Relaxation Kinetic Study of the Equilibrium between Diaquobis(ethylenediamine)nickel(II) and Tris(ethylenediamine)nickel(II)

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Abstract: The rate of addition of the third ethylenediamine to nickel(II) is greatly accelerated by the presence of two coordinated ethylenediamine molecules. Both en and $H(en)^+$ react with $Ni(en)_2(H_2O)_2^{2+}$, and temperature-jump relaxation time constants are resolved by the use of steady state approximations and computer calculations. At 25° the monodentate formation rate constants are $5.5 \times 10^6\ M^{-1}\ sec^{-1}$ for en and $1.1 \times 10^5\ M^{-1}\ sec^{-1}$ for $H(en)^+$. In the formation of $Ni(en)_3^{2+}$ the ring closure rate constant ($2.2 \times 10^5\ sec^{-1}$) is similar in magnitude to the monodentate en dissociation rate constant ($1.2 \times 10^5\ sec^{-1}$). As a result ring closure contributes to the limiting rate in the chelation of the third en, while this is not the case in the chelation of the first en to aquonickel ion. Acid has little effect on the rate of removal of en from $Ni(en)_3^{2+}$; the reaction is only half as slow at pH 8 as it is in strong acid.

The rate of replacement of bound water in nickel(II) complexes can be greatly affected by ligands coordinated to the nickel. It has been shown[2] that the rate of exchange of water by ammonia increases as the number of nitrogens coordinated to the nickel increases up to $Ni(dien)(H_2O)_3^{2+}$. Recent work[3] indicates that the rate of exchange continues to increase for the nickel–trien and nickel–tren complexes.[4] The same effect is seen for the present system where two ethylenediamine molecules coordinated to nickel speed its substitution reactions.

In chelate formation reactions it is seldom possible to obtain rate constants for each of the steps of monodentate formation, monodentate dissociation, and ring closure. However, the pH and concentration dependence of the relaxation times in this system permit an evaluation of all of these rate constants. The rate of chelate ring opening in $Ni(en)_3^{2+}$ is known.[5]

For most substitution reactions which involve a bidentate ligand, the replacement of the first coordinated water molecule is the rate-determining step.[6–8] The loss of a second water molecule and chelate ring closure is faster than the first step and is fast compared to the dissociation of the monodentate ligand. However, several examples have been reported where the loss of the second water molecule and chelate ring closure is rate limiting. In particular, slow six-membered chelate ring closure for the cobalt complexes of β-alanine and β-aminobutyric acid results in sterically controlled substitution. These rates are significantly slower than the formation of the respective five-membered chelate ring complexes with α-alanine and α-aminobutyric acid.[9,10] The formation of nickel malonate in the pH region 6–7 fits a mechanism in which the rate of formation of the chelated complex from the monodentate complex is slower than the rate of departure of the first water molecule from the inner hydration sphere of nickel ion.[11] This result may also be explained by the difficulty of closing a six-membered chelate ring.

In the present study, two en ligands accelerate the rate of formation and dissociation of the third en. The dissociation rate of this en molecule when it is singly bonded is greatly accelerated and its rate becomes competitive with the ring closure rate. Therefore, the rate-determining step in the formation of $Ni(en)_3^{2+}$ is no longer solely the rate of addition of monodentate en, but is influenced by the rate of ring closure.

Experimental Section

Reagents. Nickel perchlorate was prepared from nickel carbonate and perchloric acid and was recrystallized from water. Nickel solutions were standardized by the addition of excess CyDTA (*trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate), and back titration with Ca^{2+} using methyl thymol blue as indicator. Reagent grade ethylenediamine was used and was standardized by acid titration.

The ionic strength was controlled at 0.40 *M* with recrystallized $NaClO_4$. The pH was adjusted to the desired value with NaOH or $HClO_4$.

Relaxation Measurements. The temperature-jump apparatus has been described elsewhere.[2] The temperature-jump cell was thermostated to ±0.1° and the magnitude of the jump was 5.7° using a 40-kV discharge. Five to seven minutes was allowed between jumps for the solution to reattain temperature equilibrium. Each relaxation time, τ, represents an average of four to eight individual relaxation experiments. The average of the standard deviations for each set of τ values is 7.4%.

Phenol red was used to follow the reaction (555 mμ). The indicator concentration was varied from 5×10^{-6} to $2.5 \times 10^{-5}\ M$ without affecting the relaxation times. Thus, no correction for the indicator concentration is necessary. This is in agreement with the fact that the calculated α value (which takes into account the rapid protolytic equilibria)[6] is negligible for the conditions used.

Experiments in which the ratio of all forms of en to all forms of nickel was varied from 1:1 to 3:1 demonstrated that the observed relaxation involved the equilibrium between $Ni(en)_2^{2+}$ and $Ni(en)_3^{2+}$,

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[1] Address correspondence to this author.

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

[3] J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, in press.

