1}k'$	6.5	5.5	5.7		6.5	6.5	7.0
CYDTA	10^2k_{obsd}	3.7	1.80	1.15	0.65	0.34		

complexes.¹ Both dissociative paths (which obviously show an acid-catalyzed contribution) and associative paths are taking place, and if the ligation capability of the acid is low (NTA, EDDA, HEEDTA), strong intermediate mixed complexes cannot be formed and simple first-order dependences on the reactants are observed. The reaction sequence (9)–(14) can account for the observed dependences. Equations 9 and 11



are responsible for the dissociative paths (see eq 4) independent of Cu^{2+} ; the rate-determining step involves the loss of Zn^{2+} from the complex and a rapid reaction of the released ligand with Cu^{2+} (eq 12). Thus the Zn^{2+} ion, released during the reaction, does not suppress the rate, as observed by varying the excess Zn^{2+} present; this resembles Ni^{2+} in the reaction of NiEDTA^{2-} with Cu^{2+} , in contrast with the reactions of Cu^{2+}

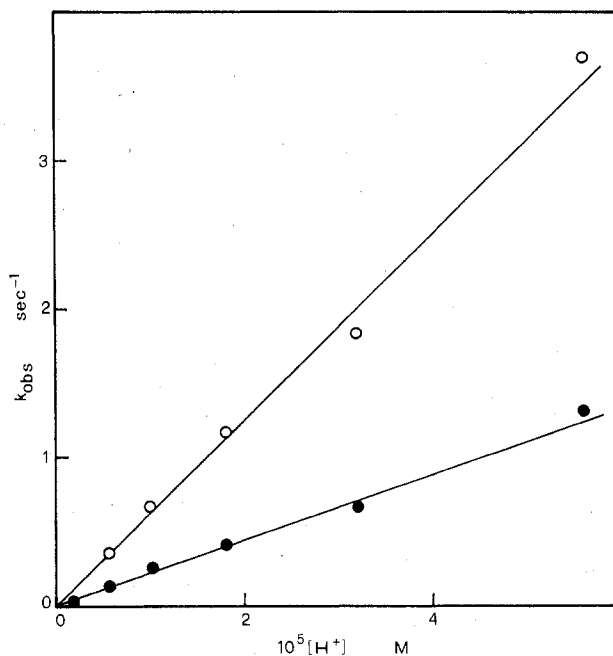


Figure 5. Variation of k_{obsd} as a function of $[\text{H}^+]$ and temperature for the reaction of ZnCYDTA^{2-} : closed points, 20.0°C ; open points, 37.0°C .

with the EDTA complexes of Pb^{2+} , Cd^{2+} , and Zn^{2+} .^{5,6} Equations 13 and 14 represent the overall electrophilic copper attack on partially dissociated ZnL . Together with a direct attack of Cu^{2+} on ZnL (eq 13), another path with $[\text{H}^+]^{-1}$ dependence must be present (see eq 5). Possible explanations for the inverse $[\text{H}^+]$ behavior would be the existence of hydroxo complexes of ZnL or the attack of hydrolyzed copper species on ZnL . The first possibility can be ruled out; in fact the equilibrium $\text{ZnNTA}^- + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})\text{NTA}^{2-}$ has been reported^{2b} to have an equilibrium quotient $K_{\text{ZnOHNTA}} = 10^{3.55}$. Thus, even at the higher investigated pH, ZnNTA^- should be hydrolyzed to a very small extent (ca. 0.001%) and no higher hydrolysis is expected for ZnEDDA .

