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.

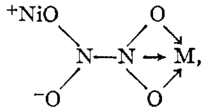
TABLE V

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

Experimental kinetic ratio

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

Model



$M = \mathrm{Zn}^{++}$ or Cu^{++}

Kinetic ratio based on the relative stabilities of intermediates

$$\frac{K_{\mathrm{CuYNi}}}{K_{\mathrm{ZnYNi}}} = \frac{10^{11.09-18.79}}{10^{7.66-16.50}} = 10^{1.14} = 14$$

Similarly, for the reverse reaction to that studied here, the rate constant $k_{\mathrm{Ni}}^{\mathrm{CuL}}$ (calculated from the forward rate constant and the equilibrium constant for reaction 1) is $7.5 \times 10^{-4}\ M^{-1}\ \mathrm{sec.}^{-1}$, which compared to $k_{\mathrm{Ni}}^{\mathrm{CuY}}$ gives a ratio of 0.71. On the basis of the proposed mechanism this ratio is 0.8. Copper-EDTA is more stable thermodynamically but is less stable kinetically because of the greater stability of the nickel intermediate prior to the first nickel–nitrogen bond formation.

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

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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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Multidentate Ligand Kinetics. V. Copper(II) and Cyclohexylenediaminetetraacetatonickelate(II)

BY D. W. MARGERUM AND T. J. BYDALEK

Received January 17, 1963

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 series[5] 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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[1] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **32**, 1682 (1949).

[2] G. Schwarzenbach, R. Gut, and G. Anderegg, *ibid.*, **37**, 936 (1954).

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

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

[5] T. J. Bydalek and D. W. Margerum, *ibid.*, **2**, 678 (1963).

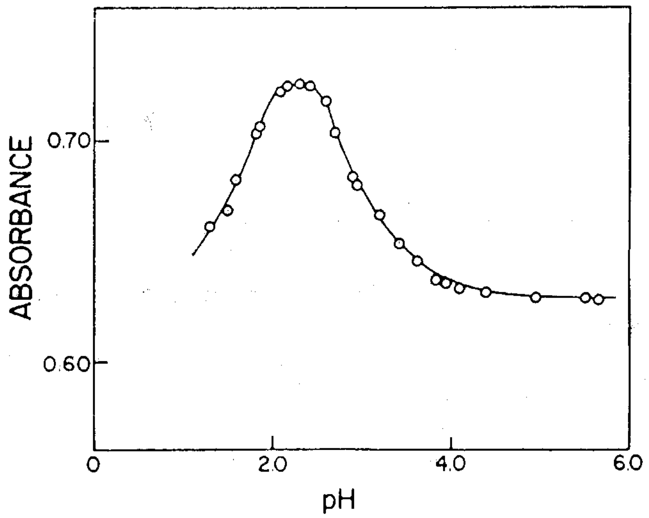

Fig. 1.—The absorbance of the copper-CyDTA complex changes with pH due to the three forms: CuH_2Cy, $CuHCy^-$, and $CuCy^{-2}$. Conditions are such that the dissociation of $CuCy_T$ is negligible: $[CuCy_T] = 1.13 \times 10^{-3}$ *M*, $\mu = 1.25$, 25.0°, $\lambda = 700$ mμ, 5-cm. cell.

step proposed was the breaking of the nickel–nitrogen bond of this intermediate. Sterically CyDTA cannot bond both nickel and copper to its nitrogen atoms. On the other hand, this ligand could simultaneously bond copper to one nitrogen atom and nickel to one of the more distant acetate groups if the rate-determining step were the dissociation of the last nickel–acetate bond. Thus, depending on the mechanism the copper reaction with nickel-CyDTA might proceed by (1) an extremely weak attack by copper if the nickel is bonded to a nitrogen atom up to the rate-determining step and copper cannot form a favorable intermediate complex or (2) a strong copper attack if nickel acetate dissociation is the rate-determining step, thus permitting the copper formation to proceed to a favorable nitrogen-bonded copper intermediate.