[4] Tren is $N(CH_2CH_2NH_2)_3$, trien is $(CH_2NHCH_2CH_2NH_2)_2$, dien is $HN(CH_2CH_2NH_2)_2$, and en is $H_2NCH_2CH_2NH_2$.

[5] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960).

[6] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962).

[7] F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).

[8] J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).

[9] K. Kustin, R. F. Pasternak, and E. M. Weinstock, *ibid.*, **88**, 4610 (1966).

[10] A. Kowalak, K. Kustin, R. F. Pasternak, and S. Petrucci, *ibid.*, **89**, 3126 (1967).

[11] V. Nickel, H. Hoffman, and W. Jaenicke, *Ber. Bunsenges. Physik. Chem.*, **72**, 526 (1968).

Table I. Equilibrium Constants at 25° and 0.75 *M* Ionic Strength[a]

$$K_{H(en)} = \frac{[H(en)^+]}{[H^+][en]} = 10^{10.18} \qquad K_2 = \frac{[Ni(en)_2{}^{2+}]}{[Ni(en)^{2+}][en]} = 10^{6.48}$$

$$K_{H_2en} = \frac{[H_2en^{2+}]}{[H^+][H(en)^+]} = 10^{7.47} \qquad K_3 = \frac{[Ni(en)_3{}^{2+}]}{[Ni(en)_2{}^{2+}][en]} = 10^{5.05}$$

$$K_1 = \frac{[Ni(en)^{2+}]}{[Ni^{2+}][en]} = 10^{7.60}$$

[a] F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **74**, 2373 (1952); *ibid.*, **74**, 5243 (1952).

Table II. Experimental Conditions and Comparison of Observed and Calculated Relaxation Times[a]

pH	$[Ni(en)_2{}^{2+}]$ × 10³, *M*	$[Ni(en)_3{}^{2+}]$ × 10³, *M*	[en] × 10⁶, *M*	$[H(en)^+]$ × 10³, *M*	$[H_2(en)^{2+}]$ × 10³, *M*	τ^{-1}_{obsd} × 10^{-2}, sec⁻¹	τ^{-1}_{calcd} × 10^{-2}, sec⁻¹
7.20	2.45	0.21	0.80	0.97	2.27	0.83 ± 0.14[b]	1.24
7.29	5.36	0.91	1.60	1.56	2.97	1.37 ± 0.06	1.98
7.26	8.03	1.72	1.99	2.09	4.26	1.84 ± 0.15	2.45
7.20	8.04	1.47	1.70	2.05	4.80	2.01 ± 0.07	2.24
7.29	10.5	2.87	2.54	2.49	4.74	2.61 ± 0.11	3.06
7.18	15.8	4.34	2.56	3.22	7.92	2.98 ± 0.20	3.38
7.20	22.7	8.41	3.46	4.15	9.74	4.50 ± 0.14	4.59
7.18	29.7	12.2	3.83	4.82	11.8	5.23 ± 0.23	5.36
7.11	37.3	14.9	3.73	5.52	15.9	5.49 ± 0.12	5.53
7.20	35.6	17.3	4.55	5.47	12.8	7.02 ± 0.50	6.46
7.70	2.60	0.80	2.85	1.08	0.80	1.49 ± 0.19	2.05
7.78	4.74	2.31	4.56	1.44	0.88	2.80 ± 0.27	3.32
7.76	6.68	4.03	5.62	1.86	1.20	3.68 ± 0.14	4.48
7.72	6.82	3.85	5.28	1.92	1.36	3.64 ± 0.17	4.15
7.74	8.68	5.64	6.07	2.10	1.42	4.38 ± 0.31	5.07
7.72	12.2	9.46	7.25	2.63	1.86	5.95 ± 0.35	6.73
7.68	17.5	15.1	8.07	3.21	2.49	8.20 ± 0.27	8.32
7.68	22.6	20.9	8.65	3.44	2.67	9.80 ± 0.38	10.2
7.71	26.8	27.7	9.60	3.58	2.59	12.6 ± 0.4	12.2
7.71	50.1	21.0	3.91	1.45	1.05	20.4 ± 1.7	19.2
8.13	2.17	1.41	6.04	0.85	0.23	2.59 ± 0.19	2.61
8.20	3.94	3.30	7.82	0.94	0.22	4.17 ± 0.45	4.19
8.30	5.22	5.71	10.2	0.97	0.18	5.81 ± 0.13	5.82
7.98	6.41	5.94	8.65	1.72	0.67	5.59 ± 0.09	4.73
8.30	6.86	7.72	10.5	1.00	0.19	6.80 ± 0.83	7.27
8.18	9.46	11.1	11.0	1.38	0.34	9.80 ± 0.38	8.56
8.09	11.5	21.8	17.6	2.73	0.82	11.4 ± 0.8	11.2
8.22	14.6	27.0	17.3	1.98	0.44	14.2 ± 1.6	13.4
8.11	21.0	32.9	14.6	2.16	0.62	16.4 ± 1.7	16.1
8.19	23.2	31.6	12.7	1.56	0.37	18.2 ± 1.6	18.9
8.01	31.4	30.3	9.00	1.68	0.61	18.5 ± 3.4	19.8

