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# Equilibria and Kinetics of Chelation of Nickel(II) by a Solubilized 1-(2-Pyridylazo)-2-naphthol (β-PAN) Dye

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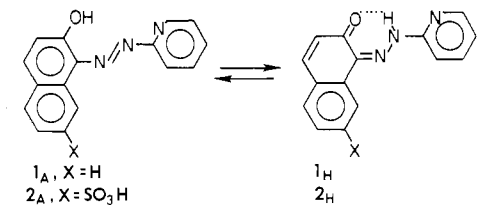
The chelation kinetics and equilibria with a sulfonated β-PAN dye were studied in aqueous buffers at pH 5.7–8.2 and an ionic strength of 0.04 M. In a moderate excess of nickel, the initial rapid chelation gives a kinetically controlled mixture of the 1:1 (MD) and 1:2 ($MD_2$) complexes in which the concentration of $MD_2$ exceeds its equilibrium level. Equilibration of the initial mixture in a pH 7.0 MES buffer had a half-time of almost 5 h. Formation of the experimentally determined excess of $MD_2$ in competitive consecutive reactions requires that $k_{MD_2} \simeq 300k_{MD}$. The large value of $k_{MD_2}$ is ascribed to an enhanced value of $K_{os}$ whereby prior complexation of one dye facilitates addition of a second through a stacking interaction. The rate of formation of MD has a pH-independent path and is subject to specific- and general-base catalysis. The pH-independent path is assigned to the reaction of $Ni^{2+}$ with the predominant quinone hydrazone tautomer, which is abnormally slow ($k_{LH} = 2.7 \times 10^2\ M^{-1}\ s^{-1}$) because of a rate-limiting ring closure requiring a slow transfer of a strongly hydrogen-bonded proton to solvent or buffer. The specific-base catalysis is associated with ionization of the dye ligand. The value of $k_{L^-}$ ($1.1 \times 10^6\ M^{-1}\ s^{-1}$) is larger than can be accounted for by a conventional dissociative-interchange mechanism and suggests the operation of an internal conjugate-base mechanism.

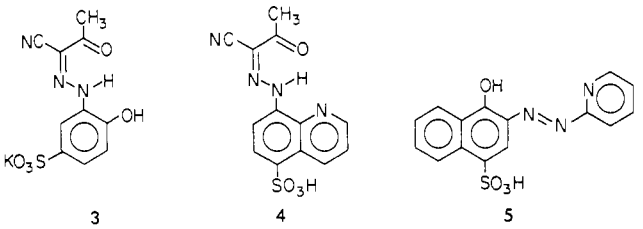
(Pyridylazo)naphthols and -phenols form an interesting class of chelating agents for first-row transition metals, and a number of studies of the kinetics of chelation with several such ligands have appeared. Some anomalies in the kinetics and stoichiometries of the reactions have been pointed out.[1] In our study of two 2-(2-pyridylazo)-1-naphthol (α-PAN) dyes we showed that kinetic rather than thermodynamic control of the initial products gave a mixture that contained more of the 1:2 complex than was present at equilibrium.[1] Equilibration from the initial mixture was very slow. The excess 1:2 complex ($MD_2$) was formed via the 1:1 complex (MD) by consecutive competitive reactions (eq 1 and 2) whereby $k_{MD_2} > k_{MD}$.

$$M + D \xrightarrow{k_{MD}} MD \quad (1)$$

$$MD + D \xrightarrow{k_{MD_2}} MD_2 \quad (2)$$

We were interested in the study of a 1-(2-pyridylazo)-2-naphthol (β-PAN) dye to extend the scope of the study of PAN dyes and because of our interest in the effect of tautomerism in the dye ligand on the chelation kinetics.[2] An earlier kinetic study of β-PAN (**1**) in dilute aqueous solution showed that the undissociated dye was a very unreactive ligand toward Ni(II), Cu(II), and Zn(II) compared to other pyridylazo ligands.[3] Since the predominant form of the dye is the hydrogen-bonded quinone hydrazone ($\mathbf{1}_H$),[4–6] it was proposed that the stable hydrogen bond holds the ligand in a conformation that is unfavorable for final ring closure so that ring closure becomes rate-limiting.[3] We have studied the chelation of Ni(II) by two cyano keto azo dyes (**3** and **4**) that also exist predominantly as hydrazones in the neutral forms, and we were able to measure directly the rates of ring closure from accumulated intermediates.[2] We found that the rates of ring closure of the undissociated dyes[7] were much slower than expected and suggested two reasons the hydrazones might be unreactive, including that proposed by Hubbard and Pacheco.[3] We also found that the dissociated ligands, which exist only as the azoenolates, had slow rates of ring closure, and we concluded that steric factors and tautomerism both contributed to slow ring closure. The earlier study of β-PAN[3] was made at a single pH (5.8), so it was not possible to assess the importance of steric factors that might remain when the possibility of tautomerism is removed by ionization of the ligand.