In fact the first mechanism is fully supported because there is no appreciable copper ion attack on nickel-CyDTA below pH 4. The system studied in this work is

$$\begin{bmatrix} \mathrm{NiCy^{-2}} \\ \uparrow\downarrow \\ \mathrm{NiHCy^{-}} \\ \uparrow\downarrow \\ \mathrm{NiH_2Cy} \end{bmatrix} \underset{k_{\mathrm{Ni}}{}^{\mathrm{Cy_T}}}{\overset{k^{\mathrm{NiCy_T}}}{\rightleftarrows}} \mathrm{Ni^{+2}} + \mathrm{Cy_T} \qquad (1)$$

$$\mathrm{Cy_T} + \mathrm{Cu^{+2}} \underset{k^{\mathrm{CuCy_T}}}{\overset{k_{\mathrm{Cu}}{}^{\mathrm{Cy_T}}}{\rightleftarrows}} \mathrm{CuCy_T} \qquad (2)$$

where the terms Cy_T, $NiCy_T$, and $CuCy_T$ refer to the sum of all protonated and unprotonated forms of each species of CyDTA. The various acid forms of the nickel and copper complexes equilibrate rapidly compared to their dissociation and reaction 2 is rapid compared to reaction 1. The rate of formation of copper-CyDTA therefore is equal to the rate of acid dissociation of nickel-CyDTA.

$$\frac{d[\mathrm{CuCy_T}]}{dt} = -\frac{d[\mathrm{NiCy_T}]}{dt} = k^{\mathrm{NiCy_T}}[\mathrm{NiCy_T}] \qquad (3)$$

This rate constant is resolved into the appropriate rate constants for the H^+ reaction with $NiCy^{-2}$, $NiHCy^-$, and NiH_2Cy and these constants are compared to the corresponding constants for EDTA.

Experimental

The experimental procedures were similar to those reported previously.[3–5] A constant ionic strength of 1.25 was maintained with sodium perchlorate 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. After the H_4Cy form of *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (LaMont Laboratories) was recrystallized twice from water and dried it was standardized by direct titration (murexide indicator) against a standard copper solution. Results were within 0.6% of the theoretical. Solutions of Na_2NiCy and Na_2CuCy were prepared by adding excess metal perchlorate to CyDTA and removing the excess metal ion as the metal hydroxide before adjusting the solution to pH 5.

The reaction was followed spectrophotometrically at the 700 mμ absorption band of copper-CyDTA. The absorbances of all species in eq. 1 and 2 except Cy_T are appreciable and must be taken into consideration. As the pH is varied the molar absorptivity of the equilibrium mixture of $CuCy^{-2}$, $CuHCy^-$, and CuH_2Cy changes with the relative concentration of the species. At this wave length no appreciable variation is noted for the corresponding nickel complexes. The molar absorptivities used in the kinetic runs are summarized in Table I along with the acid dissociation equilibrium constants found for the copper–CyDTA complexes.

TABLE I

MOLAR ABSORPTIVITIES AT 700 mμ[a]

Species	Molar absorptivity
$CuCy^{-2}$	$\epsilon_{CuCy} = 111$
$CuHCy^-$	$\epsilon_{CuHCy} = 140$
CuH_2Cy	$\epsilon_{CuH_2Cy} = 109$
$NiCy_T$	$\epsilon_{NiCy} = 2.2$
Cu^{+2}	$\epsilon_{Cu} = 7.4$
Ni^{+2}	$\epsilon_{Ni} = 2.1$

[a] $\mu = 1.25$, 25.0°, $K_{NiHCy} = 1.8 \times 10^{-3}$, $K_{NiH_2Cy} = 1.6 \times 10^{-2}$.

In terms of the absorbance measurements the concentration of product in eq. 2 is

$$[\mathrm{CuCy_T}] = \frac{A - A_i}{b(\epsilon_{\mathrm{CuCy_T}} + \epsilon_{\mathrm{Ni}} - \epsilon_{\mathrm{Cu}} - \epsilon_{\mathrm{NiCy}})} \qquad (4)$$

where ϵ_{CuCy_T} is the apparent molar absorptivity of the mixture of protonated copper complexes and A_i is the initial absorbance of the reactants at zero time. There was no spectrophotometric indication of any stable mixed complexes of copper, nickel, and CyDTA.

The kinetic runs were followed under conditions where the reverse reactions were negligible and gave rate constants reproducible to 5% or better.

Results

Protonation of Copper-CyDTA and Nickel-CyDTA.—Figure 1 shows the change of absorbance of copper-CyDTA with pH (below pH 2 excess $[Cu^{+2}]$ was present to ensure complete complexation and the absorbance is corrected for the copper ion contribution). Approximate values of K_{CuHCy} and K_{CuH_2Cy} can be obtained from the points of inflection[6] in Fig. 1. Suc-

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(6) H. Irving, H. S. Rossotti, and G. Harris, *Analyst*, **80**, 83 (1955).

cessive approximations in the form of plots of absorbance against $[H^+]$ and the evaluation of the limiting slope give the values

$$K_{CuHCy} = \frac{[H^+][CuCy^{-2}]}{[CuHCy^-]} = 2.1 \times 10^{-8} \qquad (5)$$

and

$$K_{CuH_2Cy} = \frac{[H^+][CuHCy^-]}{[CuH_2Cy]} = 1.9 \times 10^{-2} \qquad (6)$$

at 25.0° and $\mu = 1.25$. These constants were used to evaluate ϵ_{CuCy_T} as the pH was varied.

