second of these formulations is the correct one.

Cyanide, however, has a greater affinity for hematin than does imidazole, and in Hambright's work all the hematin was converted immediately to the monocyano adduct. This, and not hematin, is the species which is then cleaved. This would appear to support the mechanism in which the imidazole adduct is the reactive species (eq 8).

However, the splitting of the cyano adduct with a rate proportional to $[HCN][CN^-]$ does not strictly correspond to the splitting of the imidazole adduct, since this latter reaction has a rate proportional to $[H_2Im^+]$. While there is no reason that both reactions must have similar rate laws, this would be an attractive feature. One possible explanation for this difference is that if the hematin itself is the reactive species in our system, as in eq 6, Hambright's system would have differed from ours in that the rapid reaction to form the cyanide adduct would prevent the hematin from reacting.

An adduct between hematin and either imidazole or 1,10-phenanthroline has not previously been reported. However, our observations are strikingly similar to those of Abbott.[9,10] He observed adducts between bis(imidazole)-iron(III) cation and 1,10-phenanthroline, imidazole, and 2-methylimidazole. As was the case in our measurements, other compounds studied, even similar ones such as bipyridyl and N-methylimidazole, did not form adducts.[10] Also the size of Abbott's equilibrium constants, 90 and 500 M^{-1} for imidazole and 1,10-phenanthroline, respectively,[10] are similar to those we have observed, 220 and 580 M^{-1}.

Abbott has postulated that this interaction may occur by an overlap between the two π clouds and, given the list of compounds which form adducts, this is quite plausible. However, it has been shown that significant hydrogen bonding occurs between free and complexed imidazoles when bis-(imidazole)iron(III) porphyrin is dissolved in the presence of excess imidazole.[11] Since hydrogen bonding should increase the donating ability of the imidazole ligands, this should energetically favor the bis(imidazole) complex and would thus explain Abbott's observations. However, our results cannot be explained in terms of hydrogen bonding.

For experimental reasons neither we nor Abbott's group have examined cyanide to see if it forms adducts. However, Hambright's work indicates that cyanide does behave like imidazole and 1,10-phenanthroline. It should be noted that cyanide, like the others, is unsaturated and that one molecule quickly adds to the iron porphyrin. Unlike the others cyanide does cause a small spectral change. However, this change is too small to be caused by direct interaction with the metal or by any significant change in structure.

Finally we are unable to explain why only certain molecules form porphyrin adducts. This question will have to await further work.

Acknowledgment. We wish to thank Dr. Daniel Huchital for helpful discussions and Dr. Edwin Abbott for permission to quote unpublished results. The support of the Research Corporation is gratefully acknowledged.

Registry No. TPPFeOFeTPP, 12582-61-5; HIm, 288-32-4; $H_2Im^+Cl^-$, 1467-16-9; $[TPPFe{\cdot}2HIm]^+$, 52155-41-6.

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Kinetics of the Nickel(II)–N,N′-Diglycylethylenediamine Reaction with Ethylenediaminetetraacetate

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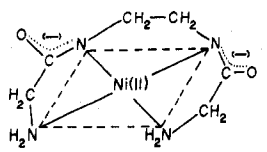
The reaction of deprotonated nickel(II)–N,N′-diglycylethylenediamine with ethylenediaminetetraacetate has been studied over the pH range of 8.55–11.47. The ligand exchange reaction proceeds through two paths. The first of these is dissociative, $k_d = 2.1 \times 10^{-4}$ s^{-1}, and the second involves direct replacement by deprotonated EDTA, $k_{EDTA^{4-}} = 3.33 \times 10^{-3}$ M^{-1} s^{-1}, and monoprotonated EDTA, $k_{HEDTA^{3-}} = 8.13 \times 10^{-3}$ M^{-1} s^{-1}. The overall reaction is accelerated through reaction with bicarbonate ion to form a protonated intermediate. This complex is more reactive than $NiH_{-2}DGEN$ and the exchange reaction is initiated at a nonterminal coordination site. The reaction is retarded at higher pH values by the loss of a proton from the parent complex.

