previous work and therefore are not presented in detail.[11]

Horrocks[21] has presented an equation relating the contact shift to the free energy change when there is a diamagnetic $\rightleftharpoons$ paramagnetic equilibrium in solution. Assuming that the monoadduct of $Ni(dtp)_2$ is diamagnetic in the picoline systems, we have tried to fit the temperature dependence of the chemical shift when the experimental free energy change for the reaction is used. While the fit is adequate at low temperatures (260–290°K), we find a divergence at higher temperatures (290–340°) between the experimental points and the calculated contact shift.[11] While several hypotheses are available to explain this behavior, we suggest that the high-temperature behavior might be accounted for by some kind of fluxional behavior. The fluxional nature of five-coordinate geometries is well known.[22] Perhaps one geometrical structure is diamagnetic but as the temperature is increased, another structure with a triplet ground state becomes preferred.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(22) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

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Kinetics and Mechanism of the Ligand Substitution Reactions of the Ethylenediamine-N,N′-diacetate and Nitrilotriacetate Complexes of Nickel(II) with 4-(2-Pyridylazo)resorcinol

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Kinetics and mechanism of the ligand substitution reactions of the ethylenediamine-N,N′-diacetatonickel(II) (Ni^{II}–EDDA: NiEDDA) and the nitrilotriacetatonickelate(II) (Ni^{II}–NTA: $NiNTA^-$) complexes with 4-(2-pyridylazo)resorcinol (PAR: H_2R) have been studied spectrophotometrically at $\mu = 0.10$ and at 25.0°. In the Ni^{II}–EDDA system two distinct reaction steps are observed. The Ni^{II}–EDDA complex reacts rapidly with PAR to form an intermediate Ni^{II}–EDDA–PAR complex ($RNiEDDA^{2-}$ and $RNiHEDDA^-$), which undergoes subsequent unwrapping of EDDA. The first observable step of the reaction follows the rate law $d([RNiEDDA^{2-}] + [RNiHEDDA^-])/dt = k_1[NiEDDA][HR^-]$. The rate law for the second step is written as $d[NiR_2{}^{2-}]/dt = k_2[RNiEDDA^{2-}] + k_{2,H}[RNiHEDDA^-]$. Values of k_1, k_2, and $k_{2,H}$ are $(1.0 \pm 0.3) \times 10^3\ M^{-1}\ sec^{-1}$, $(2.7 \pm 0.2) \times 10^{-4}\ sec^{-1}$, and $(5.1 \pm 0.4) \times 10^{-3}\ sec^{-1}$, respectively. In the Ni^{II}–NTA system the rate equation of the formation of an intermediate $RNiNTA^{3-}$ is $d[RNiNTA^{3-}]/dt = k_1[NiNTA^-][HR^-]$ where the value of k_1 is $(4.2 \pm 0.3) \times 10^2\ M^{-1}\ sec^{-1}$. Some discussions are made on the effect of coordinated ligands on the lability of remaining water. The stability constant of the intermediate $RNiEDDA^{2-}$ is determined at 25.0° and $\mu = 0.1$ ($NaClO_4$): $K^{R}{}_{RNiEDDA} = [RNiEDDA^{2-}]/[NiEDDA][R^{2-}] = 10^{8.2 \pm 0.2}$.

Introduction

For the ligand substitution reactions of metal chelates with multidentate ligands, it has been proposed that the substitution proceeds through an intermediate in which a central metal ion is bonded with both leaving and entering ligands and that the cleavage of the bond between the metal and leaving ligand is the rate-determining step.[1–4] In order to detect spectrophotometrically an intermediate with two different multidentate ligands and to provide a direct experimental evidence for the proposed mechanism, we have taken up ethylenediamine-N,N′-diacetic acid (EDDA: tetradentate) and nitrilotriacetic acid (NTA: tetradentate) as leaving ligands and 4-(2-pyridylazo)resorcinol (PAR: tridentate) as an entering ligand. The present paper describes the result on the ligand substitution reactions

$$Ni^{II}\text{–EDDA} + PAR \rightleftharpoons Ni^{II}\text{–PAR} + EDDA \qquad (1)$$

$$Ni^{II}\text{–NTA} + PAR \rightleftharpoons Ni^{II}\text{–PAR} + NTA \qquad (2)$$

The divalent anions of PAR and EDDA and trivalent anion of NTA are represented as R^{2-}, $EDDA^{2-}$, and NTA^{3-}, respectively.

Experimental Section

Reagents. EDDA.—Reagent grade EDDA, obtained from Dojin-do Chemical Co., Kumamoto, Japan, was purified by recrystallization from aqueous methanol. Care was taken to use fresh solutions of EDDA because cyclization of the free ligand occurs.[5]

NTA.—Reagent grade NTA, obtained from Dojin-do Chemical Co., was recrystallized twice from distilled water.

Sodium Perchlorate.—Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid. Heavy-metal impurities in sodium perchlorate were precipitated as hydroxides at pH 9 and extracted as PAN complexes (PAN:

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(1) D. W. Margerum and H. M. Rosen, *Inorg. Chem.*, **7**, 299 (1968).

(2) M. Tanaka, S. Funahashi, and K. Shirai, *ibid.*, **7**, 573 (1968).

(3) S. Funahashi and M. Tanaka, *Bull. Chem. Soc. Jap.*, **43**, 763 (1970).

(4) S. Funahashi, S. Yamada, and M. Tanaka, *ibid.*, **43**, 769 (1970).

(5) R. B. LeBlanc, *Anal. Chem.*, **31**, 1840 (1959).