The protonation of $NiCy^{-2}$ was studied by potentiometric titration as shown in Fig. 2. The acid dissociation constants were evaluated by a graphical method described by Schwarzenbach.[7] The graphical solution is given in Fig. 3, where

$$A = \frac{(a-1)[NiCy_T] + [H^+]}{\frac{(2-a)[NiCy_T]}{[H^+]} - 1}$$

$$B = \frac{-(a-1)[NiCy_T] + [H^+]}{[H^+](a[NiCy_T] + [H^+])}$$

and a is the mole ratio of NaOH to $NiCy_T$ used in Fig. 2. The graphical solution gives

$$K_{NiHCy} = \frac{[H^+][NiCy^{-2}]}{[NiHCy^-]} = 1.8 \times 10^{-8} \qquad (7)$$

and

$$K_{NiH_2Cy} = \frac{[H^+][NiHCy^-]}{[NiH_2Cy]} = 1.6 \times 10^{-2} \qquad (8)$$

at 25.0° and $\mu = 1.25$. These constants are used in the resolution of the kinetic data into rate constants for each species.

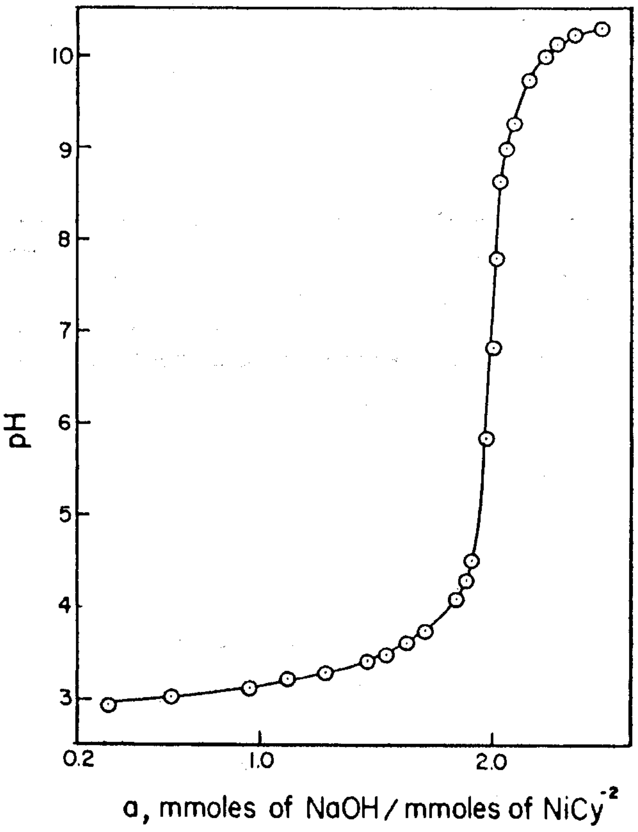

Fig. 2.—The pH dependence of nickel-CyDTA used to calculate the acid dissociation constants of NiH_2Cy and $NiHCy^-$: $[NiCy_T] = 2.26 \times 10^{-2}$ M, $\mu = 1.25$, 25.0°.

Kinetics of the Forward Reaction.—All the reactions between copper and nickel-CyDTA showed a first-order dependence in $[NiCy_T]$ and a zero order dependence in $[Cu^{+2}]$ consistent with eq. 1, 2, and 3. In Table II, for example, a fivefold variation in $[Cu^{+2}]$ at pH 2.12–2.16 does not significantly affect the rate constant, k^{NiCy_T}. This first-order rate constant is quite pH dependent, changing by more than three orders of magnitude in the pH range studied. In contrast, for the same reaction conditions with EDTA in place of CyDTA, the copper attack predominates over the acid attack and the reaction is first order in copper concentration and almost independent of acidity. Thus, the cyclohexene group in place of the ethylene group makes a great difference in the kinetics.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR NICKEL-CyDTA DISSOCIATION USING COPPER AS THE SCAVENGER[a]