N,N′-Diglycylethylenediamine (DGEN) forms a yellow square-planar complex with Ni(II) in which both of the DGEN amide protons have been ionized.[1,2] The mode of coordination of the ligand to nickel is through the two terminal amine groups and the two deprotonated amide nitrogens. The deprotonated complex is designated by $NiH_{-2}DGEN$.



Ionization of the protons is virtually complete by pH 8. Nickel(II) also facilitates the ionization of amide protons from coordinated polypeptides and polyamides. As with DGEN the deprotonated complexes are generally formed by pH 8.[3–5]

The displacement of short-chain polypeptides from nickel(II) and copper(II) by multidenatate ligands such as ethylenediaminetetraacetate and triethylenetetramine proceeds through proton transfer limited[5–7] or direct replacement paths.[8,9] In these studies the polypeptide is believed to unwrap from the metal stepwise starting with the carboxyl terminus. When the third residue in glycylglycylglycine is replaced by L-histidine (glygly-L-his), the reactivity pattern is altered to a proton-assisted mechanism that is initiated at a nonterminal position.[10–12]

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In this report we present the kinetics and mechanism for the reaction of $NiH_{-2}DGEN$ with ethylenediaminetetraacetate, EDTA. The reaction is influenced by the lability of the terminal amine donors, the loss of a proton from the parent complex, and proton transfer from bicarbonate. This reaction, like displacement reactions with glygly-L-his, may be initiated at a nonterminal position. A direct replacement path provides an indication of the internal flexibility of the coordinated DGEN.

Experimental Section

Diglycylethylenediamine (DGEN) was synthesized by the method of Cottrell and Gill[13] and isolated as the dihydrochloride salt. The observed melting point was 247 °C which is the same as the reported value. The $Ni(ClO_4)_2$ stock solution, 0.092 M, was prepared from the recrystallized salt, and standardized by comparison to ethylenediaminetetraacetate (EDTA). Stock solutions of $NaClO_4$ (2.0 M), Na_2CO_3 (0.20 M), $NaHCO_3$ (0.20 M), and EDTA (0.100 M) were prepared by dissolution of the salts in doubly distilled water.

Solutions of $NiH_{-2}DGEN$ were prepared by dissolving an analytically weighed portion of DGEN in water followed by the addition of an aliquot of stock $Ni(ClO_4)_2$. The solutions contained 100% excess DGEN. The pH of the solution was then raised slowly through the addition of dilute NaOH to a pH of at least 9.2. At this pH, both amide protons have been ionized, and the complex is diamagnetic.[1,2]

It has been previously noted that oxygen influences the reactivity of some nickel–polypeptide complexes. This was observed in these studies, and thus all solutions were deoxygenated with N_2 prior to mixing. The solutions used for the kinetic runs were prepared 2 to 3 h prior to the experiment. The pH of the solutions was monitored with Radiometer Model 26 using a glass electrode and SCE. The electrodes were standardized with certified buffers. The pH of a reaction solution was measured after completion of the kinetic run. Constant pH was maintained throughout a kinetic run by EDTA or added bicarbonate–carbonate buffer. The acid dissociation constants used were $pK_a(HEDTA^{3-}) = 10.26$ and $pK_a(HCO_3^-) = 10.2$.

The visible and ultraviolet spectra of $NiH_{-2}DGEN$ were obtained with a Cary Model 14 spectrophotometer using a 10-cm cell. The complex exhibits an absorption maximum at 412 nm. This maximum does not shift as the pH is varied from 9.2 to 11.8; however, there are shifts at shorter wavelengths (275–300 nm). As the pH is increased the shoulder observed in this region exhibits a slight increase.

