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Kinetics of Ternary Complex Formation between Nickel Terpyridine and a Tridentate Quinolylazo Dye. Formation and Decay of Intermediates

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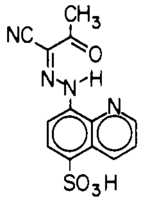
Complexation of α-(8-quinolylazo)-α-acetoacetonitrile dye in 1 mM nickel(II) 2,2′:6′,2″-terpyridine (Ni(terpy)$^{2+}$) at pH 6-8 gives complex spectral changes corresponding to the accumulation and decay of a short-lived ($\tau < 1$ s) and a long-lived ($\tau \simeq 30$ min) intermediate. Rate constants for formation and decay of the intermediates were evaluated as a function of pH and concentration by stopped-flow and conventional spectrophotometry and suitable choice of monitoring wavelengths. The rate of conversion of the long-lived intermediate to the final product ($(3.42 \pm 0.24) \times 10^{-3}$ s^{-1}) is independent of pH, buffer concentration, and Ni(terpy)$^{2+}$ concentration. The ligand can form either of two tridentate chelates with a 5- and 6-membered ring, and the slow relaxation is attributed to the isomerization of a rapidly formed, metastable tridentate chelate to a more stable form. The conversion of the short-lived to the long-lived species is attributed to a slow ring closure from a bidentate intermediate. The ring closure from the Ni(terpy)$^{2+}$ intermediate is 480 times faster than from the corresponding Ni^{2+} intermediate. The results show that when ring closure is rate limiting in chelation reactions, replacement of Ni^{2+} by Ni(terpy)$^{2+}$ can accelerate steps removed from the outer-sphere association.

Recent work from our laboratory suggests that the presence of a planar aromatic ligand in a nickel chelate can accelerate the addition of a second similar ligand even when the rate-determining step (rds) in the overall chelation is ring closure.[1,2] Such accelerations are known for chelations where the rds is the initial bond formation.[3,4] These accelerations have been attributed to enhanced outer-sphere association through stacking interactions.[3,4] To our knowledge, no studies have been made of the effect of a bound aromatic ligand on subsequent complexation when the rds in the complexation is ring closure. One difficulty in such studies is that intermediates rarely accumulate. The experimental rate constants are complex composites of rate constants for individual steps in the overall chelation, and there is no direct measure of which step may be affected.

Our study of the chelation of Ni^{2+} by the dye ligand **1** revealed that conditions could be found where an intermediate accumulates so that its rate of formation and decay could be measured.[5] The chelation rate of Ni^{2+} was one of the slowest reported in the literature, and ring closure was clearly indicated as the rds. A study of the kinetics of ternary complex formation between **1** and nickel(II) terpyridine (Ni(terpy)$^{2+}$) seemed to provide a unique opportunity to study the kinetic effect of an attached terpy ligand on a rate-determining ring closure. We have found conditions in the reaction of **1** with Ni(terpy)$^{2+}$ where as many as two intermediates accumulate, and their formation and decay rates have been measured.



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Experimental Section

The preparation and purification of **1**[6] and of Ni(terpy)(OAc)$_2$(H$_2$O) and its solutions[1] have been described. The buffers used were described earlier.[2] Kinetic measurements were made at 25 °C and an ionic strength of 0.04 M (0.01 M buffer ion and 0.03 M sodium perchlorate). Rapid rates were measured with a Durrum stopped-flow instrument interfaced with an OLIS Model 3820 data system. The slower rates were monitored at a single wavelength on a Cary 118C recording spectrophotometer with the chart drive as a time base. For the slowest relaxation in the reaction of **1** with Ni^{2+}, absorbance readings to the fourth decimal place were obtained from the digital panel meter of the spectrophotometer. Timing was with a stopwatch, and first-order rate constants were obtained by the Guggenheim method. For the slower runs, the two solutions were brought to temperature and mixed in the cell with a mechanical pipet. Runs were made under pseudo-first-order conditions with an excess of Ni(terpy)$^{2+}$. The concentration of dye was $(0.5-1.0) \times 10^{-5}$ M.