pH	$[NiCy_T]$ initial, $M \times 10^4$	$[Cu^{+2}]$ initial, $M \times 10^3$	k^{NiCy_T}, sec.$^{-1}$ $\times 10^6$
1.52	4.23	1.34	48.8
1.68	14.1	1.34	31.6
1.70	14.1	1.34	30.8
1.70	4.23	1.34	28.0
1.83	4.23	1.34	18.7
1.85	4.23	0.67	19.7
1.90	8.46	1.34	17.5
1.97	4.23	2.01	13.0
2.02	35.2	1.34	11.2
2.12	4.23	1.34	8.21
2.15	4.23	0.268	6.75
2.16	4.23	0.670	6.83
2.35	4.23	1.34	2.98
2.40	8.46	1.34	2.96
2.70	4.23	0.670	1.11
2.90	4.23	3.35	0.516
3.09	4.23	1.34	0.363
3.52	28.2	0.670	0.095

[a] $\mu = 1.25$, 25.0°.

Resolution of the Acid Dissociation Rate Constant.—

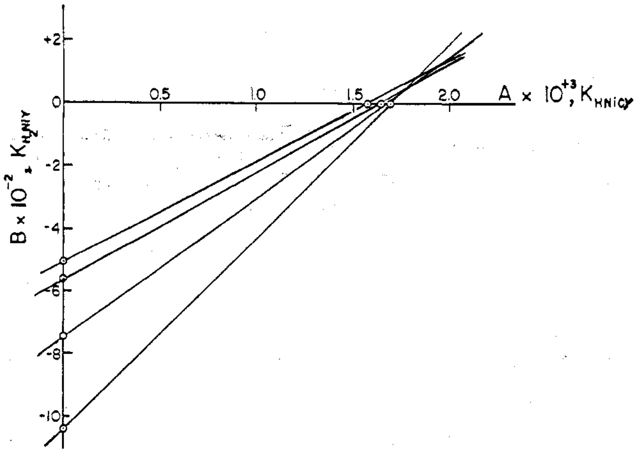

Fig. 3.—Graphical evaluation of K_{NiHCy} and K_{NiH_2Cy} using data from Fig. 2.

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[7] G. Schwarzenbach, A. Willi, and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).

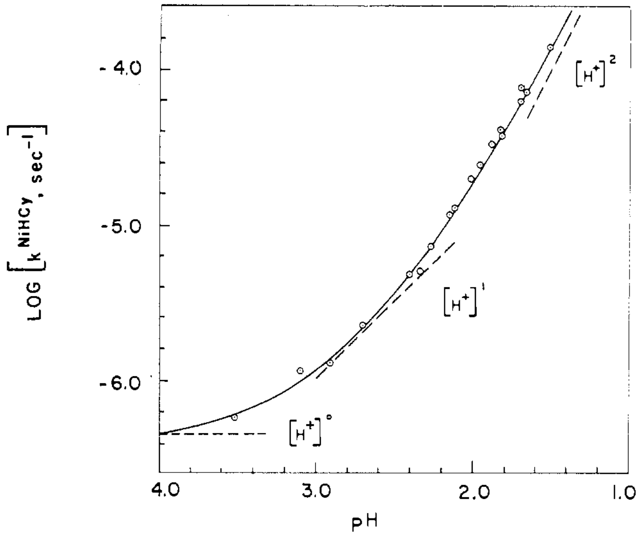

Fig. 4.—The pH dependence of the dissociation of nickel CyDTA in terms of the apparent first-order constant for dissociation of $NiHCy^-$. The slopes show a contribution of $[H^+]^0$ $[H^+]^1$, and $[H^+]^2$ terms.

This rate constant can be written in terms of $[NiHCy^-]$ rather than $[NiCy_T]$

$$k^{NiHCy} = k^{NiCy_T}[NiCy_T]/[NiHCy^-]$$

where the right-hand ratio is calculated from the constants in eq. 7 and 8. Figure 4 plots log k^{NiHCy} against pH where the points are experimental and the curve is calculated on the basis of the resolution of the acid terms. As the dashed lines show the slope approaches 2 at low pH indicating an expression

$$\frac{d[CuCy_T]}{dt} = k_{2H}{}^{NiHCy}[H^+]^2[NiHCy^-]$$

At intermediate pH values the slope approaches unity indicating the term $k_H{}^{NiHCy}[H^+][NiHCy^-]$, while at somewhat higher pH the slope is less than unity corresponding to the contribution of $k^{NiHCy}[NiHCy^-]$. It was possible to neglect the contribution of this last term at higher $[H^+]$ and appropriate linear plots were used to evaluate the two higher acid terms. By correcting for the $[H^+]$ term at lower acidity it again was possible to use linear plots to evaluate the less acid term and to confirm the value of $k_H{}^{NiHCy}$.

