Since these complexes are undissociated in solution, the tetrahedral configuration can be achieved only if one of the potential donor atoms of the Schiff base does not form a bond to the metal ion. The sulfur atom is probably the unbonded atom because of its low donor power with respect to that of the nitrogen atoms. The complexes of $Co(MABen\text{-}N(C_2H_5)_2)X_2$ (X = Cl, Br, I),[1] which have an $NH\text{-}CH_3$ group in the place of the $S\text{-}CH_3$ group studied here, form five-coordinate complexes which suggests that the previous suggestion is correct.

The high-spin complex $Co(MSBen\text{-}N(C_2H_5)_2)(NCS)_2$, which is monomeric and undissociated in dichloroethane solution, exhibits a spectrum different from that of the preceding complexes (Figure 4). The absorption bands, which occur at 5800, 13,000, 16,000, 17,500, and 18,500 cm^{-1}, can be correlated with those of $Co((CH_3)_5\text{-}dien)X_2$[5] which have been shown to possess a five-coordinate structure by X-ray crystal structure analysis.[6] The first two bands have been assigned[14] as transitions from the ground state to the $^4E''(F)$ and $^4E'(F)$ states in a D_{3h} symmetry field, respectively, and the other bands are derived from transitions to the levels which originate from the splitting of the ^4P level of the free ion.

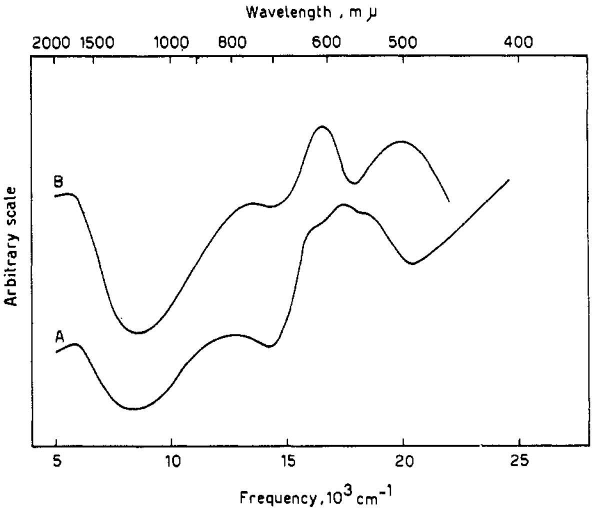

Figure 4.—Reflectance spectra of: A, $Co(MSBen\text{-}N(C_2H_5)_2)(NCS)_2$; B, $Co((CH_3)_5dien)(NCS)_2$ (M. Ciampolini, private communication).

The infrared spectrum of the complex $Co(MSBen\text{-}N(C_2H_5)_2)(NCS)_2$ exhibits two bands at 2060 and 2075 cm^{-1} assignable to the C–N stretching vibrations of the two thiocyanate groups. The values of the frequencies are in the range of those found for nitrogen-bonded thiocyanate complexes.[10]

Acknowledgment.—Thanks are expressed to Dr. J. Gelsomini for the microanalyses and to Mr. G. Vignozzi for assisting in the preparation of compounds. G. P. S. is grateful to the Scientific Affair Division of NATO for a grant.

[14] M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966); M. Ciampolini and N. Nardi, *Inorg. Chem.*, **6**, 445 (1967).

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Multidentate Ligand Kinetics. XII. Ethylenediaminetetraacetate Ion Reaction with Mono- and Bis(diethylenetriamine)nickel(II) Complexes

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The stepwise process by which one multidentate ligand displaces another from a metal ion is observed in the reactions of $Ni(dien)_2^{2+}$ and $Ni(dien)^{2+}$ with EDTA. The bis-dien complex does not react directly with EDTA but must completely lose one dien first. The mono-dien complex reacts rapidly with EDTA to give $Ni(dien)EDTA^{2-}$ and this complex undergoes successive unwrapping of dien and increasing coordination to EDTA. Two successive first-order steps are observed before $NiEDTA^{2-}$ and dien are produced. Excess $Ni(dien)^{2+}$ can slow the reaction with EDTA owing to the formation of a bridged EDTA species, [Ni(dien)EDTA(dien)Ni]. Difference spectral studies indicate another possible bridged species, $[Ni(dien)(EDTA)Ni(EDTA)(dien)Ni]^{2-}$.

Introduction

The mechanism by which one multidentate ligand displaces another from a metal ion depends on the ability of both ligands to coordinate the metal simultaneously. It may be necessary to replace segments of the initially bound ligand by solvent before an incoming ligand can gain a coordination foothold. The more segments which must be unwrapped from the metal the slower the reaction. Thus, the EDTA[1] reaction with nickel–trien is faster than its reaction with nickel–tetren[2] and both are much faster than the EDTA reaction with nickel–CyDTA.[3] In the latter case complete dissociation of CyDTA from nickel occurs before EDTA reacts. In the present study the tridentate

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[1] Abbreviations used are: dien, diethylenetriamine; trien, triethylenetetramine; tetren, tetraethylenepentamine; EDTA, ethylenediaminetetraacetate ion; CyDTA, cyclohexylenediaminetetraacetate ion.

[2] D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

[3] W. J. Huber, M.S. Thesis, Purdue University, 1964.

ligand diethylenetriamine is displaced from nickel, again using EDTA. On the basis of previous mechanisms[2] the mono-dien complex was expected to react rapidly and the bis-dien complex to be much less reactive. Both predictions are confirmed and it is shown that one dien from the bis complex dissociates completely before EDTA reacts. Several mixed complexes are observed in which EDTA and dien are coordinated to nickel. Additional evidence of the stepwise nature of ligand–ligand exchange reactions is found in the kinetic sequence in which nickel–dien–EDTA complexes react to give nickel–EDTA.