[a] 25° and 0.40 μ. [b] Standard deviation.

and not that between $Ni(en)^{2+}$ and $Ni(en)_2{}^{2+}$. This is expected from the measured rates of dissociation of $Ni(en)^{2+}$ and $Ni(en)_2{}^{2+}$.[5] For most experiments, the ratio of total forms of en to total forms of nickel was kept constant at 2.6 because the best experimental data were obtained for these conditions. However, the ratio of $[en]_T$ to $Ni(en)_2{}^{2+}$ ($[en]_T = [en] + [H(en)^+] + [H_2en^{2+}]$) changes by a factor of 10 over the pH and concentration range studied.

The concentrations of all species ($Ni(en)^{2+}$, $Ni(en)_2{}^{2+}$, $Ni(en)_3{}^{2+}$, en, $H(en)^+$, H_2en^{2+}) in solution were calculated using a species concentration computer program written by Perrin and Sayce[12] and run on the CDC 6500 computer. The equilibrium constants used for these calculations are given in Table I. The experimental conditions and the concentrations of each species are given in Table II.

Stopped-Flow Kinetics. Solutions of $Ni(en)_3{}^{2+}$, 0.02 *M*, were prepared from its perchlorate salt. A slight amount of dissociation of the tris complex occurred as equilibrium was established and this raised the pH of the $Ni(en)_3{}^{2+}$ solution to approximately 10.3. A 2,6-lutidine buffer with an initial pH between 5.7 and 6.7 was mixed with the $Ni(en)_3{}^{2+}$ solution in the stopped-flow experiments (final pH range 6.7–7.2). The resulting dissociation of $Ni(en)_3{}^{2+}$ was followed at 25° on a Durrum–Gibson stopped-flow apparatus with 2-cm cell length, by monitoring the disappearance of $Ni(en)_3{}^{2+}$ at 543 mμ. These experiments gave relaxation curves as a result of $[H^+]$ jump and were comparable to the temperature-jump relaxation.

Additional $[H^+]$-jump experiments with $Ni(en)_3{}^{2+}$ were run on the stopped-flow at 3.5° to determine if any of the $Ni(en)_3{}^{2+}$ exists in solution with the third en group as a monodentate ligand. The reaction was followed at 610 mμ using bromocresol green as indicator. The rate of dissociation of $Ni(en)_3{}^{2+}$ at 3.5° is 8 sec⁻¹,[15] and the pK_a of the indicator is 4.7. A sufficient concentration of $HClO_4$ was used to ensure a final pH of less than 4 for the $Ni(en)_3{}^{2+}$ within the time of initial observation (5 msec). The calculation of the amount of acid uptake possible by any monodentate en bound to nickel was corrected for the small amount of dissociation and hydrolysis which occurs on dissolution of $Ni(en)_3(ClO_4)_2$. Correction also was made for the kinetic dissociation expected within 5 msec at 3.5°. The results showed that no detectable amount (less than 5% for these experiments) of the $Ni(en)_3{}^{2+}$ exists as a monodentate species in solution.

Results and Discussion

Only one relaxation curve could be observed at each set of conditions. The relaxations were simple exponentials; the relaxation times were concentration and pH dependent. At constant pH the experimental data gave good straight line plots for eq 1, as shown in

$$\tau^{-1} = k_f([Ni(en)_2{}^{2+}] + [en]_T) + k_r \qquad (1)$$

Figure 1. Equation 1 corresponds to the chemical reaction

$$Ni(en)_2{}^{2+} + en_T \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ni(en)_3{}^{2+} \qquad (2)$$

where $[en]_T = [en] + [H(en)^+] + [H_2en^{2+}]$. The reaction scheme shown in Figure 2 was used to explain

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(12) D. D. Perrin and I. G. Sayce, *Talanta*, **14**, 833 (1967).

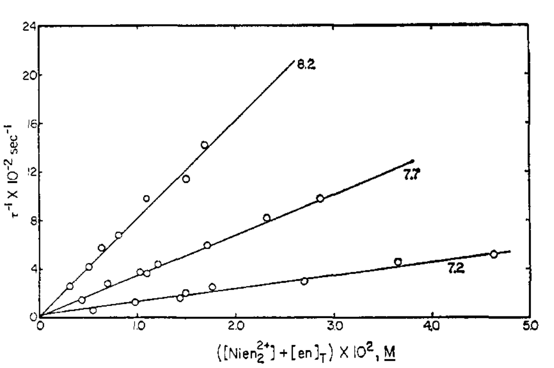

Figure 1. Relaxation times at pH 7.2, 7.7, and 8.2 for equilibrium between $Ni(en)_2(H_2O)_2{}^{2+}$, (en), $H(en)^+$, and $Ni(en)_3{}^{2+}$ at 25.0° and 0.40 μ.