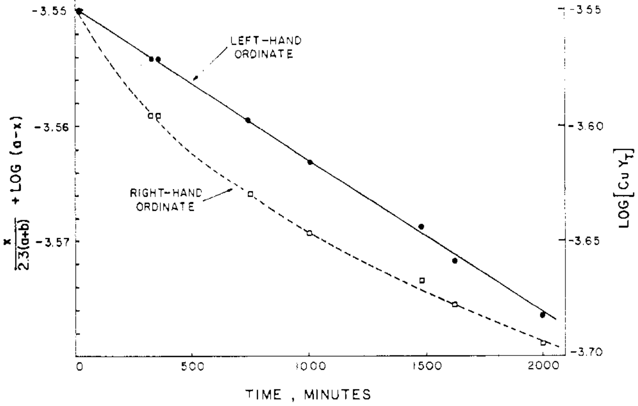

Fig. 5.—Reaction of Ni^{+2} with $CuCy_T$ where the rate-determining step is between Ni^{+2} and the equilibrated Cy_T; pH 3.09 (see Table IV). The right-hand ordinate shows the failure of a first-order fit while the left-hand ordinate corresponds to eq. 11 and 12.

In order to compare the various rate constants with one another and with the EDTA constants it is more convenient to write all as second-order rate constants (see Table III).

$$\text{rate} = k_H{}^{NiCy}[H^+][NiCy^{-2}] + k_H{}^{NiHCy}[H^+][NiHCy^-] + k_H{}^{NiH_2Cy}[H^+][NiH_2Cy] \quad (9)$$

Table III

Second-Order Rate Constants for the Reaction of Hydrogen Ion with Ni-CyDTA and Ni-EDTA[a]

CyDTA		EDTA	
$k_H{}^{NiCy}$	$= 2.5 \times 10^{-4}$	$k_H{}^{NiY}$	$= 8.0 \times 10^{-4}$
$k_H{}^{NiHCy}$	$= 5.88 \times 10^{-4}$	$k_H{}^{NiHY}$	$= 20 \times 10^{-4}$
$k_H{}^{NiH_2Cy}$	$= 22.3 \times 10^{-4}$	$k_H{}^{NiH_2Y}$	$= 42.0 \times 10^{-4}$

[a] 25.0°, $\mu = 1.25$, M^{-1} sec.$^{-1}$.

Kinetics of the Reverse Reaction and Estimation of the Ni-CyDTA Stability Constant.—The stability constant for the nickel-CyDTA complex has not been measured because of the sluggishness of the system. A study of the nickel reaction with copper-CyDTA was used to check the proposed mechanism and to estimate the nickel-CyDTA equilibrium constant. A large excess of nickel ion is needed in order to reverse reactions 2 and 1 so that a significant amount of $CuCy_T$ is reacted. Using the steady state approximation and operating under conditions where the dissociation of $NiCy_T$ can be neglected gives the reverse rate expression

$$\frac{-d[CuCy_T]}{dt} = \frac{k_{Ni}{}^{Cy_T}[Ni^{+2}]k^{CuCy_T}[CuCy_T]}{k_{Ni}{}^{Cy_T}[Ni^{+2}] + k_{Cu}{}^{Cy_T}[Cu^{+2}]} \quad (10)$$

From eq. 10 it can be seen that a sufficiently large excess of $[Ni^{+2}]$ might shift the rate-determining step from the reverse of reaction 1 to the reverse of reaction 2. However, this is not the case even when the ratio of $[Ni^{+2}]/[Cu^{+2}]$ is greater than 100. Thus, the reverse reactions tested did not fit kinetic plots of log $[CuCy_T]$ against time but corresponded to the situation where $k_{Cu}{}^{Cy_T}[Cu^{+2}] >> k_{Ni}{}^{Cy_T}[Ni^{+2}]$ with the same rate-determining step observed in the forward reactions (eq. 1). Figure 5 gives the appropriate kinetic plot where $a = [CuCy_T]_{\text{initial}}$, $b = [Cu^{+2}]_{\text{added}}$, and $x = [NiCy_T]_{\text{formed}}$. Thus, $[CuCy_T] = a - x$, $[Cu^{+2}] = b + x$, and the rate expression is

$$\frac{dx}{dt} = k_{Ni}{}^{Cy_T}\left[\frac{k^{CuCy_T}}{k_{Cu}{}^{Cy_T}}\right][Ni^{+2}]\ \frac{(a - x)}{(b + x)} = k'\frac{(a - x)}{(b + x)} \quad (11)$$