Experimental Section

Diethylenetriamine (Aldrich Chemical Co.) was distilled at 45° (0.5 mm) and stored in the dark. $Ni(dien)_2Cl_2$ was prepared for the difference spectra studies by the addition of excess dien to a saturated solution of $NiCl_2$. The purple crystals were recrystallized from water–ethanol and standardized with NaCN. Other solutions of $Ni(dien)_2^{2+}$ and $Ni(dien)^{2+}$ were prepared by stoichiometric addition of solutions of dien with nickel nitrate or nickel perchlorate.

A thermostated Cary 14 spectrophotometer was used for the kinetic studies of EDTA and $Ni(dien)_2^{2+}$ (385 mμ). Spectral scans of the reaction product showed complete conversion to $NiEDTA^{2-}$ in agreement with the known log K stability constants:[4] $Ni(dien)^{2+}$ (10.7), $Ni(dien)_2^{2+}$ (8.2), $Hdien^{+}$ (9.94), H_2dien^{2+} (9.13), $NiEDTA^{2-}$ (18.6), $HEDTA^{3-}$ (10.26), and H_2EDTA^{2-} (6.16). A stopped-flow apparatus[5] was used for the EDTA and $Ni(dien)_2^{2+}$ studies (390 mμ). KNO_3 rather than $NaClO_4$ was used for ionic strength control because of the limited solubility of $Ni(dien)(ClO_4)_2$. Difference spectra were measured on the Cary 14 using double-sectioned quartz 2-cm cells (each section = 1.00 cm). The cells were well matched and gave no absorbance when the same solutions were in reference and sample.

In a few cases a cyanide ion quench method[2] was used in which $Ni(dien)_2^{2+}$ is converted rapidly to $Ni(CN)_4^{2-}$ without appreciable reaction of $NiEDTA^{2-}$. The intense absorption bands of $Ni(CN)_4^{2-}$ provide a very sensitive way of following the reaction progress of dilute reactants. However this was not a satisfactory method when excess dien was present because the dien catalyzed the cyanide ion reaction with $NiEDTA^{2-}$. Results are reported here only where dien catalysis did not interfere.

Results and Discussion

EDTA and $Ni(dien)_2^{2+}$.—The velocity of the exchange reaction with the bis-dien complex was sufficiently slow at pH 8 to be studied by manual mixing techniques. The presence of excess dien suppressed the rate. The concentrations of EDTA and of dien were varied as shown in Table I. At lower concentrations of dien (10^{-2} M or less) the rate of formation of $NiEDTA^{2-}$ was first order in the concentration of $Ni(dien)_2^{2+}$ and independent of EDTA. At higher dien concentrations (0.31 M) and low EDTA concentrations, linear second-order plots were obtained (first order in $[Ni(dien)_2^{2+}]$ and in [EDTA]). Intermediate conditions did not give simple reaction-order plots and the kinetic data are analyzed in terms of the initial reaction velocity, $V_i = -d[Ni(dien)_2^{2+}]_i/dt = d[NiEDTA^{2-}]_i/dt$. The values of V_i were obtained from the initial slopes of ln $(A_\infty - A)$ plots where A is the absorbance. The dependence of V_i on dien and EDTA concentrations in Table I suggests the following reaction mechanism (protons are omitted in eq 1 and 2) where a first-order dissociation of the bis complex precedes the reaction with EDTA

Table I

Initial Reaction Velocities for the Formation of $NiEDTA^{2-}$ from $Ni(dien)_2^{2+}$ at 25.0°

Excess $[dien]_i$, M	$[EDTA]_i$, $M \times 10^3$	$V_i/[Ni(dien)_2^{2+}]_i$, $sec^{-1} \times 10^3$
$[Ni(dien)_2^{2+}]_i = 1.00 \times 10^{-3}$ M, pH 7.95 ± 0.05, $\mu = 1.0$ M $NaClO_4$, dien Added as the Free Amine		
0	2.02	11.1
0	4.04	10.7
0	6.06	9.9
0	8.08	10.8
0	10.10	10.0
0.01	2.02	11.2
0.01	4.04	11.6
0.01	6.06	11.4
0.01	8.08	12.3
0.01	10.10	12.2
0.02	2.02	8.8
0.02	10.10	11.8
0.04	2.02	7.6
0.04	10.10	12.0
0.06	2.02	7.4
0.06	10.10	11.4
0.08	2.02	6.5
0.08	10.10	11.7
0.10	2.02	6.7
0.10	4.04	8.9
0.10	6.06	10.3
0.10	8.08	10.5
0.10	10.10	11.5
0.20	1.01	3.4
0.20	1.52	4.0
0.20	2.02	5.0
0.20	2.52	5.7
0.20	3.03	6.4
0.31	0.40	1.08
0.31	0.51	1.33
0.31	0.61	1.60
0.31	0.61	1.61
0.31	0.71	1.87
0.31	0.81	2.10
0.31	0.81	2.16
0.31	0.91	2.45
0.31	1.01	2.47
0.31	2.02	3.05
0.31	3.03	4.02
0.31	4.04	4.54
$[Ni(dien)_2^{2+}]_i = 1.30 \times 10^{-4}$ M, pH 8.76 ± 0.02, $\mu = 0.10$ M $NaClO_4$, CN^- Quench		
0	0.57	1.32
0	0.76	1.34
0	1.30	1.29

$$Ni(dien)_2^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(dien)^{2+} + dien \qquad (1)$$

$$Ni(dien)^{2+} + EDTA \xrightarrow{k_2} products \qquad (2)$$

A steady-state approximation can be used for $Ni(dien)^{2+}$ because it is not present in appreciable amounts in the presence of either dien or EDTA. This leads to eq 3 which fits qualitatively the observed kinetic behavior.

$$V_i = \frac{k_1k_2[Ni(dien)_2^{2+}]_i[EDTA]_i}{k_{-1}[dien]_i + k_2[EDTA]_i} \qquad (3)$$