The reaction of $NiH_{-2}DGEN$ with EDTA was monitored by measuring the disappearance of the yellow $NiH_{-2}DGEN$ complex at 412 nm (ϵ 220 M^{-1} cm^{-1}). A typical kinetic reaction involved the preparation of 500 mL of an oxygen-free solution, 3.0×10^{-4} M in $NiH_{-2}DGEN$, 0.10 M in $NaClO_4$, and of desired pH. An aliquot of this solution was transferred to a beaker, under nitrogen, and a known quantity of O_2-free EDTA solution (0.10 M in $NaClO_4$) was added. A Cary Model 14 spectrophotometer was used to record the absorbance values, using 10-cm cells. The reactions were run at 25 °C in the presence of excess EDTA, and plots of $-\ln (A - A_\infty)$ vs. time were linear. The observed pseudo-first-order rate constants are the slopes of such plots and were calculated by computer using a linear least-squares program. The reported rate constants are an average of at least two kinetic runs. Extrapolation of absorbance readings to zero time was always within 3% of the expected value. The products of the reaction are $NiEDTA^{2-}$ and DGEN. The presence of 100% excess DGEN does not appear to influence the rate of the reactions.

Results and Discussion

The reaction of $NiH_{-2}DGEN$ with excess EDTA at pH 8.55 was found to proceed through two paths. One of these paths is independent of the EDTA concentration and the second exhibits first-order dependence in EDTA. In addition, both paths are first order in the nickel complex. A rate equation consistent with these observations is shown in eq 1. Under

$$-d[NiH_{-2}DGEN]/dt = (k_d + k[EDTA]_T)[NiH_{-2}DGEN] \quad (1)$$

pseudo-first-order conditions the observed rate constant, k_{obsd}, is given by eq 2. A plot of k_{obsd} vs. EDTA total concentration

$$k_{obsd} = k_d + k[EDTA]_T \quad (2)$$

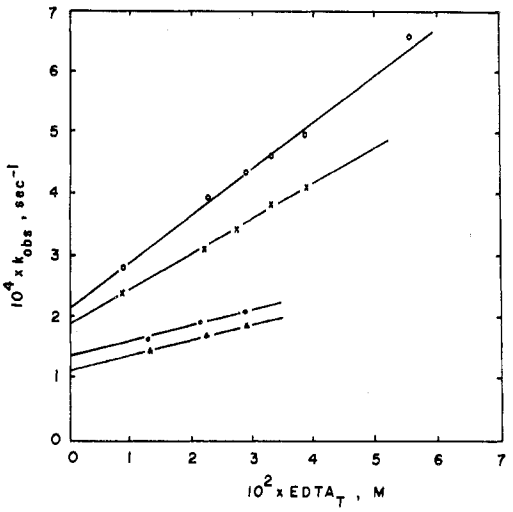


Figure 1. Dependence of the observed pseudo-first-order rate constant on EDTA concentration: ○ for pH 8.55, × for pH 10.65, ● for pH 11.19, ▲ for pH 11.45.

is shown in Figure 1 and the kinetic data are presented in Table A.[23] When the reaction is run at pH 10.65, 11.19, and 11.45, both the slope and the intercept decrease from the values observed at pH 8.55 (see Figure 1). Over this pH range, the speciation of $EDTA_T$ changes from the monoprotonated form, $HEDTA^{3-}$, to the deprotonated form, $EDTA^{4-}$. This speciation change accounts for the slope changes in Figure 1.

The decrease in the intercept values is attributed to the loss of proton from $NiH_{-2}DGEN$. This mixed complex is not as reactive as $NiH_{-2}DGEN$. Spectral evidence for such a complex is observed through very small band shifts in the 275–300-nm region with the absorbance increasing slightly as the mixed complex forms. The shift is not sufficient to permit evaluation of the stability constant.

A reaction sequence consistent with these observations is

$$NiH_{-2}DGEN \overset{K_a}{\rightleftharpoons} NiH_{-2}DGEN(H_{-1})^- + H^+ \quad (3)$$

$$NiH_{-2}DGEN \xrightarrow{k_d} \text{products} \quad (4)$$

$$NiH_{-2}DGEN + EDTA^{4-} \xrightarrow{k_1} \text{products} \quad (5)$$

$$NiH_{-2}DGEN + HEDTA^{3-} \xrightarrow{k_2} \text{products} \quad (6)$$

The rate equation for the reaction over pH range 8.55–11.47 is shown in eq 7, assuming equilibrium concentrations of

$$d[\text{products}]/dt = (k_d + k_1[EDTA^{4-}] + k_2[HEDTA^{3-}])\frac{[Ni]_T}{K_a/[H^+] + 1} \quad (7)$$

$NiH_{-2}DGEN(H_{-1})^-$, where $[NiH_{-2}DGEN]$ is equal to $[Ni]_T/(K_a/[H^+] + 1)$ and $[Ni]_T = [NiH_{-2}DGEN] + [NiH_{-2}DGEN(H_{-1})^-]$.