1-(2-pyridylazo)-2-naphthol) with purified carbon tetrachloride four times at pH 9 and as oxinates with carbon tetrachloride four times at pH 7. Sodium perchlorate was then recrystallized once from distilled water.

Methods of preparation of the other reagents (sodium hydroxide, nickel perchlorate, boric acid, borax, and PAR) have been described previously.[6]

Kinetic Measurements.—The kinetics of the ligand substitution reaction between the nickel complex and PAR was studied spectrophotometrically at 495 nm using a photoelectric spectrometer, Type 6 (Hirama Rikakenkyujo, Kawasaki, Japan), equipped with a thermostated 2.0-cm cell compartment. A Coolnics circulator, Type CTE-1B (Komatsu Solidate Co., Komatsu, Japan), was utilized in circulating thermostated water through the block. The temperature in the cell was maintained at 25 ± 0.1°. Supplementary spectra were taken on a JASCO Model ORD/UV-5 optical rotatory dispersion recorder.

The procedure for a typical kinetic run is outlined as follows. The nickel complex solution was prepared by mixing nickel perchlorate solution with EDDA solution or NTA solution. Borate buffer solution was added to adjust pH of the solution. The ionic strength of the solution was held constant ($\mu = 0.10$) by sodium perchlorate. A quartz cell with light path length of 2.0 cm containing the nickel complex solution was placed in a thermostated compartment of a spectrophotometer. The PAR solution was brought to temperature equilibrium in a thermostated bath. The reaction was started by mixing the nickel complex solution and the PAR solution. The transmittance at 495 nm of the reaction solution was recorded as a function of the reaction time by a recorder (an X-Y recorder, Type VR-631; Matsushita Communication Industrial Co., Yokohama, Japan).

All pH values were measured with a Radiometer PHM-4d (Copenhagen) with a Type G202B glass electrode and a Type K401 calomel electrode which was carefully calibrated with a standard buffer solution (potassium dihydrogen phosphate, 0.025 *M;* disodium hydrogen phosphate, 0.025 *M*) prepared as described by Bates.[7]

Results

Ligand Substitution Reaction of the Ni^{II}–EDDA Complex with PAR.—Under the present experimental conditions, the Ni^{II}–PAR complex forms the 1:2 complex, NiR_2^{2-},[6] the Ni^{II}–EDDA complex is NiEDDA,[8] and the dominant species of PAR is the monoionic species HR^-, as evident from the stability constants of PAR.[9] The molar absorption coefficients of NiR_2^{2-} and HR^- at 495 nm are 7.85×10^4 and 1.11×10^3, respectively. Reaction 1 is much favored to the right so that the reaction of the Ni–EDDA complex with PAR goes to completion and the reverse reaction can be neglected in the kinetic study.

The overall ligand substitution reaction is described as

$$NiEDDA + 2HR^- \longrightarrow NiR_2^{2-} + EDDA' \qquad (3)$$

where EDDA′ refers to EDDA not combined with nickel. PAR is in a sufficient excess over the Ni–EDDA complex, so that the reaction can be regarded as pseudo first order in NiEDDA. Plots of log ($E_\infty - E_t$) *vs. t* are not linear until the later stage of the reaction (*E* is absorbance of the reaction system). Figure 1 represents a first-order plot of the data. The points are taken from a continuous trace, and excellent linear plots were obtained for all points taken after about 200 sec. Extrapolation to zero reaction time gives a higher absorbance, E_i, than that of the reactants and indicates the rapid formation of an intermediate. The first part of the trace also gives a linear first-order plot as seen in Figure 2, the E_i value taken from the intercept of Figure 1 being assumed to correspond to the absorbance at equilibrium of the first part of the reaction. This fact suggests a consecutive reaction. We assume the reaction scheme

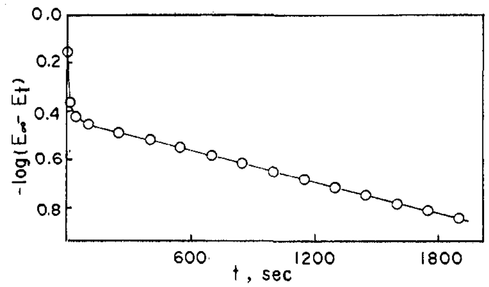

Figure 1.—Typical first-order plot of the slower step using the final absorbance (E_∞) and the observed absorbance (E_t).

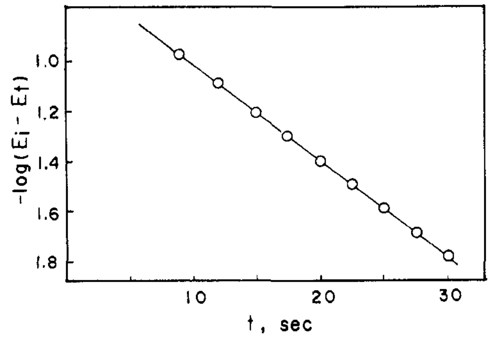

Figure 2.—First-order plot of the faster step in Figure 1 using the intercept of Figure 1 to give E_i.

$$NiEDDA + HR^- \overset{k_1}{\rightleftharpoons} RNiEDDA' + H^+ \qquad (4)$$

$$RNiEDDA' \xrightarrow[+HR^-]{k_{0,2(H)}} NiR_2^{2-} + EDDA' \qquad (5)$$

where RNiEDDA′ indicates all species of intermediates which will be discussed later. A series of kinetic runs was performed at various hydrogen ion concentrations in order to determine the effect of hydrogen ion. In Table I are given the conditional rate constant $k_{0,1(R)}$ for the fast reaction and the conditional rate constant $k_{0,2(H)}$ for the subsequent slow reaction obtained under various experimental conditions. According to these results the conditional rate constant $k_{0,1(R)}$ is proportional to the concentration of PAR and independent of the other concentration terms, such as EDDA, hydrogen ion, and Ni–EDDA complex (runs no. 1–15 in Table I). Therefore, the rate equation for the fast reaction, that is, for the formation of an intermediate RNiEDDA′, is

$$\frac{d[RNiEDDA']}{dt} = k_{0,1(R)}[NiEDDA] = k_1[NiEDDA][HR^-] \qquad (6)$$

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(6) S. Funahashi and M. Tanaka, *Inorg. Chem.*, **8**, 2159 (1969).