Absorption curves ($A(\lambda)$) were constructed at various times during the rapid reactions from stopped-flow traces of $A(t)$ recorded at 5- or 10-nm wavelength intervals. Absorbance values for a given time were recalled from the computer memory for each wavelength to give the $A(\lambda)$ for that time. The occurrence and location of isosbestic points were confirmed by measurements at 1-nm intervals in the indicated wavelength region. Absolute absorbance values were recorded with water as a reference.

Results

Reaction with Ni(terpy)$^{2+}$ gave two or three spectral relaxations, depending on the pH and Ni(terpy)$^{2+}$ concentration. In 1 mM Ni(terpy)$^{2+}$ and pH >6.8, two rapid relaxations with lifetimes of 1 s or less were monitored by stopped-flow spectrophotometry. A slower relaxation had a half-time of over 3 min and could be decoupled from the rapid changes and followed with a conventional spectrophotometer. The slow change was observed under nearly all the conditions studied. Except at low pH values (5.5), the amplitude of the slowest relaxation varied little with the pH or Ni(terpy)$_2{}^{+}$ concentration. In $(0.5-1.0) \times 10^{-4}$ M Ni(terpy)$^{2+}$, a single rapid relaxation preceded the slow change. The spectral changes establish the presence of a short-lived intermediate, the accumulation of which depends upon the reactant concentration, and a long-lived intermediate which is present under most conditions.

Figure 1 shows the absorption curves of the long-lived intermediate and of the final reaction product. The curve defined by the data points is that of a mixture of the long-lived intermediate and 1 mM Ni(terpy)$^{2+}$. This curve was constructed from stopped-flow measurements at pH 8.32 and 6.97 after the absorbance changes from the two rapid relaxations had ceased on the stopped-flow time scale (0.3 and 1.0 s, respectively). Subtraction of the contribution from the Ni(terpy)$^{2+}$ gives the curve of the long-lived intermediate (dashed curve). The curve of the final product was the same at all pH values. The curve of the long-lived intermediate was unchanged in the pH range 7.0-8.3. This shows that the intermediate and the product contain no ionizable proton that can dissociate in the pH range where the dye ligand is ionized.

The kinetic data for conversion of the long-lived intermediate to the final product are summarized in Table I. The data show that the rate is independent of pH, Ni(terpy)$^{2+}$ concentration, buffer concentration, and the wavelength of measurement. The table also lists first-order rate constants for the slowest relaxation in the reaction of **1** with Ni^{2+}. We had reported earlier[5] that there

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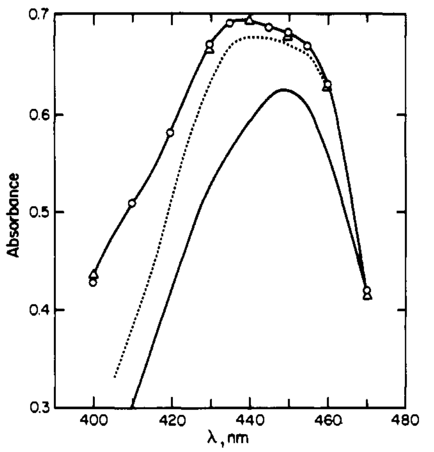

Figure 1. Absorption curves of the final ternary complex of **1** with 1 mM $Ni(terpy)^{2+}$ (—) and of the long-lived intermediate (--). Both curves are corrected for the contribution from $Ni(terpy)^{2+}$. The data points describe the uncorrected curve of the intermediate obtained from stopped-flow measurements at pH 8.32 (○) and 6.97 (△). Where a single data point is shown, identical values were obtained at both pH values.

Table I. Kinetic Data for Conversion of the Long-Lived Intermediates from $Ni(terpy)^{2+}$ and Ni^{2+} to the Final Product[a]

pH	$[B^-]$,[b] M	λ, nm	10^3k_{obsd}, s^{-1}
		$Ni(terpy)^{2+}$	
7.09[c]	0.01	440	3.43[d]
8.27[e]	0.01	440	3.27[d]
5.54[c]	0.01	440	3.36[f]
6.18[c]	0.01	440	3.34[f]
7.10[c]	0.01	440	3.39[f]
8.21[e]	0.01	440	3.39[f]
8.24[e]	0.01	390	3.66[f]
6.16[c]	0.0025	440	3.37[f]
6.17[c]	0.01	440	3.43[f]
6.16[c]	0.02	440	3.51[f]
k_{obsd}(Ni(terpy)) ± 95% confidence limits = (3.42 ± 0.24) × 10^{-3} s^{-1}			
		Ni^{2+}	
8.27[e]	0.01	430	1.17[g]
7.25[e]	0.01	430	1.11[h]
6.49[c]	0.01	430	1.14, 1.14[h]
$k_{obsd}(Ni^{2+})$ ± 95% confidence limits = (1.14 ± 0.06) × 10^{-3} s^{-1}			