The intercepts of Figure 1 are defined in eq 8 and can be

$$k_{intercept} = k_d/(K_a/[H^+] + 1) \quad (8)$$

utilized to evaluate K_a. Rearrangement of eq 8 utilizing $K^1 = K_a/K_w$ provides

$$\frac{1}{k_{intercept}} = \frac{K^1[OH^-]}{k_d} + \frac{1}{k_d} \quad (9)$$

and a plot of $1/k_{intercept}$ vs. $[OH^-]$ is shown in Figure 2. The intercept of this plot provides $k_d = 2.1 \times 10^{-4}$ s^{-1}, and from

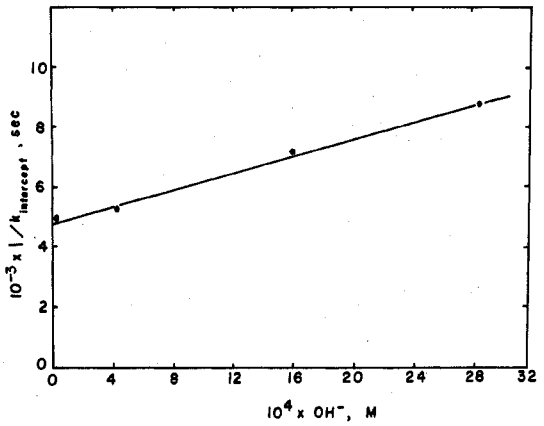


Figure 2. Resolution of k_d and K_a. Intercept = $1/k_d$ and slope = K_a/k_d.

Table I. k_d Values for Deprotonated Nickel(II) Complexes

Complex	k_d s^{-1}	Ref
$NiH_{-2}DGEN$	2.1×10^{-4}	This work
$NiH_{-2}glyglygly^-$	5×10^{-2}	5
$NiH_{-2}glyglaCN^-$ [a]	8×10^{-5}	14
$NiH_{-3}glyglyglygly^{2-}$	1.6×10^{-5}	7
$CuH_{-2}glygly$-L-his	7.5×10^{-4}	10
$CuH_{-2}glyglygly^-$	1.2×10^{-1}	6
$NiH_{-2}glyglyglyCN^{2-}$	2.7×10^{-3}	15

[a] gla = glycylamide.

the slope, K_a, equals 2.9×10^{-12} M.

The value of k_d is significantly less than the corresponding value observed for $NiH_{-2}glyglygly^-$; however, it is comparable to values observed for the tetraglycine and the amide complexes. The dissociation rate constants for other complexes are summarized in Table I.

Triglycine and DGEN have comparable modes of coordination to Ni(II) except that the carboxyl terminus of triglycine is replaced by an amine donor in DGEN. This change results in a factor of 250 decrease in the dissociation rate constant. In the triglycine complex, the carboxyl coordination is believed to be the most labile and the rate-determining step is associated with the breakage of a nickel–imide bond. In the DGEN complex the amine coordination is not as labile and the rate constant of 2.1×10^{-4} s^{-1} is assigned to the breakage of a nickel–amine bond. A value of 4.8×10^{-4} s^{-1} has been observed for the dissociation of CN^- from $Ni(CN)_4^{2-}$.[16]

Comparison of the two copper systems cited in Table I indicates a reduction of 160 when one goes from $CuH_{-2}glyglygly^-$ to $CuH_{-2}glygly$-L-his. In these systems carboxyl coordination is replaced by an imidazole nitrogen and the reduction in rate is assigned to the breakage of the copper–nitrogen bond.[11,12]