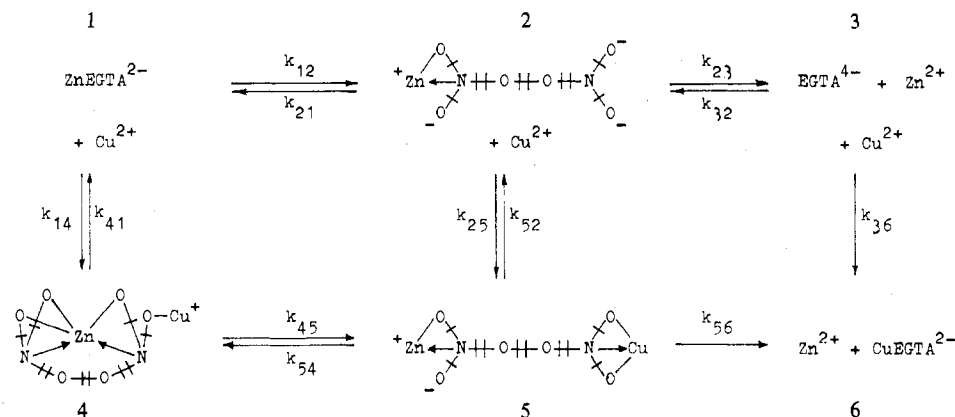
The $[\text{H}^+]^{-1}$ dependence suggests the CuOH^+ species as the active one, according to eq 14. Higher hydrolyzed species, such as $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}_3(\text{OH})_2^{4+}$, and so on,^{2a} would give different pH dependences and can therefore be neglected. An interaction between ZnHL and $\text{Cu}_2(\text{OH})_2^{2+}$ would give the observed pH dependence but this seems not to be the case; otherwise ZnHL would also be reactive with Cu^{2+} and an acid-catalyzed term would also be present. The large hydroxide ion effect cannot be simply assigned to accelerated water loss from CuOH^+ . For NTA, EDDA, and HEEDTA the Zn–L bond dissociation steps appear to be important rather than Cu–L bond formation; thus labilization in the coordination sphere of the entering metal should not play an important role.^{1d,1f,6} Repulsion between the metal centers in the intermediates⁶ is also important and can be reduced by the OH^- ligand. This effect depends on the intermediate structure

Table III. Kinetic and Activation Parameters for the Investigated Reactions (20.0°C , $\mu = 0.10 \text{ M}$)^a

ligand	k_{ZnL}, s^{-1}	$k_{\text{H,ZnL}}, M^{-1} s^{-1}$	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal mol}^{-1} \text{K}^{-1}$	$k_{\text{Cu,ZnL}}, M^{-1} s^{-1}$	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal mol}^{-1} \text{K}^{-1}$	$k_{\text{CuOH,ZnL}}, M^{-1} s^{-1}$ ^b
NTA	0.030	4.0×10^3	9.0	-12	9.0	16.6	+2	4.8×10^3
EDDA	0.30	6.0×10^4	13.2	+8	80	12.9	-6	8.0×10^4
HEEDTA	7.0×10^{-3}	1.8×10^3	6.8	-20	18	13.1	-8	
EGTA	10	1.4×10^5	11.0	+3	1.2×10^4	11.4	-1	
DTPA	18	3.0×10^5	14.4	+15	2.0×10^4	12.8	+5	
CYDTA		2.25×10^2	10.0	-14				

^a The uncertainty in the rate constant values is ± 8 –12%, in the enthalpies of activation is ± 0.8 –1.1 kcal mol^{-1} , and in the entropies of activation is ± 2.7 –3.6 $\text{cal mol}^{-1} \text{K}^{-1}$. ^b Obtained from $k'_{\text{Cu,ZnL}} = k_{\text{CuOH,ZnL}} \beta_{11}$ (see eq 5 and Table I).

Scheme I



and coordinated ligand net charge; this can be why the $[H^+]^{-1}$ term has not been found for all the Zn-L systems studied.

Turning now to ligands with more donor groups (EGTA and DTPA), a more stable intermediate can occur, and a lowering of reaction order from one to zero on the entering metal ion can be predicted. For these reactions a multistep mechanism is expected; for EGTA, for example, see Scheme I.

The scheme outlines the multistep mechanism. Equilibria 1,2 and 2,3 refer to proton-assisted (protons are omitted for simplicity) unwrapping of EGTA; vertical steps are the reactions with Cu^{2+} ; reactions 4,5 and 5,6 represent the Cu-assisted unwrapping of the ligand and chelation upon Cu^{2+} . The sequence 1,2,3,6 is the dissociative path independent of Cu^{2+} which predominates at high $[H^+]$ and low $[Cu^{2+}]$.

The copper-dependent path must be 1,2,5,6 or 1,4,5,6 or a combination of both. By assuming the steady-state condition for species 2 and 5 (reaction 1,4 is a rapid equilibration) it follows that

$$d[CuEGTA^{2-}]/dt = k_{obsd}[ZnEGTA^{2-}] \quad (15)$$

where

$$k_{obsd} = \frac{\{k_{12}k_{25} + k_{45}K_{41}(k_{21} + k_{25}[Cu^{2+}])\}k_{56}[Cu^{2+}]}{\{k_{21}(k_{56} + k_{54} + k_{52}) + k_{25}(k_{56} + k_{54})[Cu^{2+}]\}(1 + K_{41}[Cu^{2+}])} \quad (16)$$