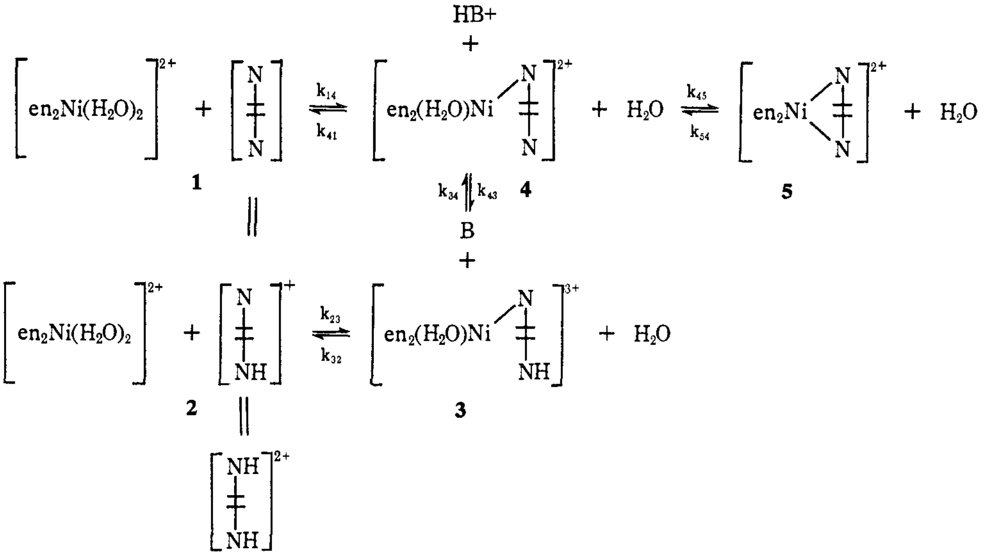

Figure 2. Proposed mechanism for the reaction of en and $H(en)^+$ with $Ni(en)_2(H_2O)_2{}^{2+}$, where B and HB^+ are a base and its conjugate acid in the rapid proton transfer reaction between **3** and **4**.

these observations. The observed pH dependence suggested reaction paths **1** to **4** and **2** to **3**. The presence of a single relaxation could result if **3** and **4** were present in negligible concentrations, but also could result if they were the products of the reaction. The latter alternative is very unlikely because $Ni(en)_3(NO_3)_2$ is known from an X-ray study[13] to have all six nitrogens coordinated, and the stability constant, K_3, is too large for a monodentate complex in solution. Indeed, the stopped-flow experiments established that less than 5% of the $Ni(en)_3{}^{2+}$ exists in solution in the monodentate state and the actual amount is believed to be much less than 5%. Since intermediates **3** and **4** are not present in appreciable concentration as products or reactants separate relaxations are not observed for steps **1–4–5** and **2–3–4–5**.

It is worth noting that several other mechanisms were tested which did not fit the experimental data. Path **1–4–5** was tested but the observed pH dependence could not be explained. The only mechanism found which fit the complete range of experimental data is that presented in Figure 2.

Although the reaction mechanism in Figure 2 is fairly simple, attempts to solve the relaxation behavior in accord with general methods for multiple-step systems[14,15] lead to very complicated relaxation expressions. These expressions are not easily solved in terms of rate constants and they give a spectrum of relaxation times. As a different approach we used the steady state approximation to resolve the rate constants. Equation 1 was established experimentally so that the k_f and k_r values are known for each of the three pH conditions. These rate constants can be written in terms of the proposed mechanism in Figure 2. The expression for k_f and k_r were obtained by assuming steady-state conditions for intermediates **3** and **4**.

$$\begin{aligned} k_f = {} & \{(k_{32} + k_{34}[B])k_{14}k_{45} + k_{23}k_{45}k_{34}K_{H(en)}[H^+][B]\}/ \\ & \{(1 + K_{H(en)}[H^+] + \beta_{2H}[H^+]^2) \times \\ & ((k_{45} + k_{41})(k_{32} + k_{34}[B]) + k_{32}k_{43}[HB^+])\} \end{aligned} \qquad (3)$$

$$k_r = \frac{(k_{32} + k_{34}[B])k_{41}k_{54} + k_{54}k_{43}k_{32}[HB^+]}{(k_{45} + k_{41})(k_{32} + k_{34}[B]) + k_{32}k_{43}[HB^+]} \qquad (4)$$

where B is the base which accepts the proton in step **3–4** and $\beta_{2H} = K_{H(en)}K_{H_2en}$. The proton transfer step is normally fast and in this case does not appear to be rate limiting despite the speed of the coordination substitution reactions. There are several possible sources of B: H_2O, en, OH^-, and $H(en)^+$. Of these, OH^- and $H(en)^+$ are the major contributors to the proton transfer rate. The rate of transfer to H_2O would not make an appreciable contribution unless species **3** is a much stronger acid than H_2en^{2+}, which is unlikely. For OH^-, $k_{34} \simeq 10^{11}$ M^{-1} sec^{-1}, and for $H(en)^+$, k_{34} is 10^8–10^9 M^{-1} sec^{-1}.[16] The OH^- contribution does not predominate in the pH range 7.2–8.2 in the reaction with $H(en)^+$, as B probably is the main proton acceptor in path **3–4**.