[a] 25 °C; I = 0.04 M. [b] Concentration of the buffer base. [c] MES buffer. [d] $[Ni(terpy)^{2+}]_0$ = 0.12 mM. [e] HEPES buffer. [f] $[Ni(terpy)^{2+}]_0$ = 1 mM. [g] $[Ni^{2+}]_0$ = 0.119 mM. [h] $[Ni^{2+}]_0$ = 1.99 mM.

were no spectral changes with Ni^{2+} after those that were complete within several minutes. Careful reexamination has revealed a small change (3% maximum at 430 nm) that occurs over 45 min from which rate constants could be obtained. These concentration- and pH-independent constants are smaller than those obtained with $Ni(terpy)^{2+}$ by a third. The slow spectral changes with **1** and Ni^{2+} are not those corresponding to the interconversion of 1:1 and 1:2 metal–dye complexes.[6]

Low Concentrations of $Ni(terpy)^{2+}$. The single rapid relaxation leading to the long-lived intermediate in 5 × 10^{-5} M $Ni(terpy)^{2+}$ is first order through 90% reaction. The derived rate constant is the same at two wavelengths. Under these conditions, there is no accumulation of the short-lived intermediate and the rate constant for formation of the long-lived intermediate was measured by stopped-flow as a single isolated first-order reaction. The pseudo-first-order rate constants were measured in the pH range 4.4–8.4. At the higher pH values, formation of the long-lived intermediate is essentially complete and second-order formation rate constants (k_f) were obtained by dividing k_{obsd} (s^{-1}) by $[Ni(terpy)^{2+}]$. At pH <5.5, a back-reaction is detectable and k_{obsd} is given by eq 1 where k_d is the rate constant for dissociation of

$$k_{obsd} = k_f[Ni(terpy)^{2+}] + k_d \qquad (1)$$

the long-lived intermediate. Plots of k_{obsd} vs. $[Ni(terpy)^{2+}]$ at pH 4.38, 4.69, and 4.99 gave k_d = 7 × 10^{-3} s^{-1} from the intercepts. An approximate stability constant for the long-lived intermediate of 7 × 10^6 M^{-1} is obtained from this estimate and the value of k_f for the ionized ligand (4.6 × 10^4 M^{-1} s^{-1}, see below).

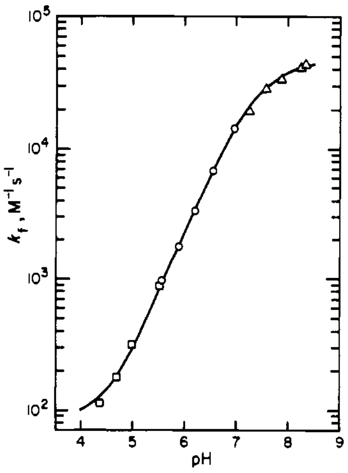

Figure 2. Semilog plot of k_f as a function of pH for formation of the long-lived intermediate under conditions where the short-lived intermediate does not accumulate. $[Dye]_0$ = 5 × 10^{-6} M; $[Ni(terpy)^{2+}]_0$ = 5 × 10^{-5} M; 25 °C; I = 0.04 M. The buffers were acetate (□), MES (○), and HEPES (△). The continuous curve was calculated with eq 5, the experimental pK_a (7.32), and the values k_{LH} = 80 M^{-1} s^{-1} and k_{L^-} = 4.6 × 10^4 M^{-1} s^{-1}.