(7) R. G. Bates, "Determination of pH, Theory and Practice," Wiley, New York, N. Y., 1964.

(8) S. Chaberek, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 6228 (1952).

(9) W. J. Geary, G. Nickless, and F. H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962)

TABLE I

THE LIGAND SUBSTITUTION REACTION OF THE NICKEL(II)–ETHYLENEDIAMINE-N,N′-DIACETATE COMPLEX WITH 4-(2-PYRIDYLAZO)RESORCINOL[a]

Run no.	C_{EDDA}, M	C_R, M	pH	$k_{0,1(R)}$, sec^{-1}	k_1, M^{-1} sec^{-1}	$k_{0,2(H)}$, sec^{-1}
1	5.60×10^{-6}	8.00×10^{-5}	9.21	8.48×10^{-2}	1.06×10^{3}	5.22×10^{-4}
2	5.60×10^{-6}	8.00×10^{-5}	9.45	7.84×10^{-2}	0.98×10^{3}	3.88×10^{-4}
3	5.60×10^{-6}	8.00×10^{-5}	9.61	7.60×10^{-2}	0.95×10^{3}	3.72×10^{-4}
4	5.60×10^{-6}	8.00×10^{-5}	9.73	8.16×10^{-2}	1.02×10^{3}	3.53×10^{-4}
5	5.12×10^{-6}	3.99×10^{-5}	9.04	4.83×10^{-2}	1.21×10^{3}	5.53×10^{-4}
6	1.28×10^{-5}	3.99×10^{-5}	9.04	4.15×10^{-2}	1.04×10^{3}	4.95×10^{-4}
7	1.92×10^{-5}	3.99×10^{-5}	9.04	3.75×10^{-2}	0.94×10^{3}	4.57×10^{-4}
8[b]	6.40×10^{-5}	3.99×10^{-5}	9.04	4.87×10^{-2}	1.22×10^{3}	5.48×10^{-4}
9	6.40×10^{-5}	2.39×10^{-5}	9.04	2.69×10^{-2}	1.12×10^{3}	4.48×10^{-4}
10	6.40×10^{-5}	3.99×10^{-5}	9.03	4.80×10^{-2}	1.20×10^{3}	5.37×10^{-4}
11	6.40×10^{-5}	3.99×10^{-5}	9.41	4.59×10^{-2}	1.15×10^{3}	3.76×10^{-4}
12	6.40×10^{-5}	5.98×10^{-5}	9.03	6.58×10^{-2}	1.10×10^{3}	5.83×10^{-4}
13	6.40×10^{-5}	9.97×10^{-5}	9.02	1.01×10^{-1}	1.01×10^{3}	6.29×10^{-4}
14	6.40×10^{-5}	9.97×10^{-5}	9.23	8.89×10^{-2}	0.89×10^{3}	4.91×10^{-4}
15	6.40×10^{-5}	9.97×10^{-5}	9.42	9.03×10^{-2}	0.91×10^{3}	4.30×10^{-4}
16	6.40×10^{-5}	9.97×10^{-5}	7.80	. . .[c]	. . .[c]	3.09×10^{-3}
17	6.40×10^{-5}	9.97×10^{-5}	8.09	. . .	. . .	2.32×10^{-3}
18	5.60×10^{-6}	2.00×10^{-4}	8.42	. . .	. . .	1.72×10^{-3}
19	5.60×10^{-6}	2.00×10^{-4}	8.59	. . .	. . .	1.28×10^{-3}
20	5.60×10^{-6}	2.00×10^{-4}	8.82	. . .	. . .	9.48×10^{-4}
21	5.60×10^{-6}	2.00×10^{-4}	9.21	. . .	. . .	5.57×10^{-4}
22	5.60×10^{-6}	2.00×10^{-4}	9.30	. . .	. . .	4.67×10^{-4}
23	5.60×10^{-6}	2.00×10^{-4}	9.46	. . .	. . .	4.45×10^{-4}
24	5.60×10^{-6}	2.00×10^{-4}	9.74	. . .	. . .	3.49×10^{-4}

[a] $C_{Ni} = 5.09 \times 10^{-6}$ M; $\mu = 0.10$ (NaClO$_4$); borate buffer: $[B] = 0.008$ M; 25.0 ± 0.1°. [b] $C_{Ni} = 3.05 \times 10^{-6}$ M. [c] Not determined.