The reciprocal expression in eq 4 is tested quantitatively in Figures 1 and 2.

$$\frac{[Ni(dien)_2^{2+}]}{V_i} = \frac{k_{-1}[dien]_i}{k_1k_2[EDTA]_i} + \frac{1}{k_1} \qquad (4)$$

Although there is a little scatter, both sets of data give consistent results with a k_1 value of 0.012 ± 0.001 sec^{-1} from the intercepts and from the slopes a value of 1.6 ± 0.1 sec for k_{-1}/k_1k_2. Hence at pH 7.95 ± 0.05 the k_{-1}/k_2 ratio is 1.9×10^{-2}. The value of k_{-1} can be calculated from k_1 and the stability constant of the complex under the experimental conditions. On this basis $k_{-1} = 1.2 \times 10^3$ M^{-1} sec^{-1} and $k_2 = 6.3 \times 10^4$ M^{-1} sec^{-1} at pH 7.95 with an ionic strength of 1.0 M.

The limited data from the cyanide ion quench method gave good first-order plots and a k_1 value of 1.3×10^{-3}

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(4) L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1964.

(5) D. W. Margerum and J. D. Carr, *J. Am. Chem. Soc.*, **88**, 1639 (1966).

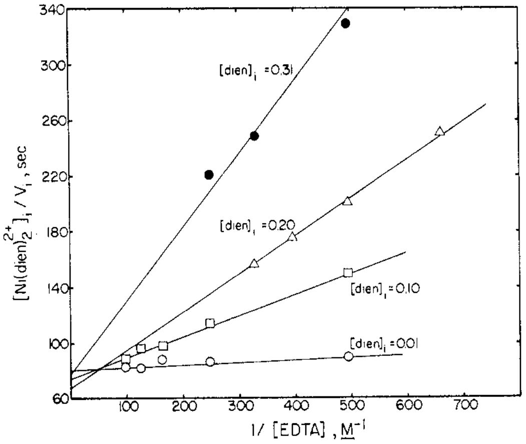

Figure 1.—Double-reciprocal dependence of the initial velocity and EDTA concentration for the reaction of $Ni(dien)_2^{2+}$ with EDTA at various dien concentrations, 25.0°, pH 7.95 ± 0.05, and 1.0 M $NaClO_4$. The values of the (slope)/$[dien]_i$ are 1.6, 1.7, 1.4, and 1.7 sec for $[dien]_i$ equal to 0.01, 0.10, 0.20, and 0.31 M, respectively.

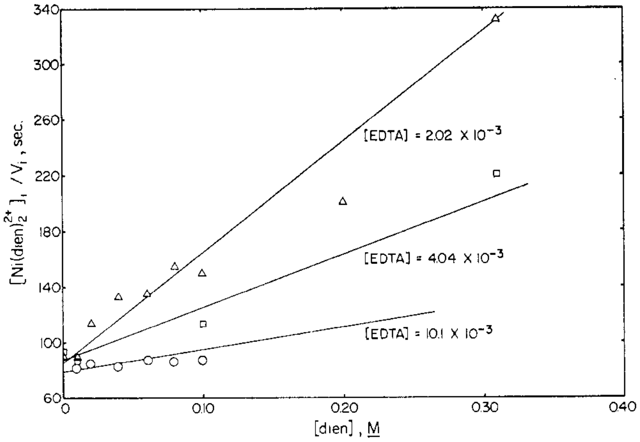

Figure 2.—Reciprocal dependence of the initial velocity on the concentration of excess dien for the reaction of $Ni(dien)_2^{2+}$ with various concentrations of EDTA at 25.0°, pH 7.95 ± 0.05, and 1.0 M $NaClO_4$. The values of the (slope) × [EDTA] are 1.6, 1.5, and 1.6 sec for $[EDTA]_i$ equal to 2.02 × 10^{-3}, 4.04 × 10^{-3}, and 10.1 × 10^{-3} M, respectively.

sec^{-1} at pH 8.76, $\mu = 0.1$ M. The large decrease in the value of k_1 as the pH increases is reasonable for the reaction of H^+ with $Ni(dien)_2^{2+}$ in the dissociation step. The reaction is

$$\mathrm{Ni(dien)_2^{2+} + H^+ \rightleftarrows Ni(dien)^{2+} + Hdien^+}$$

and an approximate value for the forward rate constant, $k_H^{Ni(dien)_2}$, is 1×10^6 M^{-1} sec^{-1} and of the reverse rate constant, $k_{Hdien}^{Ni(dien)}$, is 1.7×10^4 M^{-1} sec^{-1}.

EDTA and $Ni(dien)^{2+}$.—The reaction of the mono-dien complex with EDTA is fast, requiring stopped-flow methods. A rapid reaction was expected from the mechanism given in eq 1 and 2, but when $Ni(dien)_2^{2+}$ was the reactant it was not possible to distinguish between the addition of EDTA and the loss of dien from $Ni(dien)^{2+}$. By starting with the mono-dien complex the additional steps involved in the formation of $NiEDTA^{2-}$ can be examined.