The effect of pH on k_f for formation of the long-lived intermediate, under conditions where no other intermediates are detected, is shown in Figure 2. The continuous curve was calculated by assuming that the quinolinium species (LH_2^+) is kinetically insignificant and that the rate law is given by eq 2 and 5. The

$$-d[L]_T/dt = v_T = (k_{LH}[LH] + k_{L^-}[L^-])[Ni(terpy)^{2+}] \qquad (2)$$

$$[L]_T = [LH] + [L^-] = [LH](1 + K_{a2}/[H^+]) \qquad (3)$$

$$\frac{v_T}{[Ni(terpy)^{2+}][L]_T} = k_f = \frac{[LH]}{[L]_T}\left(k_{LH} + \frac{k_{L^-}K_{a2}}{[H]^+}\right) \qquad (4)$$

$$k_f = (k_{LH} + k_{L^-}K_{a2}/[H^+])/(1 + K_{a2}/[H^+]) \qquad (5)$$

value of pK_{a2} is 7.32.[5] The incomplete complexation and the insolubility of the dye in acidic solution precluded measurements at pH <4.4 where it was expected that k_f would reach a constant value corresponding to k_{LH}. Instead, k_{LH} was treated as an adjustable parameter. The values of k_{LH} and k_{L^-} for formation of the long-lived intermediate that were used for the fit in Figure 2 were 80 M^{-1} s^{-1} and 4.6 × 10^4 M^{-1} s^{-1}, respectively.

High Concentrations of $Ni(terpy)^{2+}$. The spectral changes that accompany the *two* rapid relaxations in 1 mM $Ni(terpy)^{2+}$ leading to the long-lived intermediate are shown in Figure 3. The most notable feature of the curves is the appearance of an isosbestic point near 405 nm after about 50 ms. Because the curves vary with pH in the pH range where the two rapid relaxations are observed, the position of the isosbestic point shifts from 404 nm at pH 8.3 to 409 nm at pH 6.9. The amplitude of the absorbance change at the isosbestic point decreases with decreasing pH. The overall spectral changes correspond to the formation and decay of a short-lived intermediate to give the long-lived intermediate. The isosbestic point that appears after 50 ms corresponds to the wavelength at which the short- and long-lived intermediates have equal absorptivities. Kinetic measurements made at the isosbestic point isolate the formation of the short-lived intermediate from its subsequent decay.

The solubility limit of $Ni(terpy)^{2+}$,[3] the low amplitude of the absorbance change at the isosbestic point, and the need to redetermine its location at each pH value made reliable measurement of the formation rate constant of the first intermediate over a range of conditions difficult. Replicate measurements of k_{obsd} (s^{-1}) at pH 8.21 and three concentrations of $Ni(terpy)^{2+}$ in the range

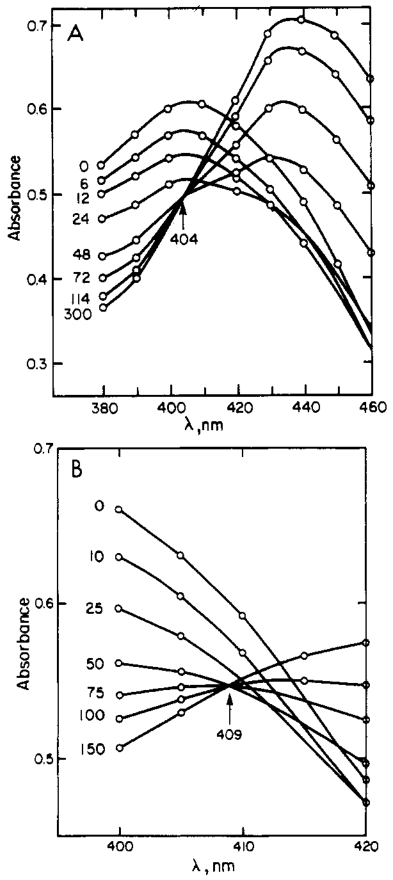

Figure 3. Constructed absorption curves at different reaction times during the rapid changes in 1 mM Ni(terpy)$^{2+}$: (A) pH 8.30; (B) pH 6.90. Data points are omitted for clarity near where the curves cross. The indicated reaction times in milliseconds are uncorrected for the instrument dead time. The curves are uncorrected for the contribution from the Ni(terpy)$^{2+}$.

Table II. Kinetic Data for the Formation of the Short-Lived Intermediate from Ni(terpy)$^{2+}$ [a]

pH	λ,[b] nm	k_{obsd}, s^{-1}	pH	λ,[b] nm	k_{obsd}, s^{-1}
8.21	404	47 (3)[c]	7.23	408	49
7.84	405	51	6.94	409	49

[a] 25 °C; I = 0.04 M; [Ni(terpy)$^{2+}$] = 1 mM. k_{obsd} ± 95% confidence limits = 48 ± 6 s^{-1}. [b] Location of the isosbestic point. [c] Mean and standard deviation from seven determinations given in parentheses.