When the assumption is made that the proton transfer reaction is fast ($k_{34}[B] \gg k_{32}$), then the expressions for

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(13) L. N. Swink and M. Atoji, *Acta Cryst.*, **13**, 639 (1960).

(14) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, p 907.

(15) G. W. Castellan, *Ber. Bunsenges. Physik. Chem.*, **67**, 898 (1963).

(16) E. Grunwald and M. Cocivera, *Discussions Faraday Soc.*, **39**, 105 (1965).

k_f and k_r are given in eq 5 and 6, where $K_{HB} = [HB^+]/([H^+][B])$.

$$\{k_f = k_{14}k_{45} + k_{23}k_{45}K_{H(en)}[H^+]\}/ \left\{(1 + K_{H(en)}[H^+] + \beta_{2H}[H^+]^2) \times \left[(k_{45} + k_{41}) + \frac{k_{32}k_{43}}{k_{34}} K_{HB}[H^+]\right]\right\} \quad (5)$$

$$k_r = \frac{k_{54}k_{41} + k_{54}k_{32}(k_{43}/k_{34})K_{HB}[H^+]}{(k_{45} + k_{41}) + \dfrac{k_{32}k_{43}}{k_{34}}K_{HB}[H^+]} \quad (6)$$

In order to evaluate the individual rate constants, eq 5 and 6 were combined with eq 1 and with $K_3 = k_{14}k_{45}/(k_{41}k_{54})$ to give eq 7

$$\tau^{-1} = \left(\frac{a + bK_{H(en)}[H^+]}{c + d[H^+]}\right) \times \left(\frac{[Ni(en)_2{}^{2+}] + [en]_T}{1 + K_{H(en)}[H^+] + \beta_{2H}[H^+]^2}\right) + \frac{a/K_3 + k_{54}d[H^+]}{c + d[H^+]} \quad (7)$$

where $a = k_{14}k_{45}$, $b = k_{23}k_{45}$, $c = k_{41} + k_{45}$, and $d = k_{32}(k_{43}/k_{34})K_{HB}$. The value for k_{54} is 87 sec^{-1} (determined by Ahmed and Wilkins). In addition to the 23 experimental values seen in Figure 1, another eight relaxation constants at other pH values and at higher concentrations were used in the computation of eq 7 (see Table II for all the values). A nonlinear weighted regression computer program (Computer Science Center, Purdue University) solved eq 7 for the constants a, b, c, and d. The values of these constants are given in Table III. As a test of the constancy of the values, different sets of initial estimates for the constants were used in the computer program and the same values resulted.

Table III. Kinetic Constants Determined by Regression Analysis and the Resulting Individual Rate and Stability Constants.

$a = k_{14}k_{45} = 1.22 \times 10^{12}\ M^{-1}\ sec^{-2}$
$b = k_{45}k_{23} = 2.5 \times 10^{11}\ M^{-1}\ sec^{-2}$
$c = k_{41} + k_{45} = 3.45 \times 10^5\ sec^{-1}$
$d = k_{32}(k_{43}/k_{34})K_{HB} = 4.7 \times 10^{12} M^{-1}\ sec^{-1}$
Monodentate en formation: $k_{14} = 5.5 \times 10^6\ M^{-1}\ sec^{-1}$
Monodentate en dissociation: $k_{41} = 1.2 \times 10^5\ sec^{-1}$
en ring closure: $k_{45} = 2.2 \times 10^5\ sec^{-1}$
en ring opening: $k_{54} = 87\ sec^{-1}$ (ref 5)
$H(en)^+$ formation: $k_{23} = 1.1 \times 10^5\ M^{-1}\ sec^{-1}$
Ratio en/$H(en)^+$ monodentate formation: $k_{14}/k_{23} = 50$
Stability constant of monodentate species: $k_{14}/k_{41} = 44\ M^{-1}$
Stability constant for ring closure: $k_{45}/k_{54} = 2.5 \times 10^3$

The constants determined by the computer calculations were used in eq 5 to calculate the k_f values at the three pH values shown in Figure 1. The calculated values are compared to the graphical slopes in Table IV and the agreement is excellent. The constants also were used to calculate the τ^{-1} values for the individual relaxation experiments shown in Table II. Again the agreement is very good with more than half of the calculated values falling within the standard deviation of the experimental values. The observed standard deviations are for individual solutions, and slight errors in the pH measurement could easily lead to disagreement with the calculated values.