Several seconds is required for EDTA (0.2–1.0 M) to react with $Ni(dien)^{2+}$ (0.02 M) to give $NiEDTA^{2-}$, whereas the k_2 value found for reaction 2 predicts reaction times of less than 1 msec. Extrapolation of the stopped-flow data to zero reaction time gives a higher absorbance than that of the reactants and indicates the rapid formation of a nickel–dien–EDTA complex in accord with the k_2 value. Hence, the addition of EDTA to $Ni(dien)^{2+}$ occurs much more rapidly than the displacement of dien. The reaction observed by the stopped-flow spectrophotometer is the conversion of nickel–dien–EDTA to nickel–EDTA. Oscilloscopic traces of the reaction (per cent transmittance against time) showed a definite and reproducible break at 0.2 sec. Neither the time nor the % T position depended on the concentration of EDTA, provided EDTA was in excess. Figure 3 is a first-order plot of the data (A_∞ = absorbance at equilibrium) which shows the reaction after 0.2 sec to be first order. The points are taken from a continuous trace, and excellent linear plots were obtained for all points taken after 0.2 sec. The first part of the trace also gives a linear first-order plot as seen in Figure 4 using an A_∞' value taken from the intercept of Figure 3. The faster reaction has a rate constant, k_3, about ten times larger than that for the slower reaction, k_4. Table II summarizes values for k_3 and k_4 under a variety of pH and EDTA concentrations. The agreement of the data is good considering the small absorbance changes involved and the need to reproduce A_∞' values for k_3. The values of $(A_\infty' - A_0)/(A_\infty - A_0)$ did not depend on EDTA or pH, and equaled 0.47 ± 0.07 for the reactions with [EDTA] = 0.0448–0.1120 M. When [EDTA] = 0.024 M and $[Ni(dien)^{2+}]$ = 0.020 M, the $(A_\infty' - A_0)/(A_\infty - A_0)$ ratio drops slightly owing to interference from another reaction to be discussed. When EDTA is in excess, all evidence points to two successive first-order reactions rather than to two parallel first-order reactions.

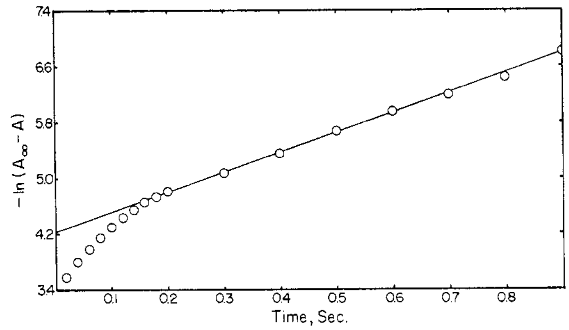

Figure 3.—Reaction of mono(diethylenetriamine)nickel(II) with EDTA shows a very rapid addition followed by a two-step decay to give nickel–EDTA and dien. This first-order plot of the slower step using the final absorbance (A_∞) and the observed absorbance (A) gives $k_4 = 2.8$ sec^{-1}. Conditions: $[Ni(dien)^{2+}]$ = 0.020 M, [EDTA] = 0.090 M, pH 9.16, 1.0 M KNO_3, 25.0°, 390 mμ, 0.2-cm cell path.

The reaction mechanism must account for two first-order reactions occurring after the addition of EDTA

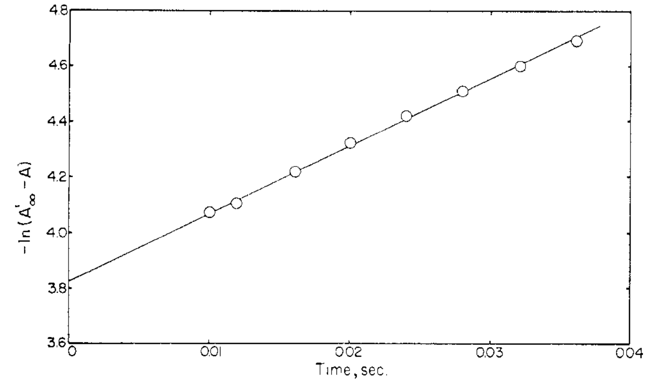

Figure 4.—First-order plot of the faster decay reaction in Figure 3 using the intercept of Figure 3 to give A_∞'. Separate runs were generally made in order to expand the time scale on the oscilloscope. The slope gives k_3 = 25 sec^{-1} for the first decay reaction of nickel–dien–EDTA.

Table II

Successive First-Order Rate Constants Following the Addition of EDTA to Ni(dien)$^{2+}$ [a]

pH	[EDTA], *M*	k_3, sec^{-1}	k_4, sec^{-1}
8.42	0.0680	24, 24	2.3, 2.3
8.46	0.0224	23, 26	3.4, 3.5
8.46	0.0448	25, 33	2.2, 2.1
8.50	0.0900	22, 24	2.6, 2.6
8.51	0.1120	21, 23	2.6, 2.8
9.04	0.0224	27, 34	2.4, 2.3
9.13	0.0448	29, 29	2.4, 2.1
9.13	0.0680	24, 22	2.3, 2.4
9.16	0.0900	27, 25	2.8, 2.9
9.16	0.1120	33, 28	3.0, 3.4
9.85	0.0224	22, 24	1.9, 2.1
9.90	0.0448	24, 21	2.2, 2.6
9.92	0.0680	28, 23	2.6, 2.3
9.92	0.1120	28, 28	2.7, 2.4
9.95	0.0900	30, 28	2.6, 2.7
		Av = 26.0	Av = 2.55
		σ = 3.5	σ = 0.40

pH	[EDTA], *M*	k_{-5}, sec^{-1}
8.60[b]	0.0112	0.77, 0.61
9.54[b]	0.0112	0.74, 0.90
		Av = 0.76

[a] $[\mathrm{Ni(dien)(NO_3)_2}]_i$ = 0.020 *M*, temperature 25.0°, μ = 1.0 *M* KNO_3. [b] The pH dropped 0.3–0.4 unit in these reactions because of the absence of excess EDTA which helps to buffer the other reactions. Nevertheless good first-order plots were obtained.