0.5–1.0 mM showed considerable scatter, but indicated a nonlinear dependence on [Ni(terpy)$^{2+}$] that seemed to approach a saturation value. Values of k_{obsd} measured at several pH values in 1 mM Ni(terpy)$^{2+}$ are given in Table II. The data show that the rate of formation of the short-lived intermediate is independent of pH in the range 6.9–8.2.

Figure 3 shows that at wavelengths near 460 nm, small absorbance changes occur during the first 50 ms when the rapid change occurs at the shorter wavelengths, and a larger change occurs after the most rapid relaxation is complete. This gives an S-shaped curve of $A(t)$ at the longer wavelengths (Figure 4). The lengths of the induction periods (τ_i, time to the inflection points) correspond to about 90% completion of the formation of the first intermediate. The absorbance change beyond the inflection point in the 460-nm curves is exponential (Figure 4), and the derived first-order rate constant measures the rate of conversion of the short-lived to the long-lived intermediate. Values of τ_i were evaluated by subtracting the calculated exponential curve from the experimental curve and noting the times when the residuals become small and random. The τ_i values did not change with pH. This provides additional confirmation that the lifetimes for forming the short-lived intermediate from the reactants are pH independent. The decay rates of the short-lived intermediate decreased with decreasing pH, however, so that the pH range over which the two rates could be decoupled was limited to 6.8–8.4. Figure 5 shows the effect of pH in this range on the first-order rate constant for converting the first intermediate to the long-lived one. The continuous curve was calculated with a "kinetic" pK_a of 7.0 and a value of k_{X^-} of 21 s^{-1}, where X$^-$ is the ionized short-lived intermediate. The results show that the first intermediate retains an ionizable ligand group with a pK_a that is 0.3 lower than that of the uncomplexed dye ligand.

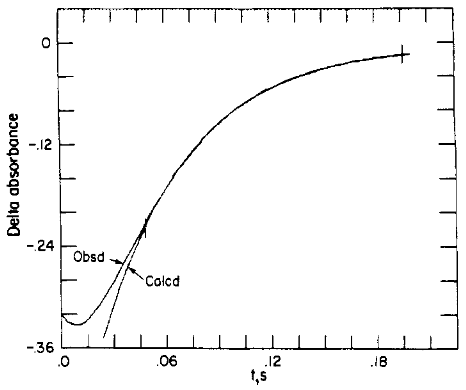

Figure 4. Absorbance change at 460 nm for formation of the long-lived intermediate from the first intermediate in 1 mM Ni(terpy)$^{2+}$, pH 8.21. The superimposed calculated curve is a pure exponential function.

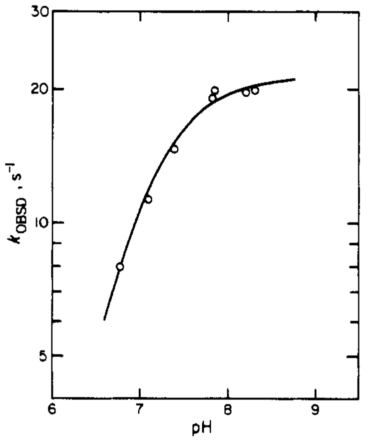

Figure 5. Effect of pH on the first-order rate constant for conversion of the first intermediate to the long-lived intermediate. The continuous curve was calculated with pK_a = 7.0 and k_{X^-} = 21 s^{-1}.

Discussion

Slowest Relaxations. The rate constants for formation of the final product from the long-lived intermediate seem too small to involve a ring closure. A slow ring closure requiring a slow proton transfer[2] is ruled out by the magnitude of the pK_a values, the absence of general base catalysis, and the fact that the slow relaxation is observed at all degrees of ionization of the ligand. We propose that the slow relaxation involves an isomerization of a rapidly formed metastable tridentate chelate to a more stable tridentate chelate. The dye is capable of forming either of two chelates, each with a 5- and a 6-membered ring, depending upon whether the N$_\alpha$ or N$_\beta$ atom of the azo bridge is a ligand atom (structures A and B in Scheme I). At this time we do not know which is the more stable.