Table IV. Comparison of k_f Values.

pH	k_f(graphical), $M^{-1}\ sec^{-1}$	k_f(calcd), $M^{-1}\ sec^{-1}$
7.2	1.08×10^4	1.09×10^4
7.7	3.38×10^4	3.50×10^4
8.2	7.95×10^4	7.44×10^4

The k_r values from the graphical intercepts are too inaccurate to provide an exact check on the constants. Some of the graphical values (which ranged from 20 to 45 sec^{-1}) were a little low compared to the calculated k_r values of 40–55 sec^{-1} from pH 8.2 to 7.2. However, independent $[H^+]$-jump experiments run on the stopped-flow gave an average of 38 sec^{-1} for k_r at pH 7.0–7.5. Therefore the agreement for the k_r values is considered satisfactory.

Individual rate constants and the stability constants for the intermediates can be calculated from the values of a, b, c, k_{54}, and K_3. The resulting constants are summarized in Table III.

The value of 44 M^{-1} for k_{14}/k_{41} agrees with the range of stability constants found for the ammonia complexes of nickel polyamines.[3] At 25° the ammonia complexes of nickel-dien and of nickel-*cis,cis*-1,3,5-triaminocyclohexane have values of 56 M^{-1} and 61 M^{-1}, respectively. The value with nickel-tren at 6° is 53 M^{-1}.

The rate constant, k_{14}, for the formation of the monodentate intermediate is very large for nickel(II) and illustrates the extent to which the coordinated ethylenediamine molecules make the substitution reactions of nickel more labile. On the basis of an outer-sphere association constant (K_{os}) of 0.1 M^{-1} expected for an ion and a neutral molecule,[2,17] and using a statistical correction for the number of water molecules, the value of k_{14} is larger by a factor of 6000 than predicted from the characteristic water exchange constant of aquonickel.[18] Not all of this acceleration can be attributed to the two bound ethylenediamines, however, as shown by a comparison of rate constants for the corresponding reaction with aquonickel ion in Table V.

Table V. Comparison of Rate Constants for the Reactions of $Ni(H_2O)_6{}^{2+}$ and $Ni(en)_2(H_2O)_2{}^{2+}$ with en and $H(en)^+$ at 25°

Rate constant	$Ni(H_2O)_6{}^{2+}$	$Ni(en)_2(H_2O)_2{}^{2+}$
k_{14}, $M^{-1}\ sec^{-1}$	2×10^5 [a]	5.5×10^6
k_{41}, sec^{-1}	~3[b]	1.2×10^5
k_{45}, sec^{-1}	~2×10^3 [c]	2.2×10^5
k_{54}, sec^{-1}	0.14[d]	87
k_{23}, $M^{-1}\ sec^{-1}$	6×10^2 [e]	1.1×10^5

[a] M. Eigen and R. G. Wilkins, Advances in Chemisty Series, No. 49, American Chemical Society, Washington, D.C., 1956, p 55 (calculated from dissociation rate constant corrected to 25°). [b] Value is for the dissociation of $Ni(H_2O)_5NH_3{}^{2+}$ and may be too small for monodentate en. [c] Calculated from the k_{41} and the k_{14}, k_{54}, and $K_{Ni(en)}$ values, and therefore may also be too small. [d] Reference 5. [e] Reference 8.

The value of k_{14} is larger by a factor of 27 for $Ni(en)_2(H_2O)_2{}^{2+}$ than for $Ni(H_2O)_6{}^{2+}$, or the lability per water molecule is greater by a factor of 90. The reason the difference is not greater is that the en reaction with $Ni(H_2O)_6{}^{2+}$ is itself faster than would be predicted from K_{os} and the characteristic water exchange constant.

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(17) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).
(18) See ref 14, p 1042.

This has been discussed by Rorabacher[17] and explained in terms of an internal conjugate base mechanism.

An interesting aspect of the present study is that the existence of the two competitive reaction paths (with and without H^+) permits the evaluation of the ring closure rate constant, k_{45}, and of the monodentate en dissociation rate constant, k_{41}. Both of these constants are very much larger for the intermediate **4** than the estimated constants for the corresponding intermediate with aquonickel (Table V). The effect of the two coordinated en molecules on k_{41} is so large that the ring closure rate (**4** → **5**) is no longer much faster than the rate of loss of the monodentate intermediate (**4** → **1**). As a result, chelate ring closure contributes to the limiting rate in the formation of $Ni(en)_3{}^{2+}$. Therefore, the actual rate of chelation is only faster by a factor of 17 in the formation $Ni(en)_3{}^{2+}$ compared to $Ni(en)(H_2O)_4{}^{2+}$.