from which the empirical rate (eq 6) can be obtained under the following conditions: $1 \gg K_{41}[Cu^{2+}]$ (K_{41} is 6.8 for NiEDTA + Cu and for the present system cannot be much higher);^{1d} $k_{56} \gg k_{54} \gg k_{52}$ ($k_{56} \approx k_{Zn-H_2O}/K_{ZnGly} \approx 3 \times 10^2$, $k_{54} \approx k_{Cu-H_2O}/K_{CuGly} \approx 7$, $k_{52} \approx k_{Cu-H_2O}/K_{CuIda} \approx 7 \times 10^{-3}$), since the rate of water loss of zinc is $\sim 3 \times 10^7$ s⁻¹ and the rate for copper is $\sim 3 \times 10^8$ s⁻¹; $k_{25} \gg k_{21}$ (copper is more labile than zinc);^{1a,b,7} and k_{12} and k_{45} both involve zinc dissociation steps and must be of the same order of magnitude. Thus

$$k_{obsd} = k_{12}k_{25}[Cu^{2+}]/(k_{21} + k_{25}[Cu^{2+}]) \quad (17)$$

or

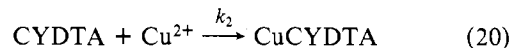
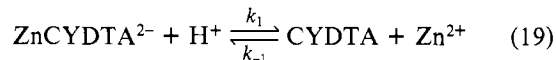
$$[Cu^{2+}]/k_{obsd} = k_{21}/(k_{12}k_{25}) + [Cu^{2+}]/k_{12} \quad (18)$$

which can be compared with eq 6 with $k_{diss}^{ZnL} = k_{12}$ and $k_{Cu}^{ZnL} = K_{12}k_{25}$.

Comparison can be made between these findings and the results already found for the ZnEDTA + Cu reaction;⁶ also in this case the rate-determining step is the rate of water loss from Cu^{2+} in step 2,5, which is shifted at higher $[Cu^{2+}]$ to the dissociation step 1,2. Then for EGTA and DTPA the formation of the dinuclear intermediates occurs after the rate-determining step. Then it follows that the rate-determining step is shifted from bond breakage in the dinuclear inter-

mediates to early steps with the increasing ligation capability of the ligand, i.e., from NTA, EDDA, and HEEDTA, on the one hand, to EDTA, EGTA, and DTPA, on the other.

For CYDTA, the cyclohexane ring restricts the flexibility of the ligand: the opening of the chelating groups is hindered and a direct attack of a metal to a CYDTA complex cannot be accommodated sterically;^{4,8,9} a prior acid-catalyzed dissociation is needed, followed by rapid recombination (steps 4,5 and 2,5 of the scheme are not possible, and the reaction is forced through 1,2,3,6). The sequence is then



from which (protons are omitted for simplicity), if $k_{-1}[Zn^{2+}] \ll k_2[Cu^{2+}]$ (due to the large value of water loss of copper),⁷ the observed kinetic dependences are obtained

$$\text{rate} = k_1[H^+][ZnCYDTA^{2-}] \quad (21)$$

Thus for all ligands the relative water loss rates from the involved metal species and the possibility of intermediate mixed complexes play an important role. In the case of EDDA, NTA, and HEEDTA the reactivity should be governed by the stability of the intermediate complex relative to the precursor reactant species. Previous metal-exchange studies have shown that the nature of the dinuclear intermediate immediately prior to the rate-determining step may be characterized by a comparison of rate constant ratios, involving similar systems, to relative stability constant ratios for the same system as shown in the equation^{3,10,11}

$$k_{M'}^{ML}/k_{M'}^{ML'} = K_R^{MLM'}/K_R^{ML'M'} \quad (22)$$

where

$$K_R = \frac{K_M \text{ segment } K_{M'} \text{ segment}}{K_{ML, \text{precursor complex}}} \quad (23)$$

Electrostatic and statistical factors are included where appropriate.^{1f,10} Equations 22 and 23 have been extensively used and proven to hold for many NiL complexes exchanged by Cu^{2+} ,^{1,3,10,11} and the experimental data showed that the intermediate immediately prior to the rate-determining step has a glycinate group bound to the leaving metal ion and the breakage of the N-Ni bond is the slow step. Taking into account these findings, some interesting comparisons can be made between the present results concerning the electrophilic attack of Cu^{2+} to Zn complexes with NTA, EDDA, and HEEDTA.¹²