The conditional rate constant $k_{0,2(H)}$, on the other hand, increases with decreasing pH and is independent of the other concentration terms such as PAR, EDDA, and Ni–EDDA complex. The plots of $k_{0,2(H)}$ *vs.* $[H^+]$ did not fall on a straight line but yielded a curve. It seems thus reasonable to assume that the increase in rate constant $k_{0,2(H)}$ with decreasing pH is attributed to the formation of the RNiHEDDA$^-$ complex, the protonated form of the intermediate RNiEDDA^{2-}. Then the kinetic equation is expressed by

$$\frac{d[NiR_2{}^{2-}]}{dt} = k_2[RNiEDDA^{2-}] + k_{2,H}[RNiHEDDA^-] \quad (7)$$

From the equilibrium relationship

$$K^H{}_{RNiHEDDA} = \frac{[RNiHEDDA^-]}{[RNiEDDA^{2-}][H^+]} \quad (8)$$

and mass balance, we have

$$\begin{aligned}[RNiEDDA'] &= [RNiEDDA^{2-}] + [RNiHEDDA^-] \\ &= [RNiEDDA^{2-}](1 + K^H{}_{RNiHEDDA}[H^+]) \quad (9)\end{aligned}$$

Combining eq 7, 8, and 9, we obtain

$$\begin{aligned}\frac{d[NiR_2{}^{2-}]}{dt} &= [RNiEDDA^{2-}](k_2 + k_{2,H}K^H{}_{RNiHEDDA}[H^+]) \\ &= \frac{k_2 + k_{2,H}K^H{}_{RNiHEDDA}[H^+]}{1 + K^H{}_{RNiHEDDA}[H^+]}[RNiEDDA'] \\ &= k_{0,2(H)}[RNiEDDA'] \quad (10)\end{aligned}$$

where $k_{0,2(H)} = (k_2 + k_{2,H}K^H{}_{RNiHEDDA}[H^+])(1 + K^H{}_{RNiHEDDA}[H^+])^{-1}$ is a conditional first-order rate constant composed of rate constants, stability constant, and hydrogen ion concentration. The conditional rate constant $k_{0,2(H)}$ can be rewritten as

$$k_{0,2(H)} = k_{2,H} + \frac{k_2 - k_{2,H}}{1 + K^H{}_{RNiHEDDA}[H^+]} \quad (11)$$

Therefore, we can determine the stability constant and rate constants by the curve-fitting method. The plot of $k_{0,2(H)}$ against pH is compared with a normalized function $y = p/(1 + x) = f(\log x)$.[6] The plot fits well one of a family of the normalized curves (Figure 3).

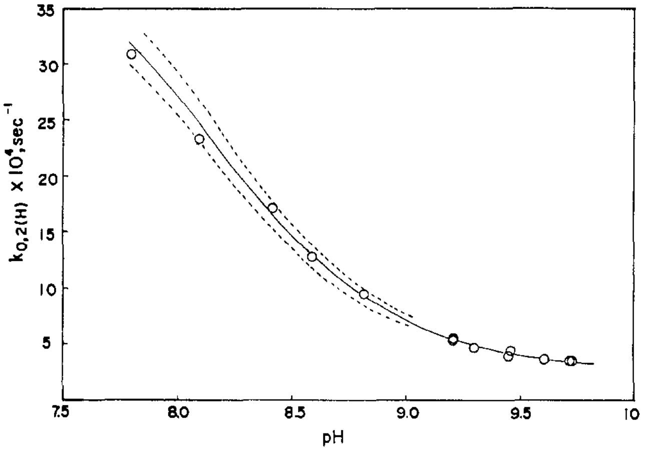

Figure 3.—Plots of $k_{0,2(H)}$ *vs.* pH. The line is the theoretical curve calculated with the values obtained by the curve fitting. The points are experimental at 25.0°. Two dotted lines show the range of deviation of $k_{2,H}$ ($k_{2,H} = (5.1 \pm 0.4) \times 10^{-3}$ sec^{-1}).

The rate constants at $\mu = 0.10$ and 25.0° are $k_1 = (1.0 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}, $k_2 = (2.7 \pm 0.2) \times 10^{-4}$ sec^{-1}, and $k_{2,H} = (5.1 \pm 0.4) \times 10^{-3}$ sec^{-1}. The stability constant $K^H{}_{RNiHEDDA}$ is $10^{8.02 \pm 0.10}$ at $\mu = 0.10$ and 25.0°. The uncertainty of constants indicates the range.

Determination of the Stability Constant of the Intermediate Ni^{II}–EDDA–PAR Complex.—When the equilibrium expressed by eq 4 is established, we have the relationships

$$C_{\mathrm{Ni}} = [\mathrm{NiEDDA}] + [\mathrm{RNiEDDA}^{2-}] + [\mathrm{RNiHEDDA}^{-}] \quad (12)$$

$$C_{\mathrm{R}} = [\mathrm{HR}^{-}] + [\mathrm{RNiEDDA}^{2-}] + [\mathrm{RNiHEDDA}^{-}] \quad (13)$$

$$E_{\mathrm{i}} = \epsilon_{\mathrm{HR}}[\mathrm{HR}^{-}] + \epsilon_{\mathrm{RNiEDDA}}[\mathrm{RNiEDDA}^{2-}] + \epsilon_{\mathrm{RNiHEDDA}}[\mathrm{RNiHEDDA}^{-}] \quad (14)$$