The ratio k_{14}/k_{23} is 50 for $Ni(en)_2(H_2O)_2{}^{2+}$, compared to a ratio of 330 for the corresponding reactions of aquonickel ion with en compared to $H(en)^+$. On the basis of electrostatics alone[19] only a sixfold difference in rate would be predicted for Ni^{2+} reacting with en and $H(en)^+$. (The center-to-center distance between nickel ion and the protonated nitrogen is about 7 Å.) The internal conjugate base mechanism[17] offers an explanation in terms of the enhanced reactivity of en due to hydrogen bonding of one amine group to coordinated water while the other amine group replaces another coordinated water. This effect should be diminished with $Ni(en)_2(H_2O)_2{}^{2+}$ compared to $Ni(H_2O)_6{}^{2+}$. In any case, the rate constant corresponding to k_{23} for $Ni(H_2O)_6{}^{2+}$ fits the normal product of $K_{os}k^{-H_2O}$, using $K_{os} = 0.018$ for a charge separation of 7 Å and a distance of closest approach of 3.5 Å for the unprotonated nitrogen.[20] The k_{23} value for the $H(en)^+$ reaction with $Ni(en)_2(H_2O)_2{}^{2+}$ is larger by a factor of 180 than for aquonickel, or the lability per water molecule is greater by a factor of 540. This increase seems to offer the best comparison for the effect of the two en molecules on the rate of water replacement, because the k_{23} value for aquonickel is a direct experimental value.[8] The electron donor ability of the four coordinated nitrogens increases the ease of water replacement, but structural features of the coordinated ligands are also important[3] in changing the value of k^{-H_2O}.

It was not possible from our experimental data to separate the constants for k_{32} and the acid–base reactions between species **3** and **4**. However, an acid stability constant has been measured for a system which is an excellent model. The ligand tam, which is $(H_2NCH_2)_4C$, cannot coordinate more than three of its amine groups to one metal.[21,22] The nickel complex (NiL^{2+}) has been shown to have three amine nitrogens coordinated and the protonation constant for the fourth amine group has been measured,[22] $[NiLH^{3+}]/([NiL^{2+}][H^+]) = 10^{7.63}$. Models indicate that the proton in this complex is the same distance from the nickel ion as it would be in species **3**. Hence, the acid stability constant, $K_{H3} = [\mathbf{3}]/([\mathbf{4}][H^+])$, should be approximately $10^{7.6}\ M^{-1}$.

At equilibrium, the following relationship exists

$$\frac{[\mathbf{3}]}{[\mathbf{4}][H^+]}\frac{[B][H^+]}{[HB^+]} = \frac{k_{43}}{k_{34}} \tag{8}$$

and $K_{H3} = (k_{43}/k_{34})K_{HB}$. It has already been shown that

$$\frac{k_{43}}{k_{34}}K_{HB} = \frac{d}{k_{32}} \tag{9}$$

and therefore eq 10 permits k_{32} to be estimated. The

$$k_{32} = \frac{4.7 \times 10^{12}}{K_{H3}} \tag{10}$$

value of k_{32} is $\sim 1.2 \times 10^5$ sec^{-1} if K_{H3} is $10^{7.6}\ M^{-1}$. This k_{32} value appears low in comparison to $k_{41} = 1.2 \times 10^5$ sec^{-1}, on the basis that electrostatic repulsion should increase the dissociation rate. However, if the internal conjugate base mechanism is correct, the dissociation constant k_{41} as well as the formation constant k_{14} are enhanced by the influence of the unbound nitrogen on a coordinated water molecule. This effect appears to be about the same as the effect of electrostatic repulsion in the k_{32} path. This point was an early stumbling block in the present interpretation of the mechanism because, if k_{32} were forced to be much larger than k_{41}, then it could not be expected that $k_{34}[B] \gg k_{32}$, yet no evidence of a proton transfer limiting step could be found.

In the proposed mechanism the $Ni(en)_2(H_2O)_2{}^{2+}$ is not specified as either the *cis* or *trans* isomer. However, in solution this complex has been shown to exist in the *cis* form.[23]

In conclusion, by combining the forward and reverse rate constants from a relaxation expression with individual rate constants derived from a steady state approximation, and by use of a computer, it has been possible to fit a detailed mechanism with a minimum number of assumptions. The resulting rate constants are internally consistent and obey a complex dependence in hydrogen ion and reactant concentrations. The mechanism is one which was expected as the result of previous studies,[24] but the rate constants were not known and the competitive reactions show some interesting effects. (1) The lability per water molecule is increased by about a factor of 540 in $Ni(en)_2(H_2O)_2{}^{2+}$ compared to $Ni(H_2O)_6{}^{2+}$. (2) In the formation of $Ni(en)_3{}^{2+}$, the ring closure rate is on the same order of magnitude as the rate of loss of the monodentate intermediate. (3) As a consequence, the dissociation rate constants for $Ni(en)_3{}^{2+}$ from pH 6 to 9 are calculated to vary from 83 to 32 sec^{-1}, and are not greatly different from the value of 87 sec^{-1} found in 0.5 *M* acid. This havior is very different from that of $Ni(en)^{2+}$, where the dissociation rate constant is much larger in acid than in neutral solutions.[5] Exchange studies of en with $Ni(en)_3{}^{2+}$ at 0° give a smaller dissociation rate constant,[25]

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but this value is measured at pH 11 where hydroxide ion may interfere. (4) The stability constant for ring closure is 2.5×10^3, so that only 0.04% of $Ni(en)_3^{2+}$ can exist in solution with five nitrogens coordinated. (5) The results support the suggestion of the internal conjugate base mechanism.