The formation of $NiH_{-2}DGEN(H_{-1})^-$ influences both reaction pathways and thus the speciation of nickel needs to be evaluated before rate constants k_1 and k_2 can be resolved. The slopes of the lines in Figure 1 are given by

$$\text{slope} = (k_1[EDTA^{4-}] + k_2[HEDTA^{3-}])(1/(K_a/[H^+] + 1)) \quad (10)$$

Utilizing K_a, total EDTA concentrations, pK_a for $HEDTA^{3-}$, pH, and the slopes from Figure 1, the values of k_1 and k_2 are found, through solution of simultaneous equations, to be 3.33 $\times 10^{-3}$ and 8.13 $\times 10^{-3}$ M^{-1} s^{-1}, respectively.

The square-planar unit resulting from coordination of short-chain polypeptides appears to exhibit extreme kinetic rigidity and thus any direct replacement reactions are subject to a variety of steric requirements in both the entering ligand and the substrate complex.[17,18] In this case, the direct reaction of $NiH_{-2}DGEN$ with $EDTA_T$ is observed because of the marked reduction in the rate of the dissociation path.

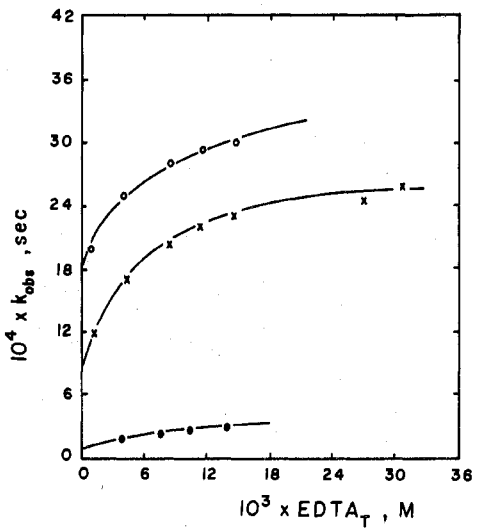


Figure 3. Influence of bicarbonate and carbonate on the reaction of $NiH_{-2}DGEN$ with EDTA: O for pH 9.20, × for pH 10.40, ● for pH 11.40.

The rate constants for the reaction of $EDTA^{4-}$ ($k_1 = 3.33 \times 10^{-3}$ M^{-1} s^{-1}) and $HEDTA^{3-}$ ($k_2 = 8.13 \times 10^{-3}$ M^{-1} s^{-1}) with $NiH_{-2}DGEN$ are small; however, it is interesting to note that $HEDTA^{3-}$ is more effective than the totally deprotonated ligand. The reverse is commonly encountered. This change is believed due to $HEDTA^{3-}$ being able to transfer its proton intramolecularly to one of the amide sites of DGEN prior to or during the rate-determining step. A concerted process of this type would facilitate the breakage of a nickel–imide bond and thus provide a path for EDTA to replace DGEN.

The kinetic and spectral evidence for the deprotonation of $NiH_{-2}DGEN$ is of considerable interest. This species can be formulated as $NiH_{-3}DGEN^-$ which implies loss of a proton from one of the amine nitrogens. There is sizable evidence for complexes of this type as intermediates in the conjugate base dissociation mechanism.[19,20] With this formulation the pK_a of the third proton would be 11.5 which is rather acidic for a coordinated amine group. Another formulation of the deprotonated species is $NiH_{-2}DGEN(OH)^-$ which implies out-of-plane coordination of hydroxide ion. Coordination of out-of-plane positions is important in these types of ligand-exchange reactions.[18] The stability constant for the formation of $NiH_{-2}DGEN(OH)^-$ is larger than what one would predict based on $HiH_{-2}GGG^-$ results.[5]

Both formulations provide the same interpretation of the kinetic results and additional studies are needed before the nature of this species can be assigned.