where C_{Ni} and C_{R} represent the total concentrations of nickel and PAR, respectively; ϵ refers to the molar absorption coefficient of relevant species; E_{i} is the absorbance at equilibrium of the reaction system which is estimated by the extrapolation to zero reaction time in Figure 1. The E_{i} value increases with increasing pH as apparent from equilibrium 4. In the present experimental condition, the E_{i} value is constant at pH higher than 9.3 where the intermediate is formed quantitatively. Thus we have the molar absorption coefficient of $\mathrm{RNiEDDA}^{2-}$; $\epsilon_{\mathrm{RNiEDDA}}$ is 3.83×10^{4} at 495 nm. Protonation of the intermediate $\mathrm{RNiEDDA}^{2-}$ is considered to occur at the most basic site of RNiEDDA, *i.e.*, at one of secondary amines in the coordinated EDDA (see Figure 7). So the molar absorption coefficient of $\mathrm{RNiEDDA}^{2-}$ does not seem to differ appreciably from that of $\mathrm{RNiHEDDA}^{-}$, the value of $\epsilon_{\mathrm{RNiHEDDA}}$ is assumed to be the same as $\epsilon_{\mathrm{RNiEDDA}}$. Then combining eq 13 and 14, we obtain

$$[\mathrm{RNiEDDA}^{2-}] + [\mathrm{RNiHEDDA}^{-}] = \frac{E_{\mathrm{i}} - \epsilon_{\mathrm{HR}}C_{\mathrm{R}}}{\epsilon_{\mathrm{RNiEDDA}} - \epsilon_{\mathrm{HR}}}$$

From eq 12 and 13, we have the concentrations of NiEDDA and PAR. Therefore we can calculate the conditional equilibrium constant K_{i} with knowledge of the concentration of hydrogen ion

$$K_{\mathrm{i}} = \frac{([\mathrm{RNiEDDA}^{2-}] + [\mathrm{RNiHEDDA}^{-}])[\mathrm{H}^{+}]}{[\mathrm{NiEDDA}][\mathrm{HR}^{-}]} = \frac{[\mathrm{RNiEDDA}^{2-}](1 + K^{\mathrm{H}}{}_{\mathrm{RNiHEDDA}}[\mathrm{H}^{+}])[\mathrm{H}^{+}]}{[\mathrm{NiEDDA}][\mathrm{HR}^{-}]}$$

Some data obtained under various experimental conditions are given in Table II. The stability constant of the intermediate $\mathrm{RNiEDDA}^{2-}$ is

$$K^{\mathrm{R}}{}_{\mathrm{RNiEDDA}} = \frac{[\mathrm{RNiEDDA}^{2-}]}{[\mathrm{NiEDDA}][\mathrm{R}^{2-}]} = \frac{K_{\mathrm{i}}K^{\mathrm{H}}{}_{\mathrm{HR}}}{1 + K^{\mathrm{H}}{}_{\mathrm{RNiHEDDA}}[\mathrm{H}^{+}]} = 10^{8.2\pm0.2}$$

where $K^{\mathrm{H}}{}_{\mathrm{HR}} = [\mathrm{HR}^{-}]/[\mathrm{R}^{2-}][\mathrm{H}^{+}] = 10^{12.3}$.[9] The constancy of the $K^{\mathrm{R}}{}_{\mathrm{RNiEDDA}}$ values obtained from the different sets of data confirms the soundness of the above assumption.

TABLE II

DETERMINATION OF THE STABILITY CONSTANT OF THE INTERMEDIATE $\mathrm{RNiEDDA}^{2-}$ [a]

$10^{5}C_{\mathrm{R}}$, M	E_{i}	pH	Log $K^{\mathrm{R}}{}_{\mathrm{RNiEDD}}$
9.97	0.332	9.02	8.3
9.97	0.269	8.09	8.1
9.97	0.244	7.80	8.0
3.99	0.143	8.03	8.3
3.99	0.182	8.54	8.3
		Av	8.2 ± 0.2

[a] $C_{\mathrm{Ni}} = 5.09 \times 10^{-6}$ M; $C_{\mathrm{EDDA}} = 6.40 \times 10^{-6}$ M; $\mu = 0.1$ ($\mathrm{NaClO_4}$); 25°.

Ligand Substitution Reaction of the $\mathrm{Ni^{II}}$–NTA Complex with PAR.—The overall ligand substitution reaction for the $\mathrm{Ni^{II}}$–NTA system is described as

$$\mathrm{NiNTA}^{-} + 2\mathrm{HR}^{-} \longrightarrow \mathrm{NiR_2}^{2-} + \mathrm{NTA}' \quad (15)$$

where NTA′ refers to NTA not combined with nickel ion. At the beginning of the reaction, any jump in absorbance at 495 nm (E_{i}) observed in the $\mathrm{Ni^{II}}$–EDDA system did not occur. The substitution reaction is of the first order in $\mathrm{Ni^{II}}$–NTA and PAR, respectively. The second-order plots were linear at least for over 90% of the reaction. Then the second-order conditional rate constant $k_{0(\mathrm{H})}$ was determined from the slope of the straight line. Some conditional rate constants at various concentrations of NTA and at various pH's are given in Table III.

TABLE III

THE LIGAND SUBSTITUTION REACTION OF THE NICKEL(II)–NITRILOTRIACETATE COMPLEX WITH 4-(2-PYRIDYLAZO)RESORCINOL[a]

C_{NTA}, M	pH	$10^{-2}k_{0(\mathrm{H})}$, M^{-1} sec^{-1}	C_{NTA}, M	pH	$10^{-2}k_{0(\mathrm{H})}$, M^{-1} sec^{-1}
5.40×10^{-6}	8.04	2.48	6.00×10^{-6}	9.12	3.78
5.40×10^{-6}	8.15	2.62	1.00×10^{-5}	8.07	2.45
5.40×10^{-6}	8.93	3.70	1.00×10^{-5}	8.28	2.87
5.40×10^{-6}	9.12	3.95	1.00×10^{-5}	8.72	3.38
5.40×10^{-6}	9.38	4.22	1.00×10^{-5}	9.11	3.53
5.40×10^{-6}	9.55	4.22	1.40×10^{-5}	9.12	3.52

[a] $C_{\mathrm{Ni}} = 5.09 \times 10^{-6}$ M; $C_{\mathrm{R}} = 5.00 \times 10^{-5}$ M; $\mu = 0.10$ ($\mathrm{NaClO_4}$); borate buffer: [B] = 0.008 M; 25.0 ± 0.1°.