but independent of pH and of EDTA concentration. The proposed reaction sequence (without protons shown) is

$$\mathrm{Ni(dien)^{2+} + EDTA \xrightarrow{k_2} [Ni(dien)EDTA^{2-}]} \qquad (2')$$

$$\mathrm{[Ni(dien)EDTA^{2-}] \xrightarrow{k_3} [Ni(dien)^*EDTA^{2-}]}$$

$$\mathrm{[Ni(dien)^*EDTA^{2-}] \xrightarrow{k_4} NiEDTA^{2-} + dien}$$

where [Ni(dien)EDTA^{2-}] has three dien nitrogens and a segment of EDTA coordinated to nickel while [Ni(dien)*EDTA^{2-}] has only two dien nitrogens but a larger segment of EDTA coordinated to nickel. Neither of these mixed complexes is stable as a final product under the reaction conditions but both are observable in the stopped-flow reaction. The values of k_3 = 26 sec^{-1} and k_4 = 2.6 sec^{-1} are strikingly similar to those observed by Melson and Wilkins[6] for the dissociation of nickel–dien in 0.5 *M* HNO_3. The following sequence was proposed where first one chelate ring and then the other opens

$$\mathrm{Ni(dien)^{2+} \xrightarrow[H^+]{k\,=\,14\ sec^{-1}} [Ni(Hdien)]^{3+}}$$

$$\mathrm{[Ni(Hdien)]^{3+} \xrightarrow[H^+]{k\,=\,2.8\ sec^{-1}} Ni^{2+} + H_3dien^{3+}}$$

We believe the same type of reaction sequence occurs with [Ni(dien)EDTA^{2-}], namely, a reaction process which depends on the first-order chelate ring-opening steps of dien. The first ring opening of the tridentate chelate is faster than the opening of the last chelate ring, and once both of the chelate rings are broken, the subsequent reactions are very much faster (*cf.* rates of loss of NH_3 from nickel complexes).[7] The effect of EDTA on the removal of mono-dien from nickel is similar to the effect of high concentrations of H$^+$, in that both prevent the opened chelate rings of dien from closing again. Hence, without strong acid or without EDTA, the rate-determining step in polyamine dissociation reactions is the last bond dissociation[8] rather than the opening of the chelate rings. Once EDTA is coordinated to nickel–dien, it rapidly occupies coordination sites left open by the polyamine dissociation.

Two mixed complexes are observed when excess EDTA is added to Ni(dien)$^{2+}$, but a third mixed complex with different kinetic properties is found when Ni(dien)$^{2+}$ is in excess. There are several kinetic differences. First, only a single first-order reaction is observed rather than two successive ones. Second, the reaction is considerably slower than when EDTA is in excess with a rate constant (k_{-5} in Table II) of 0.7 sec^{-1}. This puzzling behavior forced us to conclude that in the presence of excess Ni(dien)$^{2+}$ the Ni(dien)-EDTA complex reacted rapidly to form a bridged complex as in eq 5. The rate-determining step in the conversion of the bridged complex to NiEDTA^{2-} is the bridge dissociation (k_{-5}) which can then be followed by reactions 3 and 4. The latter reactions are no longer observable because they are faster than the k_{-5} step, and therefore a single first-order reaction is observed. EDTA is reported to act as a bridging group between metal ion centers in Sn–EDTA–Sn,[9] Hg–EDTA–Hg,[10] Pb–EDTA–Pb,[11] and Ca–EDTA–Sn.[12] It also has been postulated as a reaction intermediate in Ni–

$$\mathrm{[Ni(dien)EDTA^{2-}] + Ni(dien)^{2+} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [Ni(dien)EDTA(dien)Ni]} \qquad (5)$$

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[6] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 2662 (1963).

[7] D. W. Margerum and H. M. Rosen, *J. Am. Chem. Soc.*, **89**, 1088 (1967).

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

[9] H. G. Langer and R. F. Bogucki, *J. Chem. Soc.*, 375 (1962).

[10] R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

[11] N. Tanaka, M. Kamada, and G. Sato, *Bull. Chem. Soc. Japan*, **34**, 541 (1961).

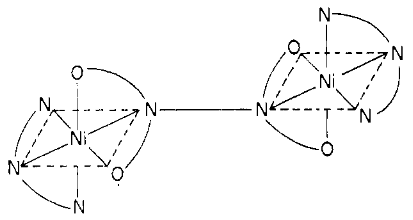
[12] R. F. Bogucki, *J. Inorg. Nucl. Chem.*, **29**, 495 (1967).

EDTA–Cu[13] and other cases.[14] The next section presents spectral evidence for stable mixed complexes of this type. The value of k_{-5} is consistent with the expected rate of dissociation of nickel from the bridged intermediate Ni–EDTA–Cu which we reported earlier[13] should be greater than 0.1 sec^{-1}.

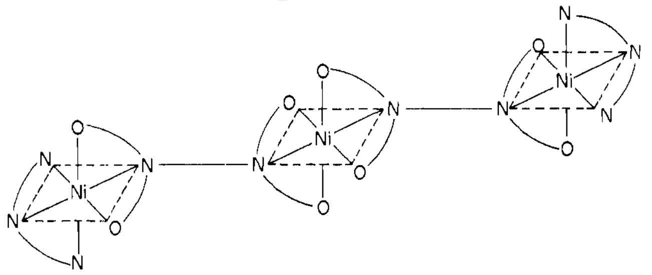
Difference Spectra using NiEDTA^{2-} and Ni(dien)$_2^{2+}$. —An equilibrium study by difference spectra was used to test for the existence of stable mixed (bridged) complexes. There should be no reaction between Ni(dien)$_2^{2+}$ and NiEDTA^{2-} unless a mixed complex forms as in eq 6. No reaction could be observed when each reactant

$$\mathrm{Ni(dien)_2^{2+} + NiEDTA^{2-} \rightleftharpoons (Ni(dien))_2EDTA} \qquad (6)$$

was 0.024 M, but a difference spectrum was found at 0.125 M (curve B, Figure 5). However, more than one mixed complex was observed, because curves A, B, and C have different maxima and minima. Solution C is believed to correspond to Ni(dien)$_2$·NiEDTA = (Ni(dien))$_2$EDTA while solution A has a higher proportion of the EDTA complex. The species proposed for A is Ni(dien)$_2$·2NiEDTA = [(Ni(dien)EDTA)$_2$Ni]$^{2-}$. Structures I and II are envisaged for these complexes.