Influence of Bicarbonate and Carbonate

The presence of bicarbonate–carbonate buffer markedly influences the reaction of $NiH_{-2}DGEN$ with EDTA. The reaction is much more responsive to lower concentrations of EDTA, as is shown in Figure 3, whereas the dependence is similar at the higher concentrations to those previously presented. It has been observed that reactions involving nickel–triglycine are subject to catalysis by bicarbonate and are also inhibited by carbonate.[7] Comparable behavior is believed to be occurring with $NiH_{-2}DGEN$ and is in addition to the two pathways previously presented. A reaction sequence that accounts for the bicarbonate dependence is shown by

$$NiH_{-2}DGEN + HCO_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} NiH_{-2}DGEN(H)^+ + CO_3^{2-} \quad (11)$$

$$NiH_{-2}DGEN(H)^+ + EDTA^{4-} \xrightarrow{k_5} \text{products} \quad (12)$$

$$NiH_{-2}DGEN(H)^+ + HEDTA^{3-} \xrightarrow{k_6} \text{products} \quad (13)$$

$$NiH_{-2}DGEN(H^+) \xrightarrow{k_d'} \text{products} \quad (14)$$

Assuming steady state for $NiH_{-2}DGEN(H^+)$ and combining eq 3–6 and 11–14 provide the rate equation for the reaction in the presence of bicarbonate buffer, eq 15. The species

$$\frac{d[\text{products}]}{dt} = \left\{ k_d + k_1[EDTA^{4-}] + k_2[HEDTA^{3-}] + k_3[HCO_3^-]\left(\frac{k_d' + k_5[EDTA^{4-}] + k_6[HEDTA^{3-}]}{k_d' + k_4[CO_3^{2-}] + k_5[EDTA^{4-}] + k_6[HEDTA^{3-}]}\right)\right\} \times \left(\frac{[Ni]_T}{K_a/[H^+] + 1}\right) \quad (15)$$

$NiH_{-2}DGEN(H)^+$ is believed to be an outside-protonated form that will subsequently rearrange to a more stable configuration after the rate-determining step. The reactions have been studied in the presence of excess EDTA, HCO_3^-, and CO_3^{2-} and at constant pH, and thus the observed pseudo-first-order rate constant is given by

$$k_{obsd} = \left\{ k_d + k_1[EDTA^{4-}] + k_2[HEDTA^{3-}] + k_3[HCO_3^-]\left(\frac{k_d' + k_5[EDTA^{4-}] + k_6[HEDTA^{3-}]}{k_d' + k_4[CO_3^{2-}] + k_5[EDTA^{4-}] + k_6[HEDTA^{3-}]}\right)\right\} \times \left(\frac{1}{K_a/[H^+] + 1}\right) \quad (16)$$

The first three terms of eq 16 have been evaluated when no bicarbonate–carbonate buffer was present and their contribution may be subtracted from k_{obsd}. If

$$k' = \{k_d + k_1[EDTA^{4-}] + k_2[HEDTA^{3-}]\}\left(\frac{1}{K_a/[H^+] + 1}\right) \quad (17)$$

then

$$k_{obsd} - k' = k_3[HCO_3^-] \times \left(\frac{k_d' + k_5[EDTA^{4-}] + k_6[HEDTA^{3-}]}{k_d' + k_4[CO_3^{2-}] + k_5[EDTA^{4-}] + k_6[HEDTA^{3-}]}\right)\left(\frac{1}{K_a/[H^+] + 1}\right) \quad (18)$$

The constant k_3 cannot be resolved unless k_d' is small compared to some of the other terms in eq 18. This appears to be the case when the $[EDTA]_T$ is greater than 4×10^{-3} M. Assuming k_d' small compared to the other terms and rearrangement of eq 18 with the inclusion of the α terms for the EDTA species provide

$$\frac{1}{k''} = \frac{1}{(k_{obsd} - k')(K_a/[H^+] + 1)} = \frac{k_4[CO_3^{2-}]}{k_3[HCO_3^-][EDTA]_T(\alpha_Y k_5 + \alpha_{HY} k_6)} + \frac{1}{k_3[HCO_3^-]} \quad (19)$$

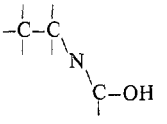
where $\alpha_Y = [EDTA^{4-}]/[EDTA]_T$ and $\alpha_{HY} = [HEDTA^{3-}]/[EDTA]_T$. A plot of $1/k''$ vs. $1/[EDTA]_T$ at constant $[CO_3^{2-}]$, $[HCO_3^-]$, and pH is shown in Figure 4.