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Reductions of *cis*- and *trans*-Diformatobis(ethylenediamine)cobalt(III) by Chromium(II). Doubly Bridging and Acid Catalysis[1a]

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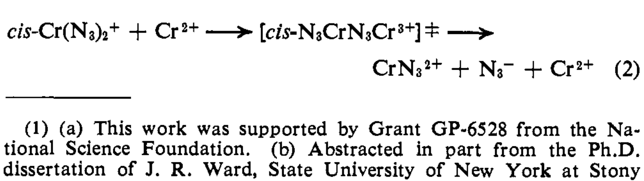
Abstract: The reductions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ by Cr^{2+} obey the rate laws $-d(\ln[cis\text{-}Co(en)_2(HCO_2)_2^+])/dt = k_0[Cr^{2+}]/(1 + Q[H^+])$ and $-d(\ln[trans\text{-}Co(en)_2(HCO_2)_2^+])/dt = (k_0 + k_1Q[H^+])[Cr^{2+}]$, respectively. At 25° and $[ClO_4^-] = 1.0\ M$, $k_0(cis) = 434 \pm 11\ M^{-1}\ sec^{-1}$, $k_0(trans) = 10.2 \pm 0.3\ M^{-1}\ sec^{-1}$, $Q(cis) = 0.44 \pm 0.07\ M^{-1}$, $k_1Q(trans) = 15.0 \pm 0.7\ M^{-2}\ sec^{-1}$. Protonation of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ is invoked to account for the observed kinetic patterns. Protonation of the *cis* complex decreases its reactivity toward chromium(II) reduction, whereas protonation of the *trans* complex increases its reactivity. Both the k_0 and k_1 paths for the *trans* complex proceed *via* inner sphere mechanisms with transfer of one formate ion from cobalt to chromium. The reaction of the *cis* complex proceeds *via* parallel singly and doubly bridged transition states with transfer of one and two formate ions, respectively, from cobalt to chromium. Various mechanistic details of these and related reactions are discussed.

The possibility that a doubly bridged transition state would provide a favorable pathway for electron transfer reactions was suggested long ago.[2] Early attempts to find evidence for this type of mechanism in the reactions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ and *cis*-CrF_2^+ with chromium(II) were unsuccessful.[3,4] In 1952, Snellgrove and King[5] provided the first conclusive evidence for a pathway involving a doubly bridged transition state: the dominant reaction that takes place when *cis*-$Cr(N_3)_2^+$ and Cr^{2+} are mixed is the exchange of chromium atoms between the two chromium species (eq 1). It was shown subsequently that, concomitant



$$cis\text{-}Cr(N_3)_2^+ + {}^*Cr^{2+} \longrightarrow \left[cis\text{-}Cr \begin{matrix} N_3 \\ \\ N_3 \end{matrix} Cr^{3+} \right]^{\ddagger} \dashrightarrow cis\text{-}{}^*Cr(N_3)_2^+ + Cr^{2+} \quad (1)$$

with the exchange reaction, but proceeding at a slower rate, a net reaction involving a singly bridged transition state (eq 2) was also important in this system.[6]

$$cis\text{-}Cr(N_3)_2^+ + Cr^{2+} \longrightarrow [cis\text{-}N_3CrN_3Cr^{3+}]^{\ddagger} \longrightarrow CrN_3^{2+} + N_3^- + Cr^{2+} \quad (2)$$

The factors governing the relative efficiencies of doubly and singly bridged paths are not apparent from the limited amount of data available, and a systematic study of a variety of systems featuring parallel singly and doubly bridged pathways seems to be called for. The report[7] that 69% of the chromium(III) produced in the chromium(II) reduction of *cis*-$Co(NH_3)_4(CH_3CO_2)_2^+$ has a unipositive charge (presumably *cis*-$Cr(OH_2)_4(CH_3CO_2)_2)^+$ encouraged the initiation of a study of the chromium(II) reductions of *cis*-dicarboxylatocobalt(III) complexes, and the results obtained with the *cis*-diformatobis(ethylenediamine)cobalt(III) complex are reported here.

In addition, because of the interest of the authors in the relative reactivities of *cis* and *trans* isomers in redox reactions,[8] the results obtained for the chromium(II) reduction of *trans*-diformatobis(ethylenediamine)cobalt(III) are also reported. The comparison of the kinetic behavior for the *cis* and *trans* isomers is of particular importance in the present system because formate ion is the conjugate base of a weak acid. For the analogous reactions of complexes containing basic ligands, namely *cis*- and *trans*-$CoA_4(CH_3CO_2)_2^+ + Cr^{2+}$ ($A = NH_3$ or $^1/_2(en)$)[7,9,10] and *cis*- and *trans*-$Co(NH_3)_4(N_3)_2^+ + Fe^{2+}$,[11] contrasting kinetic behaviors have been reported; regardless of geometry, the diacetato complexes exhibit acid-catalyzed paths, whereas for the diazido system only the *trans* isomer exhibits an acid-catalyzed path. Consequently, the hydrogen ion de-

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