I = (Nidien)$_2$ EDTA



II = [(Nidien EDTA)$_2$ Ni]$^{2-}$

The expression for the absorbance difference, ΔA, is given in eq 7 for the proposed species. The ΔA values

$$\Delta A = 2(\epsilon_{\mathrm{I}} - \epsilon_{\mathrm{Ni(dien)_2}} - \epsilon_{\mathrm{NiEDTA}})[\mathrm{I}] + 2(\epsilon_{\mathrm{II}} - \epsilon_{\mathrm{Ni(dien)_2}} - 2\epsilon_{\mathrm{NiEDTA}})[\mathrm{II}] \qquad (7)$$

in Figure 5 are all positive so that $\epsilon_{\mathrm{I}} \geqslant (\epsilon_{\mathrm{Ni(dien)_2}} + \epsilon_{\mathrm{NiEDTA}})$ and $\epsilon_{\mathrm{II}} \geqslant (\epsilon_{\mathrm{Ni(dien)_2}} + 2\epsilon_{\mathrm{NiEDTA}})$ at all wavelengths. The higher molar absorptivities would be expected only if nickel had a higher degree of coordination to the ligands in the mixed complexes. This and the relative stabilities of the complexes rule out the reaction of Ni(dien)$_2^{2+}$ and NiEDTA^{2-} to give Ni(dien)$^{2+}$ and Ni(dien)EDTA^{2-}. Solutions A, B, and C have the same initial concentration of NiEDTA^{2-} so that if the per cent of mixed complex formation were small, the ratio of [I]/[II] would be constant, and the absorbances in A, B, and C would be in proportion to the concentration of Ni(dien)$_2^{2+}$. However, this is not true for all of the ΔA values and we conclude that there must be moderate concentrations of the mixed complexes under these conditions.

The species proposed in I and II are in accord with the concentration ratios of reactants. The species have a high degree of nickel coordination and should have appreciable stability. The absorption maxima support the assignment.[15] Aquonickel has maxima at 650 and 395 mμ while Ni(dien)$_2^{2+}$ with six nitrogen donors has maxima at 540 and 340 mμ and NiEDTA^{2-} is between with maxima at 590 and 380 mμ. Species I and II have absorption peaks which in general correspond to the number of nitrogens assigned in the structures, but the spectra are a composite of absorption maxima and minima in accord with eq 7.

Species I is believed to be the same as the kinetic intermediate (eq 5) which formed under concentration conditions where it was stable relative to Ni(dien)EDTA^{2-} and Ni(dien)$^{2+}$ but not stable relative to NiEDTA^2 and Ni(dien)$_2^{2+}$.

Conclusions

Figure 6 shows the combined mechanism including the proposed intermediate complexes. EDTA does not react directly with Ni(dien)$_2^{2+}$ but must wait for the relatively slow dissociation (k_1) of one dien from the complex. The reaction is slow because of the stepwise equilibration (not shown) preceding the last nitrogen bond cleavage. After one dien is gone, the addition of EDTA occurs readily (k_2). The addition product proceeds to unwrap one nitrogen from dien (k_3) and add another segment of EDTA. This occurs again (k_4) with the breakage of the last chelate ring from the polyamine. The final step is the loss of dien with a singly bonded nitrogen. This is relatively rapid and could not be observed in the present work.

A necessary requirement for the observed kinetics is that the intermediate [Ni(dien)*EDTA^{2-}] be more stable than the intermediate [Ni(dien)EDTA^{2-}]. If this were not so, two distinct steps would not be found in the process. As shown in Figure 6 the loss of a dien nitrogen from nickel (k_3) should be followed by the rapid addition of an EDTA nitrogen in order to give a more stable intermediate. The structure shown immediately preceding the rate step k_4 is sterically crowded but is possible from models and is consistent with other polyamine–EDTA reactions[2] in that a maximum of four nitrogens from the two ligands are coordinated simultaneously.

A side product with a bridging EDTA group is possible if excess Ni(dien)$^{2+}$ is present, because the addition of an EDTA segment to Ni(dien)$^{2+}$ is so much faster than the loss of the dien. In this case the only step observed kinetically was the breakup of this bridged species (k_{-5}). The values of the rate constants

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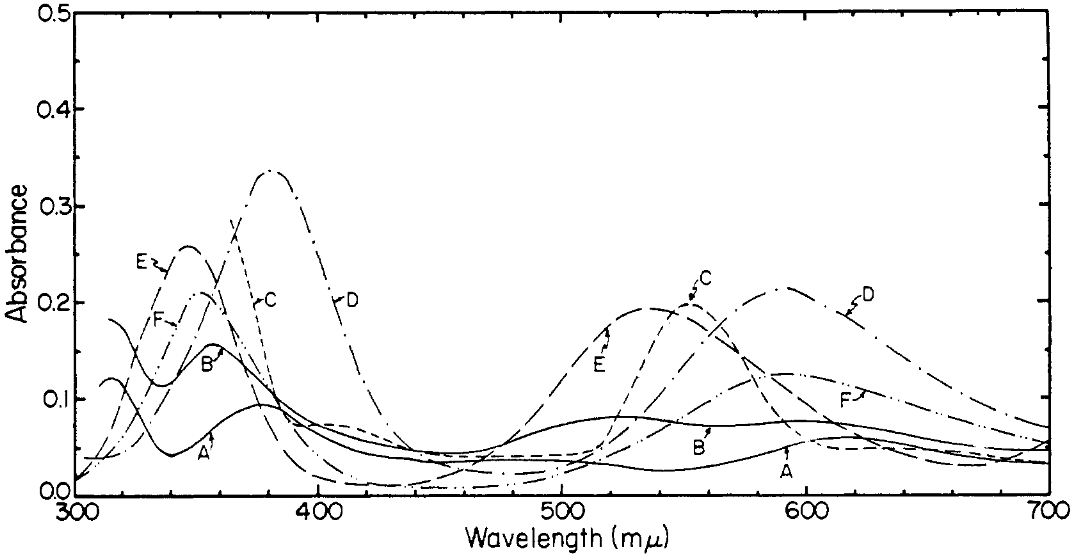