The value of k_3 calculated from the intercepts in Figure 4 and the respective HCO_3^- concentrations is 0.96 M^{-1} s^{-1}. The ratios of k_5/k_6, k_5/k_4, and k_6/k_4 may also be obtained from the slopes in Figure 4. The values of the rate constants and the ratios are summarized in Table II.

It should be noted that deviation from linearity is observed in Figure 4 at low $[EDTA]_T$. This is due to the contribution of k_d' to the right-hand side of eq 18. The result would be a larger rate constant which is in agreement with the experiment.

The constants shown in Table II and the reagent concentrations have been utilized to predict the observed rate constant, eq 16, and the results are listed in Table B.[23] Except for the experiments at low EDTA concentration, the difference between observed and calculated rate constants is approximately 10%.

The transfer of a proton to $NiH_{-2}DGEN$ from HCO_3^- is believed to involve protonation of an oxygen in one of the amide groups. Since the ligand is symmetrical, no differentiation can be made between the two sites. This proposed orientation is indicated below.



Protonation has a marked influence upon the rate of the reaction of $NiH_{-2}DGEN$ with EDTA, and there is evidence that the influence is selective. The presence of the outside proton increases the lability of the nickel–imide nitrogen bond. It is not known how much it influences the lability of the cis nickel–amine nitrogen bond. If the influence was sizable, i.e., a factor of 10 or more, k_d' would make a sizable contribution to the right-hand side of eq 18. A large contribution is not observed and, in fact, good agreement between k_{obsd} and k_{calcd} is observed for all studies when k_d' is about twice k_d or $k_d' \simeq 4 \times 10^{-4}$ s^{-1}. With this estimate of k_d', one can estimate values for k_5 and k_6. The value predicted for k_5 (see eq 12) is approximately 10 M^{-1} s^{-1}.

This predicted value is more than 10^3 times larger than the rate constant, k_1, observed for the reaction of $EDTA^{4-}$ with $NiH_{-2}DGEN$ and provides insight into the nature of the flexibility of the chelate rings. The addition of a proton to the oxygen labilizes and probably weakens the nickel–imide nitrogen bond. Molecular models indicate that sizable rotation exists within the coordinated ligand when one of the amide donors is weakly coordinated. With out-of-plane coordination and internal rotation two coordination sites are apparently available to EDTA. Coordination to the second EDTA donor is sufficient to transfer the metal from DGEN to EDTA without sequential unwrapping of DGEN. In reactions where distortion of the square plane is difficult, for example, in the crown ether complexes,[21] the rate of metal transfer is slow. In these reactions, there is insufficient flexibility to permit the replacing ligand to pluck the metal out of the square plane.

For the bicarbonate-catalyzed pathway, it is observed that $HEDTA^{3-}$ is 10 times less effective as a nucleophile than

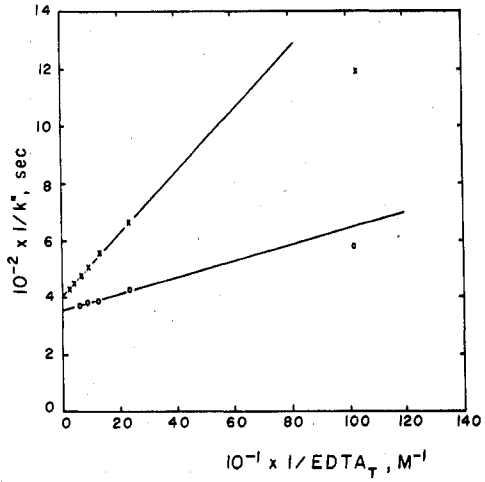


Figure 4. Dependence of k'' on $[EDTA]_T$ (see eq 19): × for pH 9.2, O for pH 10.40.