(1) ZnEDDA reacts with Cu^{2+} with a rate (k_{Cu}^{ZnEDDA}) which is 4.4 times faster than for ZnHEEDTA; if it is assumed

Table IV. Structure and Relative Stabilities of ZnL + Cu²⁺ Reaction Intermediates

no.	structure	rel stability const (log K _R)
I		log K _R = log K _{ZnGly} + log K _{CuGly} - log K _{ZnEDDA} = +1.4 (statistical factor 2)
II		log K _R = +1.0
III		log K _R = -3.9; log K _{e1} = 0.5

that a glycinate segment is responsible for Zn bonding in the rate-determining step, one can compare the relative stabilities of the intermediates I and II (see Table IV). Taking into account a statistical factor of 2 for ZnEDDA-Cu, due to the ways ZnEDDA-Cu can be formed, a reactivity ratio (EDDA/HEEDTA) of 5.2 is obtained which is in quite good agreement with the experimental value. As with NiHEEDTA, copper is thought to attack the tridentate end of the ligand rather than the bidentate end. The other case would appear anomalous since the bidentate end is more easily labilized, but a much less stable intermediate would be formed, so that structure II is rapidly formed by the labile Cu²⁺ before the opening of the last chelate ring around Zn²⁺.

(2) ZnEDDA reacts 9 times faster than ZnNTA⁻. From models I and III, EDDA should be about 10⁵ times faster than ZnNTA⁻. The disagreement between the computed and experimental ratios suggests that one or both of the following points should be taken into account: (a) the model agrees with the experimental findings when both compared ligands are ethylenediamine derivatives (two coordinating N atoms) whereas, when one N atom only is involved (as for ZnNTA⁻), a different rate for Zn-N bond breakage is concerned and eq 22 cannot be retained; (b) an increased number of bonds to copper and a decreased coordination to zinc are involved in the rate-determining step for ZnNTA-Cu. A glycinate bonded to Zn and two acetate groups bonded to Cu (log K_{CuAc₂} = 2.65) lower the reactivity ratio (EDDA/NTA) but not sufficiently to be compared with the observed one.

Also, previous findings on some NiL + Cu²⁺ reactions can be compared with the present results: (i) NiEDDA reacts with Cu²⁺ with a $k_{\text{Cu}}^{\text{NiEDDA}} = 7.5 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$.³ If the same intermediate I is assumed, one computes log K_R(NiEDDA-Cu) = -0.65.³ Thus a ratio of ca. 100 is expected from this model for the reactivity of ZnEDDA with respect to NiEDDA. The experimental ratio is ca. 1000. (ii) ZnHEEDTA and NiHEEDTA are exchanged by Cu²⁺ with a reactivity ratio of 1.2 × 10³.¹⁰ If the same intermediate structure as in II is advanced, then log K_R(NiHEEDTA-Cu) = -1.2,¹⁰ and a ZnHEEDTA/NiHEEDTA reactivity ratio of 160 is computed. Thus one order of magnitude favors the experimental reactivities for Zn²⁺ with respect to Ni²⁺ if the model of eq 22 is assumed. Then, one order of magnitude would be the difference in the rate of Zn-N bond with respect to Ni-N bond breakage.

Registry No. ZnNTA⁻, 21996-31-6; ZnEDDA, 29977-12-6; ZnHEEDTA⁻, 67598-18-9; ZnEGTA²⁻, 67612-71-9; ZnDTPA³⁻, 23759-24-2; ZnCYDTA²⁻, 19332-79-7; copper, 7440-50-8.

References and Notes

- (1) For general features and bibliography, see, for example: (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, N.Y., 1967; (b) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition-Metal Complexes", Allyn and Bacon, Boston, Mass., 1974; (c) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962); (d) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965); (e) J. R. Kuemper and W. B. Schaap, *Inorg. Chem.*, **7**, 2435 (1968); (f) R. K. Steinhaus and C. L. Barsuhn, *ibid.*, **13**, 2922 (1974); (g) E. Mentasti and E. Pelizzetti, *Ann. Chim. (Rome)*, **65**, 659 (1975); (h) T. Nozaki and N. Suemitsu, *Bull. Chem. Soc. Jpn.*, **49**, 445 (1976); see also references therein.
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- (12) The compared data are obtained under different conditions: 20.0 °C and μ = 0.10 M for the present results and 25.0 °C and μ = 1.25 M for the compared data; temperature and ionic strength effects are however probably compensated; see for example ref 11.