The integrated form of eq. 11 used for Fig. 5 is

$$\frac{x}{2.3(a + b)} + \log(a + x) = \frac{-k't}{2.3(a + b)} + \log a \quad (12)$$

which gave excellent plots for duplicate runs and thus supports the assigned mechanism. The rate constant, $k_{Cu}{}^{Cy_T}$, must be more than 10^3 times the rate constant, $k_{Ni}{}^{Cy_T}$, in order for the first term in the denominator of eq. 10 to be negligible. Table IV gives the conditions used to check the kinetics at two pH values. The stability constant used for $CuCy^{-2}$ was $10^{21.3}$ and appropriate protonation constants[8] were used in eq. 11 to calculate the ratio of rate constants.

TABLE IV

REACTION OF CuCyT WITH $Ni^{+2\,a}$

pH	$[Ni^{+2}]_{initial}$, M	$[CuCy_T]_{initial}$, M	$[Cu^{+2}]_{added}$, M	k', M sec.$^{-1}$ $\times 10^{10}$	$k_{Ni}^{Cy_T}$, M^{-1} sec.$^{-1}$
3.09	0.0116	2.82×10^{-4}	1.34×10^{-5}	1.48	19.2
2.32	0.00774	2.82×10^{-4}	None	29.4	5.16

^{a} 25.0°, $\mu = 1.25$.

The forward and reverse rate constants in eq. 1 can be used to determine the stability constant of Ni-CyDTA. The pH-independent constant

$$\left(K_{NiCy} = \frac{[NiCy^{-2}]}{[Ni^{+2}][Cy^{-4}]}\right)$$

was calculated from the rate constant k' in eq. 11 and 12, from k^{NiCy_T}, from the stability constant of $10^{21.3}$ for $CuCy^{-2}$ (measured at 20° in 0.1 M KNO_3)[2] and from our values for the acid dissociation constants of $NiHCy^-$, NiH_2Cy, $CuHCy^-$, and CuH_2Cy. The acid constants of CyDTA cancel in this calculation and are not involved in the final value and the acid constants of NiHCy, etc., have little influence. Equation 13 relates the experimental conditions in Table IV to the desired constant.

$$K_{NiCy} = \frac{k'}{[Ni^{+2}]}\,\frac{K_{CuCy}}{k^{NiCy_T}}\,\frac{\left(1 + \dfrac{[H^+]}{K_{CuHCy}} + \dfrac{[H^+]^2}{K_{CuH_2Cy}K_{CuHCy}}\right)}{\left(1 + \dfrac{[H^+]}{K_{NiHCy}} + \dfrac{[H^+]^2}{K_{NiH_2Cy}K_{NiHCy}}\right)} \quad (13)$$

The values found for K_{NiCy} were 1.0×10^{20} and 0.7×10^{20} for data at pH 2.32 and 3.09, respectively.

Discussion

Two points are particularly noticeable in comparing the kinetic reactions of nickel-CyDTA with those of nickel-EDTA: (1) The two complexes have a completely different behavior with copper ion and (2) there is a close similarity between the hydrogen ion reactions with the two complexes. This apparently contradictory behavior actually is consistent with the unwrapping mechanism proposed for these multidentate ligands and is understood readily in terms of steric effects when the molecular models are constructed. Structure I in Fig. 6 is the stable form of the metal complexes of CyDTA and the metal–iminodiacetate segment must be rotated before one nitrogen is free to add a proton as in structure II. A second metal ion cannot fit into the opening shown occupied by a proton in structure II because of the carbon and hydrogen atoms in the acetate portion of the rotated segment, nor is it possible to rotate both nitrogens so that their coördination faces are in opposite directions (structure III). With EDTA there is no ring structure to prevent the rotation of the ethylene linkage between the nitrogen atoms and therefore EDTA complexes can proceed through reaction intermediates with one metal bonded to each nitrogen atom. This is not possible with CyDTA, although it is possible to accommodate one metal ion and one proton on the nitrogen atoms as shown in structure II.