The conditional rate constant $k_{0(\mathrm{H})}$ is independent of the concentration of NTA and increases with increasing pH. We assume the following reaction scheme on the basis of the results for the $\mathrm{Ni^{II}}$–EDDA system

$$\mathrm{NiNTA}^{-} + \mathrm{HR}^{-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RNiNTA}^{3-} + \mathrm{H}^{+} \quad (16)$$

$$\mathrm{RNiNTA}^{3-} \xrightarrow{k_2} \mathrm{NiR} + \mathrm{NTA}' \xrightarrow[\text{fast}]{+\mathrm{HR}^{-}} \mathrm{NiR_2}^{2-} \quad (17)$$

RNiNTA^{3-} is not present in appreciable amounts because there is no jump in absorbance. Therefore a steady-state approximation applies for RNiNTA^{3-}. Then the rate equation of the formation of $\mathrm{NiR_2}^{2-}$ is given by

$$\frac{d[\mathrm{NiR_2}^{2-}]}{dt} = \frac{k_1k_2}{k_{-1}[\mathrm{H}^{+}] + k_2}[\mathrm{NiNTA}^{-}][\mathrm{HR}^{-}] \quad (18)$$

The conditional rate constant $k_{0(\mathrm{H})}$ corresponds to $k_1k_2/(k_{-1}[\mathrm{H}^{+}] + k_2)$, which leads to a form suitable for graphical plotting in Figure 4

$$\frac{1}{k_{0(\mathrm{H})}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}[\mathrm{H}^{+}] \quad (19)$$

From the intercept and slope of the straight line (Figure 4), we obtain $k_1 = (4.2 \pm 0.3) \times 10^{2}$ M^{-1} sec^{-1} and $k_{-1}/k_2 = (8.0 \pm 0.7) \times 10^{7}$ M^{-1} at $\mu = 0.1$ and 25.0°.

Discussion

We proposed that the ligand substitution reactions of metal chelates with multidentate ligands proceed through a reaction intermediate in which a central metal ion is bonded with both leaving and entering

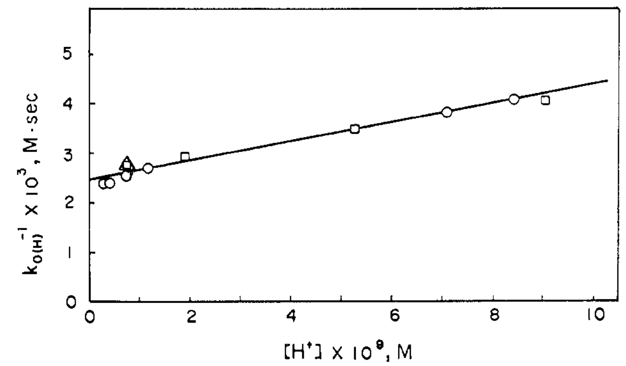

Figure 4.—Plot of $k_{0(H)}^{-1}$ *vs.* $[H^+]$ according to eq 19. Conditions: $C_{Ni} = 5.09 \times 10^{-6}$ *M;* $C_R = 5.00 \times 10^{-5}$ *M;* $\mu = 0.10$; 25.0°. C_{NTA}: ○, 5.40×10^{-6} *M;* ●, 6.00×10^{-6} *M;* □, 1.00×10^{-5} *M;* △, 1.40×10^{-5} *M.*

ligands and that the cleavage of the bond between the central metal and leaving ligand is rate determining.[2-4] As described under Results, the molar absorption coefficient of the intermediate $RNiEDDA^{2-}$ ($\epsilon_{RNiEDDA}$ is 3.83×10^4 at 495 nm) is about half that of the 1:2 Ni^{II}–PAR complex NiR_2^{2-} (ϵ_{NiR_2} is 7.85×10^4 at 495 nm). This will provide a clear evidence for an ephemeral mixed-ligand complex formed on the way to the final product NiR_2^{2-}.

In our previous paper[6] on the reactions of monohydroxo-, monoacetato-, monofluoro-, and monoazidopentaaquonickel(II) complexes with PAR, the difference of reactivity of these nickel(II) complexes has quantitatively been accounted for in terms of electron donation of coordinated ligands on the basis of Eigen mechanism[10-12] in which loss of the first water molecule coordinated to nickel is the rate-determining step. EDDA and NTA are tetradentate ligands. The available coordination sites in the 1:1 Ni^{II}–EDDA complex and the 1:1 Ni^{II}–NTA complex are at least two. The rate-determining step (k_1) of the first step of the present ligand substitution reactions may be the loss of a water molecule coordinated to the nickel complex. It is of interest to consider the effect of EDDA and NTA coordinated to a central metal ion.