The fact that the rate of the slow relaxation is independent of pH, concentration of nickel species, and buffer concentration is consistent with an isomerization requiring the opening of a chelate ring. The value of the estimated stability constant of the long-lived intermediate (7 × 10^6 M^{-1}) is large for a bidentate 8-quinolylazo chelate,[7] but is reasonable for an unstable tridentate chelate. The

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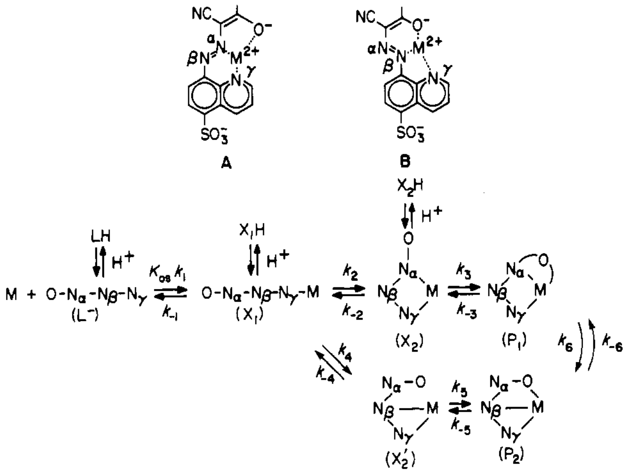
(7) The value of K_1 for complexation of 8-aminoquinoline with Ni(II) is 8 × 10^4.[8]

Scheme I



similarity of the absorption curves of the long-lived intermediate and the final product suggests that they have similar structures. If the slow relaxation is isomerization, the long-lived intermediate is actually a product that is formed by kinetic control at a branching point in the mechanism. A kinetic scheme that explains the results is given in Scheme I. Intermediates X_1 (unidentate) and X_2 and X_2' (bidentate) and two products, P_1 and P_2, are required, but the assignment of structures to them is purely arbitrary. Since an ionizable ligand proton is still present in an intermediate, it is reasonable to assume that the initial bond formation to form X_1 involves the quinoline nitrogen (N_γ).

If the metastable product is arbitrarily identified as P_1, it is formed as an initial product because $k_2 \geq k_4$. Without an independent measure of the absorptivities of P_1 and P_2, the absorbance measurements do not tell us whether P_1 is formed as the predominant initial product ($k_2 > k_4$) or whether P_1 and P_2 are formed in similar amounts at a constant ratio ($k_2 \simeq k_4$). We do know that the ratio of products is independent of metal ion concentration and of pH in the range 6–8. To simplify the discussion we will assume that $k_2 > k_4$. Conversion of P_1 to P_2 by a shift of a metal–ligand bond from N_α to N_β requires a change in conformation of the dye (e.g. structure A to structure B). Direct conversion within a partially intact chelate structure (k_6) requires rehybridization and inversion of the azo bridge with an attendant distortion of metal–ligand bond angles and bond lengths. Conversion by reversal of the k_3 and k_2 ring closures to re-form X_1 requires the cooperative breaking of two metal–ligand bonds and coupled bond rotations in the dye to change the conformation. Isomerization by either path is expected to be slow.

Rapid Relaxations. The fastest relaxation is assigned to the formation rate of a true intermediate that lies along the pathway to product. It accumulates at higher concentrations of Ni(terpy)$^{2+}$, but at the lowest concentrations it is present in low steady-state levels. Under the conditions where no short-lived intermediates accumulate, the steady-state treatment of X_1 and X_2 gives eq 6

$$k_{L^-} = \frac{K_{os}k_1k_2k_3}{k_{-1}k_{-2} + k_{-1}k_3 + k_2k_3} = 4.6 \times 10^4 \ M^{-1} \ s^{-1} \qquad (6)$$

for k_{L^-}, where K_{os} is the outer-sphere association constant. The experimental value of k_{L^-} under "steady-state" conditions is close enough to the inner-sphere water exchange rate constant in Ni(terpy)$^{2+}$ ($k_{ex} = 5.2 \times 10^4$ s^{-1})[9] that, if taken alone, one might conclude that the ring closures are rapid and the initial ligation is largely rate limiting ($k_2k_3 > k_{-1}k_{-2} + k_{-1}k_3$). The experimental value of the rate constant for decay of the ionized intermediate (21 s^{-1}) shows that this conclusion cannot be correct. The similarity in values of k_{ex} and k_{L^-} is undoubtedly adventitious, and probably results from the fact that a slow ring closure is balanced by an abnormally high value of K_{os} for the ionized ligand.[1]