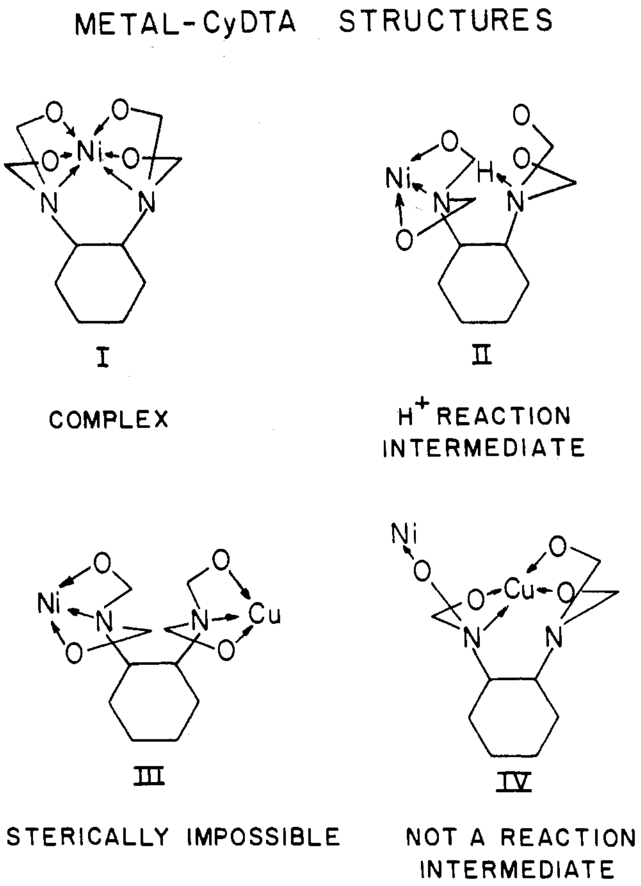

Fig. 6.—Metal-CyDTA structures.

I. One metal can coördinate both nitrogens to form the stable complex.

II. An iminodiacetate segment bonded to the metal can be rotated but the remaining segment cannot accept another metal ion at the nitrogen. It can be protonated as shown.

III. This structure is not possible due to steric hindrance of the acetate groups with one another and the ring.

IV. This structure is possible but cannot be a reaction intermediate for Cu^{+2} attack of $NiCy^{-2}$. Nor is there any evidence of an intermediate corresponding to a structure where Ni^{+2} and Cu^{+2} change places.

Table III summarizes rate constants written for the reaction of hydrogen ion with the nickel-CyDTA and nickel-EDTA complexes. For each protonated form of the complex the second order rate constant is consistently just two to three times greater for EDTA than for CyDTA. Obviously, the hydrogen ion reaction paths must be similar. Furthermore, the magnitude of these hydrogen ion rate constants corresponds closely to an intermediate with one nitrogen protonated and with the other nitrogen undergoing cleavage with nickel as the rate-determining step [see paper IV[5] for similar calculations]. This gives strong support to a CyDTA mechanism with intermediates of the type shown in structure II of Fig. 6.

The lack of copper attack on nickel-CyDTA also is consistent with structure II and supports our previous

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[8] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

arguments that the nitrogen cleavage is the rate-determining step. If the nickel–acetate cleavage was the rate step then structure IV would be possible and an appreciable rate of reaction with copper would be expected. The complete absence of any detectable attack by copper confirms both the importance of the nitrogen–nickel cleavage and the need for nitrogen bonding to the attacking metal. The cyclohexane ring prevents the complete rotation of the two iminodiacetate segments so that the dinuclear reaction intermediates so important with EDTA reactions cannot form. As a result we find that even as labile a metal ion as zinc forms sluggish CyDTA complexes.

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Contribution from the Research and Development Laboratories,
Pennsalt Chemicals Corporation, Wyndmoor, Pennsylvania

Inorganic Coördination Polymers. V. The Use of Neutral Ligands[1]

By B. P. BLOCK and JOSEPH SIMKIN

Received March 4, 1963

The attempt to make $Zn(IDP)C_6H_5PO_3$ led, instead, to $Zn_2(IDP)(C_6H_5PO_3)_2$, where IDP represents 2,2′-iminodipyridine. $Zn(py)C_6H_5PO_3$ was also prepared. It is suggested that these substances are polymers. Their thermal stabilities, however, are not high. This is related to the presence of neutral ligands and a strong bridging group.