Figure 5.—Spectra of reactants and products and the difference spectra from mixtures of $Ni(dien)_2^{2+}$ and $NiEDTA^{2-}$: A (——), difference spectrum, $[Ni(dien)_2^{2+}]:[NiEDTA^{2-}] = 0.050:0.125$, 2 cm; B (——), difference spectrum, $[Ni(dien)_2^{2+}]:[NiEDTA^{2-}] = 0.125:0.125$, 2 cm; C (– –), difference spectrum, $[Ni(dien)_2^{2+}]:[NiEDTA^{2-}] = 0.250:0.125$, 2 cm; D (–·–), spectrum, $[NiEDTA^{2-}] = 5.0 \times 10^{-3}$ *M*, 5 cm; E (— —), spectrum, $[Ni(dien)_2^{2+}] = 5.0 \times 10^{-3}$ *M*, 5 cm; F (–··–), spectrum, $Ni(dien)^{2+} = 5.0 \times 10^{-3}$ *M*, 5 cm.

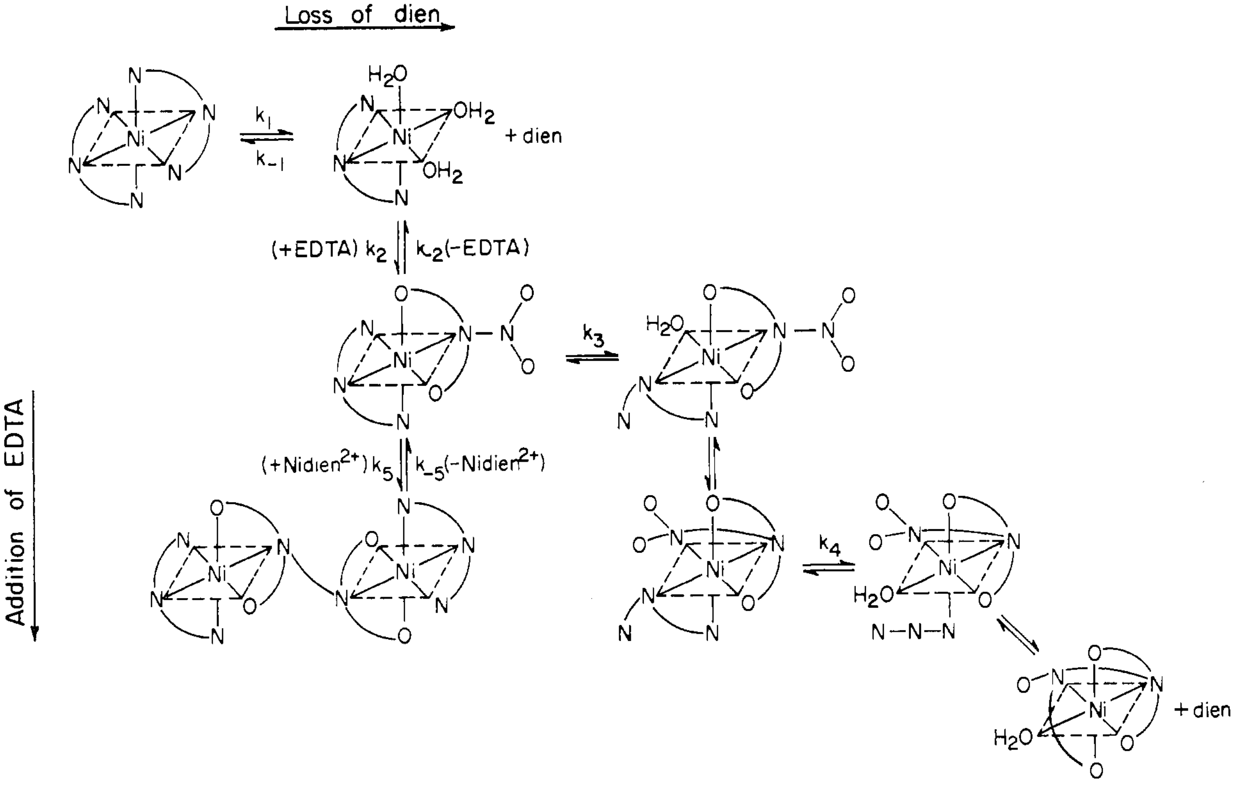

Figure 6.—Stepwise unwrapping of dien (N-N-N) with stepwise addition of EDTA $({}^{O}_{O}{>}N\text{-}N{<}{}^{O}_{O})$, showing steps identified in this kinetic study: k_1, k_2, k_3, k_4, and k_{-5}. Spectral and kinetic evidence support the existence of several of the mixed complexes consistent with the proposed structures. None of the structures is proved, not even those of $Ni(dien)_2^{2+}$ or $Ni(dien)^{2+}$, which may have three nitrogens in one plane.

are summarized in Table III. Protonated intermediates are omitted in Figure 6 to simplify the mechanism. The value of k_1 depends on $[H^+]$ even at pH 8–9. The primary EDTA ($=L^{4-}$) reactant at this pH is HL^{3-}, and k_2 corresponds to $k_{HL}^{Ni(dien)}$. However, the first nickel-dien-EDTA intermediate should lose its proton before pH 8.4 so that the k_3 and k_4 steps are independent of acidity in the pH range examined.