In the formation of the intermediates RNiEDDA and RNiNTA, a *simple* water loss mechanism does not seem operative from the following considerations. (1) PAR is tridentate, the pyridine nitrogen, the phenolic oxygen, and the diazo nitrogen atom farthest from the heterocyclic ring being coordinated to the nickel ion to form two five-membered chelate rings. The three coordination sites are very nearly planar.[13] Therefore, there should be the dissociation of at least one donor atom of the coordinated ligand in the Ni–NTA and Ni–EDDA complexes, before the incoming ligand can gain a coordination foothold. (2) The dissociation is expected also from the fact that, despite considerable electron donation anticipated in the Ni–NTA and Ni–EDDA complexes, $NiNTA^-$ and NiEDDA react more slowly with PAR than the hexaaquonickel(II) ion ($(1.7 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$).[6] (3) The rate of water loss from the Ni–NTA complex has been estimated by Margerum and Rosen:[14] $10^{5.2}$ sec^{-1}. This value is much higher than the rate constants for the formation of the intermediates RNiEDDA and RNiNTA.

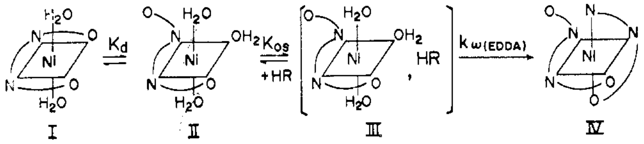

Figure 5.—Proposed reaction mechanism for the formation of the intermediate RNiEDDA. EDDA and PAR are symbolized as O–N–N–O and N–N–O, respectively. Charges are omitted for simplicity.

The reaction scheme as shown in Figure 5 is then postulated for the formation of the intermediate RNiEDDA. In Figure 5 K_d refers to the dissociation constant of I to II, K_{os} the formation constant of the outer-sphere complex III, and $k_{w(EDDA)}$ the rate constant of the loss of water from the partially dissociated Ni–EDDA in III. Based on the reaction scheme depicted in Figure 5, we have the relationship

$$k_1 = K_d K_{os} k_{w(EDDA)} \tag{20}$$

K_d was estimated from the difference in stability constants of the nickel(II)–iminodiacetate (Ni–IDA)[15] and nickel(II)–glycinate (Ni–Gly)[16] complexes

$$-\log K_d = \log K_{Ni-IDA} - \log K_{Ni-Gly} = 2.4$$

K_{os} was calculated according to the Fuoss equation,[17] the distance of 5 Å being assumed. The negative charge being remote from the coordination site in PAR, HR^- is regarded as a noncharged ligand.[6] Then we have 0.3 for K_{os}. With these calculated values for K_d and K_{os} and the experimental rate constant k_1, we can estimate the rate of loss of water from the partially dissociated Ni–EDDA complex: $k_{w(EDDA)} = 10^{5.9}$ sec^{-1} (see eq 20).[18] The same reaction scheme seems applicable to the reaction of the Ni–NTA complex with PAR, and we have $k_{w(NTA)} = 10^{5.5}$ sec^{-1} using k_1 and the estimated $K_d = 10^{-2.4}$ and $K_{os} = 0.3$.

Rate constants ($k_A/K_{os} = k_{w(A)}$) of water exchange for some monoacidopentaaquonickel(II) complexes at $\mu = 0.1$ and 25° have been estimated:[6] $k_{w(F)} = 3.7 \times 10^3$, $k_{w(H_2O)} = 5.7 \times 10^3$, $k_{w(CH_3CO_2)} = 1.5 \times 10^4$, $k_{w(N_3)} = 3.7 \times 10^4$, $k_{w(OH)} = 3.3 \times 10^4$ sec^{-1}. In Figure 6 are given plots of the logarithm of the ratio of $k_{w(A)}$ to $k_{w(H_2O)}$ *vs.* E_A, a measure of electron donation of ligand A given by Edwards.[19] There are no available data for E_{NTA} and E_{EDDA}. Then we assume the following additivity for the E_A values: E_{NTA} (for Ni-NTA

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(11) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

(12) M. Eigen and K. Tamm, *ibid.*, **66**, 93 (1962).

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(14) D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967).

(15) S. Chaberek and A. E. Martell, *ibid.*, **74**, 5052 (1952).

(16) F. Basolo and Y. T. Chen, *ibid.*, **76**, 953 (1954).

(17) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

(18) It is difficult to estimate the statistical factor which arises from the number of water molecules available for exchange and the probability that a PAR molecule in the outer sphere is in position to react. Thus we did not take these factors into consideration.

(19) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956).

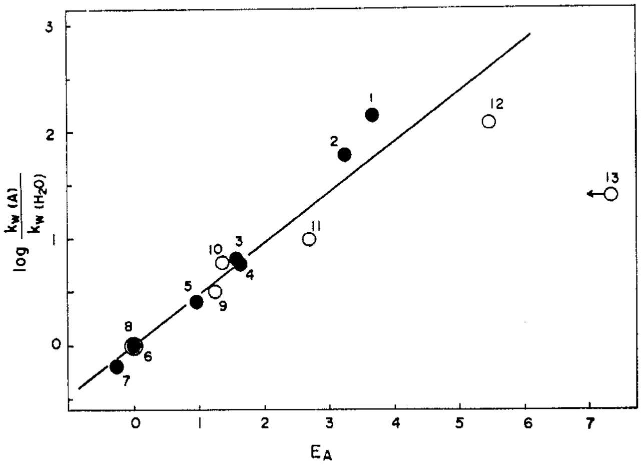

Figure 6.—Plot of log $(k_{w(A)}/k_{w(H_2O)})$ *vs.* E_A: 1, $Ni(H_2O)_3$-EDDA; 2, $Ni(H_2O)_3NTA^-$; 3, $Ni(H_2O)_5OH^+$; 4, $Ni(H_2O)_5N_3^+$; 5, $Ni(H_2O)_5CH_3CO_2^+$; 6, $Ni(H_2O)_6^{2+}$; 7, $Ni(H_2O)_5F^+$; 8, $Ni(H_2O)_6^{2+}$; 9, $Ni(H_2O)_5Cl^+$; 10, $Ni(H_2O)_5NH_3^{2+}$; 11, Ni-$(H_2O)_4en^{2+}$; 12, $Ni(H_2O)_2(en)_2^{2+}$; 13, $Ni(H_2O)_2(NCS)_4^{2-}$. 8–13 are according to data of Hunt, *et al.* (open circles).[20-23]