One difficulty in interpreting the effect of tautomerism in **3** and **4** is the fact that two possible 6–5 chelates can form, so it is uncertain whether the bridge nitrogen bearing the proton is a ligand atom. This ambiguity is removed in the β-PAN dyes, since these ligands can form only 5–5 chelates, which cannot directly involve the hydrazone nitrogen bearing the proton as a ligand atom. The hydrogen-bonded hydrazone proton can be involved only indirectly in controlling the equilibrium population of conformations in the ligand during the steps of ring closure.

I prepared a solubilized form of β-PAN (**2**) to remove the possibility that the low reactivity of **1** might have resulted from dye aggregates that can exist in dilute solutions.[8] I confirm the low reactivity of the undissociated dye toward Ni(II) and also find an exceptionally high reactivity for the ionized ligand. I also find that the initial product mixture is formed by kinetic control and that the rate of formation of the 1:2 complex via the 1:1 complex is much higher than can be accounted for by conventional considerations.

## Experimental Section

**Materials.** Sodium 2-pyridyldiazotate was prepared by dissolving 2 g of cleaned sodium metal in 30 mL of distilled ethanol and adding 17.4 g of isopentyl nitrite (Kodak Laboratory Chemicals) in portions followed by 14.0 g of 2-aminopyridine (Kodak). The mixture was refluxed for 4.5 h, cooled to room temperature, and refrigerated overnight. The solid was collected by suction filtration, washed twice with ether, and dried in a vacuum desiccator. The yield was 8.38 g.

(1) Reeves, R. L.; Calabrese, G. S.; Harkaway, S. A. *Inorg. Chem.* **1983**, *22*, 3076.
(2) Meyers, G. A.; Michaels, F. M.; Reeves, R. L.; Trotter, P. J. *Inorg. Chem.* **1985**, *24*, 731.
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(7) Throughout this paper, the ionic forms of the dye ligand refer to dissociation of the weak-acid ligand groups and not to the strong-acid solubilizing group.
(8) Reeves, R. L.; Maggio, M. S.; Harkaway, S. A. *J. Phys. Chem.* **1979**, *83*, 2359 and references cited therein.

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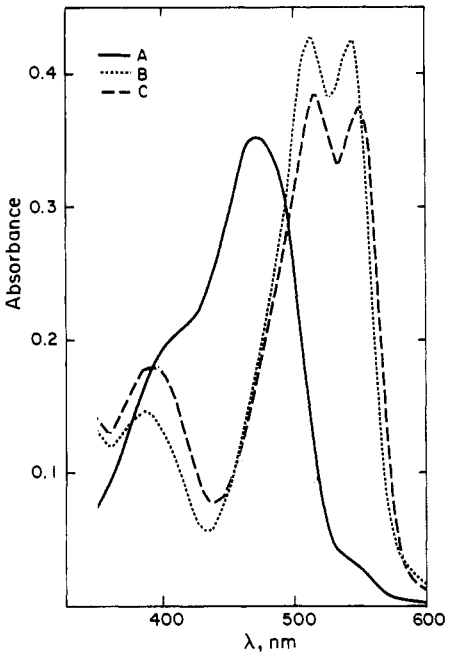


**Figure 1.** Absorption curves of dye **2** (A) and its 1:1 (B) and 1:2 complex (C) with nickel(II) ($[D]_T = 2.006 \times 10^{-5}$ M; pH 7.13 MES buffer).

A mixture of 1.34 g (0.0006 mol) of 2-naphthol-7-sulfonic acid (Pfalz and Bauer) and 1.22 g of triethylamine (0.012 mol) did not dissolve completely in 150 mL of boiling ethanol. Sodium 2-pyridyldiazotate (1.1 g, 0.0076 mol) was added to the heterogeneous mixture, and refluxing was continued for 2 h. A chromatogram showed unreacted naphthol, but with longer reaction times the dye decomposed. The crude mixture was evaporated to dryness, and the residue was chromatographed in several 200-mg batches on 8.5 × 20-cm columns of Sephadex G-25. Elution with 0.01 M sodium hydroxide separated several colored impurity bands and the luminescent naphthol. The naphthol moved just ahead of the desired dye, and they were separated only by slow elution (1 mL/min). Acidification and concentration of the combined eluates gave 430 mg of a fine precipitate of pure dye, which was collected by pressure filration on a 1 μm pore Nuclepore filter. Elemental analyses (C, H, N) were consistent with the sulfonic acid monohydrate. A second cycle of chromatographic purification separated a colored trace impurity but did not change any of the kinetic results.