A necessary condition for eq 2 and 3 to be valid is that $k_3 \gg k_{-2}$ and that the combined steps associated with k_3 and k_4 be faster than the dissociation step given by k_1. The latter condition is met easily with k_3 and

TABLE III

SUMMARY OF RATE CONSTANTS AT 25.0°

Rate constants	pH	Ionic strength	Comments
$k_1 = 1.2 \times 10^{-2}$ sec^{-1}	7.95	1.0 M NaClO$_4$	V_i plots
$k_{-1}/k_2 = 1.9 \times 10^{-2}$	7.95	1.0 M NaClO$_4$	V_i plots
$k_1 = 1.3 \times 10^{-3}$ sec^{-1}	8.76	0.1 M NaClO$_4$	CN$^-$ quench
$k_3 = 26$ sec^{-1}	8.4–10.0	1.0 M KNO$_3$	Stopped-flow
$k_4 = 2.6$ sec^{-1}	8.4–10.0	1.0 M KNO$_3$	Stopped-flow
$k_{-5} = 0.7$ sec^{-1}	8.3–9.5	1.0 M KNO$_3$	Stopped-flow
$k_{-1} = 1.2 \times 10^3$ M sec^{-1}	7.95	1.0 M NaClO$_4$	Calculated
$k_2 = 6.3 \times 10^4$ M sec^{-1}	7.95	1.0 M NaClO$_4$	Calculated
$k_{-1} = 2.1 \times 10^3$ M sec^{-1}	8.76	0.1 M NaClO$_4$	Calculated
$k_{\mathrm{H}}{}^{\mathrm{Ni(dien)_2}} \simeq 1.0 \times 10^6$ M^{-1} sec^{-1}		1.0 and 0.1 M NaClO$_4$	Estimate because of variable μ
$k_{\mathrm{Hdien}}{}^{\mathrm{Ni(dien)}} \simeq 1.7 \times 10^4$ M^{-1} sec^{-1}		1.0 and 0.1 M NaClO$_4$	
$k_{\mathrm{HL}}{}^{\mathrm{Ni(dien)}} = 6.3 \times 10^4$ M^{-1} sec^{-1}		1.0 M NaClO$_4$	Assumed $= k_2$

k_4, 2200 and 210 times larger than k_1, respectively. The value of k_{-2} can be estimated by comparing it to the dissociation rate constant of nickel iminodiacetate, $k_{\mathrm{d}}{}^{\mathrm{NiIDA}} = 1.7 \times 10^{-4}$ sec^{-1} (25°, 1.25 M NaClO$_4$).[16] Even if the coordinated dien increased the dissociation rate by a factor of 300 as it does for NH$_3$,[7] the ratio of k_3/k_{-2} would be larger than 500.

Previous work[2] indicated that the rate-determining step in the reaction of EDTA with nickel–trien and with nickel–tetren occurred when only three polyamine nitrogens were coordinated to nickel. The present study confirms the rapid addition of EDTA to the tridentate polyamine complex. The value of k_2 ($\simeq k_{\mathrm{HL}}{}^{\mathrm{Ni(dien)}}$ at pH 7.95) is 6.3×10^4 M^{-1} sec^{-1} (at $\mu = 1.0$) which is in good agreement with $k_{\mathrm{HL}}{}^{\mathrm{NiHtrien}} \simeq k_{\mathrm{HL}}{}^{\mathrm{NiH_2tetren}} \simeq 1.6 \times 10^5$ (at $\mu = 0.1$).

The ratio of $k_{\mathrm{HL}}{}^{\mathrm{Ni(dien)}}/k_{\mathrm{Hdien}}{}^{\mathrm{Ni(dien)}}$ is estimated from this study to be only 3.7, which is very much less than anticipated because there is an electrostatic attraction for the reaction of a -3 and a $+2$ ion in one case and a repulsion of a $+1$ and a $+2$ ion in the other case. The two rate constants are for the replacement of bound water by EDTA and by dien and do not involve the displacement of any portion of the dien initially coordinated in Ni(dien)$^{2+}$. It is of interest that it is the value of $k_{\mathrm{HL}}{}^{\mathrm{Ni(dien)}}$ which is less than expected from the exchange reactions of Ni(dien)$^{2+}$. The outer-sphere association constant (K_{os}) was estimated to be 13 for -3 and $+2$ ions,[17] and $k_{\mathrm{Ni(dien)}}{}^{-\mathrm{H_2O}}$ was found[7] to be 4×10^5 sec^{-1} so the predicted value of $k_{\mathrm{HL}}{}^{\mathrm{Ni(dien)}}$ was 5×10^{-6} M^{-1} sec^{-1} instead of 6.3×10^4 M sec^{-1}. On the other hand, the reaction of Hdien$^+$ with Ni(dien)$^{2+}$ ($k \simeq 1.7 \times 10^4$ M^{-1} sec^{-1}) is reasonable only for the case of enhanced water loss from Ni(dien)$^{2+}$ because the K_{os} value for two positive ions must be less than 0.1. The EDTA rate constant fits the value of water loss from the aquonickel ion (2.7×10^4 sec^{-1}) much better. This suggests the interesting possibility that the rate-determining step in the EDTA reaction involves a less labile water on Ni(dien)$^{2+}$ than the rate-determining step in the Hdien^{2+} reaction. An earlier example also seemed to distinguish the lability of different coordinated waters in a nickel ion complex.[18]

The reactions of nickel–dien and EDTA demonstrate the stepwise nature of ligand–ligand replacement reactions with multidentate ligands just as has been found for metal–metal replacement reactions.[13] The ligand–ligand reactions are generally much faster because the reaction intermediates with two multidentate ligands coordinated to one metal ion are more stable than intermediates with two metal ions coordinated to one multidentate ligand. At higher concentrations of reactants the diligand intermediates are observable, and the rate-determining steps become the chelate ring breakage steps. In the case of nickel–dien–EDTA the chelate-opening steps are very similar to those found when nickel–dien dissociates in strong acid.

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