The rate constant for formation of the short-lived intermediate in 1 mM Ni(terpy)$^{2+}$ causes the greatest difficulty of interpretation. The fact that it is independent of pH (Table II) in the pH range where the uncomplexed ligand is partially ionized rules out X_1 as the short-lived intermediate; the formation rate of X_1 should vary with the degree of ionization of the ligand. In the pH range 6.9–8.2, this rate should vary by a factor of 2.8. Assigning the short-lived intermediate to X_2 can avoid some of the difficulties, but imposes some rigid requirements. The formation of X_2 from X_1 could be independent of pH in the stated range if the unbonded ligand group is more acidic in X_1 than in LH. We were forced to such a conclusion in the complexation of Ni(terpy)$^{2+}$ with a β-PAN dye.[1] The rate of conversion of X_1 to X_2 will only be pH independent and first order if X_1 is formed rapidly during the instrument dead time in a preequilibrium that lies substantially in favor of X_1. This requirement is consistent with a rate saturation with respect to the Ni(terpy)$^{2+}$ concentration. It also requires that, in 1 mM Ni(terpy)$^{2+}$, $K_{os}k_1 \geq 5 \times 10^5$ M^{-1} s^{-1}. This limit is within the range of experimental values found for the complexation of Ni(terpy)$^{2+}$ with ionized forms of other dye ligands,[1] and it suggests that there is enhanced outer-sphere association between the Ni(terpy)$^{2+}$ complex and the entering ligand.

If the interpretations offered above are correct, the decay rate of the short-lived intermediate to P_1 must involve the final ring closure (k_3). The pH dependence of this rate constant gives a "kinetic" pK_a of 7.0 and shows that at the final ring closure stage there is still an ionizable unbonded ligand atom. This fact is the basis for our earlier assumption that the initial bond formation involves the quinoline nitrogen. The apparent pK_a of X_2H makes the proton in X_2H less acidic than in X_1H, but more acidic than in LH.

Intermediates similar to those found here were found to accumulate in the chelation of Ni^{2+} with **1**, and similar measurements and assignment of rate constants were made.[5] We are thus able to make a direct comparison of k_3(Ni(terpy)$^{2+}$) with k_3(Ni^{2+})[10] for the L$^-$ species. The value of k_3(Ni(terpy)$^{2+}$) (21 s^{-1}) is 480 times larger than the value of k_3(Ni^{2+}) (0.044 ± 0.008 s^{-1}). This shows that enhanced outer-sphere association is not the only effect that can result in overall rate enhancement from replacement of Ni^{2+} with Ni(terpy)$^{2+}$, and that an unusually slow ring closure removed from outer-sphere association can also be accelerated.

We can also compare second-order formation rate constants for the different ionic ligand species with Ni^{2+} and Ni(terpy)$^{2+}$ under conditions where X_1 and X_2 are present in low steady-state concentrations. Under these conditions, the experimental rate constants are complex composites of rate constants for individual steps. The value of k_{LH}(Ni(terpy)$^{2+}$) (80 M^{-1} s^{-1}) is 33 times larger than k_{LH}(Ni^{2+}) (2.4 M^{-1} s^{-1}). The value of k_{L^-}(Ni(terpy)$^{2+}$) (4.6×10^4 M^{-1} s^{-1}) is 38 times larger than k_{L^-}(Ni^{2+}) (1.2×10^3 M^{-1} s^{-1}).

Several facts deserve comment. The composite constants show a smaller apparent rate enhancement of Ni(terpy)$^{2+}$ over Ni^{2+} than we found for the individual rate constants for the ring closure. Apparently, other individual rate constants in the composite are also altered. Also, when ring closure is rate limiting, there appears to be less selectivity in overall formation rate constants between ligand species in the degree of rate enhancement than when the initial ligation step is rate limiting.[1]

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Registry No. **1**, 94519-60-5; Ni(terpy)$^{2+}$, 24825-68-1.

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(10) The rate constants with Ni^{2+} were measured at an ionic strength of 0.1 M.