Table II. Summary of Experimentally Determined Constants

$k_d = 2.10 \times 10^{-4}$ s^{-1}
$k_1 = 3.33 \times 10^{-3}$ M^{-1} s^{-1}
$k_2 = 8.13 \times 10^{-3}$ M^{-1} s^{-1}
$k_3 = 0.96$ M^{-1} s^{-1}
$k_5/k_6 = 9.89$
$k_5/k_4 = 1.61$
$k_6/k_4 = 0.613$
$pK_a = 11.5$

$EDTA^{4-}$ and this raises the question why $HEDTA^{3-}$ does not react more rapidly with $NiH_{-2}DGEN$ than it does. A proton and the replacing ligand are both present in the transition state and thus it is conceivable that rate constants k_2 and k_5 should be approximately the same. The fact that they differ by a factor of about 10^4 indicates that intramolecular proton transfer in these complexes is not a very facile process. This is also observed in the NiH_{-2}glygly-L-his$^-$ reactions with trien.[12] In these reactions H^+ and H_2trien^{2+} react rapidly whereas H_3trien^{3+} exhibits minimal, if any, reactivity. In both of these cases, the number of protons in the transition state is the same.

The rate constant for the reaction[7] of HCO_3^- with NiH_{-2}glyglygly$^-$ is 196 M^{-1} s^{-1} which is a factor of 220 greater than the rate constant for the reaction of bicarbonate with $NiH_{-2}DGEN$. This decrease is also comparable to the decrease in the respective values of k_d. This does not infer that the rate-determining steps are the same in each of the two reaction sequences, and it is supported by the observation that triethylenetetramine reacts slowly[22] with $NiH_{-2}DGEN$ whereas its reaction with NiH_{-2}glyglygly$^-$ is fast.[9]

Summary

The reaction of $NiH_{-2}DGEN$ with EDTA proceeds through a variety of pathways. The relative contribution is dependent upon reagent and hydrogen ion concentrations. A schematic representation is shown in Figure 5.

The reaction is inhibited by the formation of a deprotonated species designated by II. The pathway involving sequential dissociation of DGEN followed by the scavenging of Ni(II) by EDTA is designated by the sequence I → III → VIII. The direct replacement of DGEN by EDTA is designated by the sequence I → IV → VIII. The speciation of EDTA has not been designated for the pathway in Figure 5; however, both $EDTA^{4-}$ and $HEDTA^{3-}$ are reactants. Bicarbonate catalysis followed by reaction with EDTA is shown by sequence I → V → VI → VIII. Both $EDTA^{4-}$ and $HEDTA^{3-}$ are reactants in this sequence. The sequence I → V → VII → VIII involves the formation of the outside protonated species followed by sequential dissociation of DGEN and scavagening of Ni(II) by EDTA. It should be emphasized that the structures of III, IV, V, VI, and VII are proposed intermediates. In each of the paths DGEN ultimately adds two protons and, for simplicity, the respective charges have been omitted.

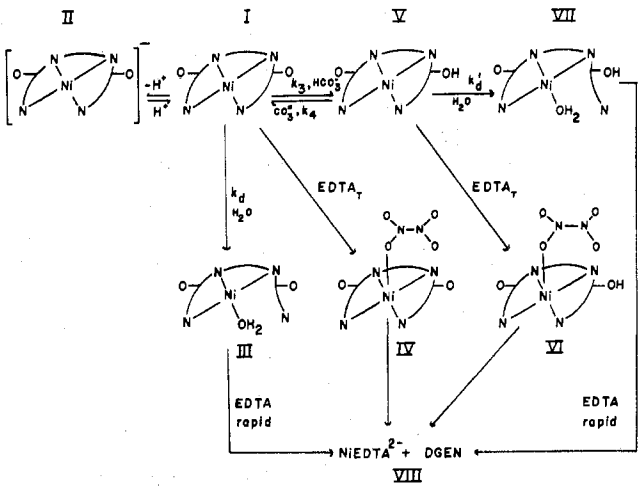


Figure 5. Summary of possible reaction pathways.

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Registry No. $NiH_{-2}DGEN$, 41582-39-2; $EDTA^{4-}$, 150-43-6; HCO_3^-, 71-52-3.

Supplementary Material Available: Tables A and B listing all kinetic data (2 pages). Ordering information is given on any current masthead page.

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