In our search for coördination polymers with inorganic backbones we have attempted the synthesis of representatives of a number of different patterns. Our efforts to make the type $(-M(AB)X-)_x$, where AB represents a uninegative, bidentate ligand and X a uninegative catenating group, resulted in a dimer for the composition $Be(AcCHAc)(OP(C_6H_5)_2O)$,[2] and we have indications that a dimer also results from attempts to make the composition $Zn(AcCHAc)(OP(C_6H_5)_2O)$.[3] Another type of polymer that we have attempted to prepare is $(-M(AA)Y-)_x$, where AA represents a neutral bidentate ligand and Y a catenating group with two negative charges. The specific composition we sought is $Zn(IDP)(C_6H_5PO_3)$, where the bidentate ligand is 2,2′-iminodipyridine (represented by IDP) and the catenating group is the phenylphosphonate anion. It was our hope that the use of a doubly charged catenating group would lead to a single bridged, rather than double bridged (as found with diphenylphosphinate[4]), structure while at the same time yielding a strong backbone.

Experimental

The reaction of $Zn(IDP)(OAc)_2$ with $C_6H_5P(O)(OH)_2$ was carried out both in methanol and in pyridine. (1) In methanol. A solution of 3.55 g. (0.0225 mole) of $C_6H_5P(O)(OH)_2$ (Eastman Organic Chemical recrystallized from methanol) in 50 ml. of methanol was added dropwise to a solution of 7.97 g. (0.0225 mole) of $Zn(IDP)(OAc)_2$[5] in 150 ml. of methanol with rapid stirring. The thick milky suspension that formed was filtered through a medium porosity filter funnel to give 6.0 g. of a white solid after washing with methanol and drying at 95°. *Anal.* Calcd. for $Zn_2(NH(C_5H_4N)_2)(C_6H_5PO_3)_2$: N, 6.8; P, 10.1; Zn, 21.3; and for $Zn(NH(C_5H_4N)_2)C_6H_5PO_3$: N, 10.7; P, 7.9; Zn, 16.7. Found: N, 6.9; P, 9.7; Zn, 21.0. The mother liquor and washings were evaporated to dryness on a steam bath, yielding 1.9 g. of residue shown by infrared spectrum to consist mainly of 2,2′-iminodipyridine.

The compound $Zn_2(IDP)(C_6H_5PO_3)_2$ exhibits a crystalline X-ray diffraction pattern and gives the infrared absorption bands shown in Table I. It does not appear to melt in a capillary tube at temperatures up to 400°, and is not soluble in organic solvents such as ethanol, benzene, acetone, chloroform, diethyl ether, and 1,4-dioxane. When a 1.95-g. sample was extracted with pyridine in a Soxhlet extractor, the soluble fraction was found to contain 2,2′-iminodipyridine as identified by infrared. The insoluble fraction, weighing 1.85 g., was shown by infrared (absorption bands in Table I) not to contain 2,2′-iminodipyridine, but pyridine instead. *Anal.* Calcd. for $Zn(C_5H_5N)(C_6H_5PO_3)$: N, 4.7; Zn, 21.8. Found: N, 4.9; Zn, 21.8.

(2) In pyridine. A solution of 1.6 g. (0.01 mole) of $C_6H_5P(O)(OH)_2$ in 50 ml. of pyridine was added to a solution of 3.5 g. (0.01 mole) of $Zn(IDP)(OAc)_2$ in 100 ml. of pyridine with stirring at room temperature. The resulting mixture, containing a white precipitate, was diluted to 250 ml. with pyridine, refluxed for 20 hr., and filtered. After the precipitate was washed with diethyl ether and dried, there was 2.8 g. of insolubles shown by infrared and X-ray spectra to be identical with the $Zn(py)(C_6H_5PO_3)$ prepared by extraction of $Zn_2(IDP)(C_6H_5PO_3)_2$ with pyridine. The filtrate upon evaporation yielded a 1.6-g. residue found by infrared and melting point of 90° (lit.[6] 95°) to be 2,2′-iminodipyridine. The weight of 2,2′-iminodipyridine in the $Zn(IDP)(OAc)_2$ taken is 1.7 g.

A dispersion of 2.20 g. (0.01 mole) of $Zn(OAc)_2 \cdot 2H_2O$ (Baker Analyzed Reagent) and 1.70 g. (0.01 mole) of 2,2′-iminodipyridine (Reilly Tar and Chemical Corp.) in 100 ml. of methanol was warmed on a steam bath and then filtered through a medium porosity filter funnel. To the filtrate was added dropwise a solution of 1.58 g. (0.01 mole) of $C_6H_5P(O)(OH)_2$ in 50 ml. of methanol with heating (steam bath) and stirring. The gelatinous mixture was filtered after 1 hr., and the precipitate was washed back into a beaker, dispersed in methanol, and refiltered. The dried product weighed 2.69 g. *Anal.* Calcd for $Zn_2(IDP)(C_6H_5PO_3)_2$ already given. Found: N, 6.8; P, 10.0;

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