with a carboxylate dissociated) = $E_{NH_3} + 2E_{CH_3CO_2}$ = 3.26, and E_{EDDA} (for Ni–EDDA with a carboxylate dissociated) = $2E_{NH_3} + E_{CH_3CO_2}$ = 3.67. The plots of the estimated values of the rate constants of the loss of a water molecule from the partially dissociated Ni^{II}–EDDA and Ni^{II}–NTA complexes lie close to the straight line. This will provide a confirmation of the dissociation of carboxylate in the Ni^{II}–EDDA and Ni^{II}–NTA complexes as illustrated in Figure 5.

In Figure 6 are also included the rate constants $k_{w(A)}$ (per H_2O moledule) at 25° of water exchange between bulk water and various complexes as determined by Hunt and his associates[20-23] (open circles in Figure 5): 4.4×10^4, 2.6×10^5, 1.4×10^5, 4.4×10^5, 5.4×10^6, and 1.1×10^6 sec^{-1} for $Ni(H_2O)_6^{2+}$, $Ni(H_2O)_5NH_3^{2+}$, $Ni(H_2O)_5Cl^+$, $Ni(H_2O)_4en^{2+}$, $Ni(H_2O)_2(en)_2^{2+}$, and Ni-$(H_2O)_2(NCS)_4^{2-}$, respectively. In estimating E_A the following additivity is again assumed: $E_{en} = 2E_{NH_3}$, $E_{(en)_2} = 4E_{NH_3}$, and $E_{(NCS)_4} = 4E_{NCS}$. The plots lie also along the straight line.[24] Although the conditions of acidity and ionic strength used in these studies are very different from our own, the inclusion of these data in Figure 6 would be useful for rough comparisons of results obtained by different techniques.

The linearity supports the view that the effect of ligands already present in a complex on the ease of replacement of the remaining water molecules is closely related to the electron-donating properties of the ligands: when a ligand coordinated to the central metal ion donates electrons to the central metal to a greater extent, the bond of the central metal with the remaining coordinated water molecules will weaken and more easily be broken.

The increase of dissociation reaction rates ($k_{0,2(H)}$) of the second step of the ligand substitution for the Ni^{II}–EDDA complex with decreasing pH points to the active role of the proton in assisting the dissociation of the leaving ligand in the complex. Since proton transfer is very rapid compared to the other reaction steps,[25] the proton is in equilibrium with the protonated intermediate ($RNiHEDDA^-$) preceding the rate-determining steps. Judging from the stability constants[26] of EDDA; log $\{[HEDDA^-]/[EDDA^{2-}][H^+]\}$ = 9.57 and log $\{[H_2EDDA]/[HEDDA^-][H^+]\}$ = 6.48, the proton in the protonated complex should be attached to a nitrogen atom in the EDDA which is the most basic (Figure 7). The dissociation rate of the $RNiHEDDA^-$ complex is 20 times faster than that of the $RNiEDDA^{2-}$ complex. The proton bound to the leaving group facilitates the dissociation of the leaving group as observed recently for the ligand substitution reaction of the Co^{II}–EGTA complex with PAR.[3,27]

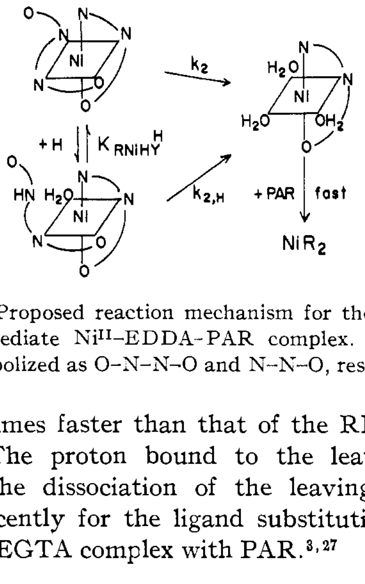

Figure 7.—Proposed reaction mechanism for the dissociation of the intermediate Ni^{II}-EDDA-PAR complex. EDDA and PAR are symbolized as O–N–N–O and N–N–O, respectively.

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[24] Deviation of the plot for $Ni(H_2O)_2(NCS)_4^{2-}$ is considerable. This may be due to back-donation from the metal: D. L. Janes and D. W. Margerum, *Inorg. Chem.*, **5**, 1135 (1966). Thus *effective* E_A for thiocyanate should be smaller. Similarly back-donation seems also important in considering the rate of water exchange of the mono(2,2′,2″-terpyridine)nickel-(II) complex ($k_{w(terpy)} = 5.2 \times 10^4$ sec^{-1} at 25°): D. Rablen and G. Gordon, *ibid.*, **8**, 395 (1969).

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[27] NOTE ADDED IN PROOF.—Values of the rate of water loss from $Ni(H_2O)_4(NH_3)_2^{2+}$ and $Ni(H_2O)_3(NH_3)_3^{2+}$ reported recently (A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 798 (1970)) fall very close to the straight line in Figure 6.