The purification of the tris(hydroxymethyl)aminomethane (Tris) and 2-(4-morpholino)ethanesulfonic acid (MES) buffers has been described.[1] Fluka purissimum grade *N*-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES) was used as received. Stock solutions of nickel perchlorate were prepared as before.[1] G. Frederick Smith reagent grade sodium perchlorate, as received, was used to adjust the ionic strength of solutions.

All glassware was first treated with an EDTA solution and then cleaned with successive treatments of detergent, ammonia, and distilled water.

**Measurements.** Rapid kinetic measurements were made on a Durrum stopped-flow spectrophotometer interfaced with an On Line Instrument System (OLIS) Model 3820 data system. Several records were averaged in the determination of each rate constant. The averaged experimental trace was fitted to a first-order function in exponential form, and any deviation from first-order kinetics was seen as a pattern in the residuals. The latter were obtained by a point-by-point subtraction of the theoretical curve from the experimental trace.

Spectra of solutions of initial product mixtures and of the slowly equilibrating solutions were measured on a Cary 118C recording spectrophotometer. Solutions were equilibrated for 40 h in the dark at room temperature before curves of equilibrium mixtures were measured. For the determination of the initial product compositions, equal volumes of dye and nickel solutions were mixed through a mixing "tee" from simultaneously driven syringes.

## Results

**Equilibria and Spectra.** The $pK_{a2}$ value for the second dissociation[7] of **2** was 10.86 at an ionic strength of 0.04 M, determined by spectrophotometric titration. This corresponds to the dissociation of the hydrogen-bonded hydrazone hydrogen and is considerably higher than the corresponding $pK_{a2}$ value of 8.14 for the α-PAN dye **5**. Test tube experiments showed that the dissociation of the pyridinium proton was complete at pH 4. The $pK_{a1}$ value of **1** in aqueous dioxane is <2.0.[9]

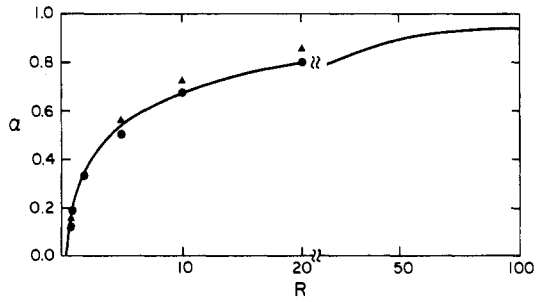


**Figure 2.** Plot of the fraction of the dye present as MD at equilibrium (α) as a function of the stoichiometric Ni:dye ratio (*R*). Measurements were made at 400 (●) and 540 nm (▲). The line was calculated from an average value of $K_{eq}$.

Figure 1 shows the absorption curves of the undissociated form of dye **2** and its 1:1 (MD) and 1:2 ($MD_2$) complexes with nickel(II). Isosbestic points occur at the following wavelengths for the indicated pairs of curves: dye and MD, 377 and 492 nm; dye and $MD_2$, 390 and 494 nm; MD and $MD_2$, 460, 548, and 585 nm. Successive additions of nickel(II) to a constant concentration of **2** in pH 7.13 MES buffer and equilibration for 40 h gave two distinct spectral changes. At stoichiometric Ni:dye ratios (*R*) up to 0.5, a family of curves with sharp isosbestic points at 390 and 494 nm was obtained. This set corresponds to a binary mixture of dye and the 1:2 complex. At $0.5 < R < 50$ a second family of curves was obtained, with the three isosbestic points and spectra corresponding to a two-component mixture of MD and $MD_2$. There was no evidence of precipitation during the equilibration. Similar results were obtained in a pH 8.2 Tris buffer. The spectral titration of **2** is thus similar to that of the α-PAN dye **5**.[1] The equilibrium corresponding to the second spectral change in the noncomplexing MES buffer for $0.5 < R < 50$ is defined by

$$MD_2 + M \rightleftarrows 2MD \qquad K_{eq} = \frac{[MD]^2}{[MD_2][M]} = \frac{K_1}{K_2} \tag{3}$$

where $K_1$ and $K_2$ are the successive formation constants for the 1:1 and 1:2 complexes defined in the customary way in terms of dissociated dye ligands.[1] Let α equal the fraction of the total dye present as MD:

$$\alpha = \frac{[MD]}{[D]_T} = \frac{A - A_{MD_2}}{A_{MD} - A_{MD_2}} \tag{4}$$

where $A_{MD}$, $A_{MD_2}$, and $A$ are the absorbances at an appropriate wavelength of pure MD, pure $MD_2$, and a mixture, respectively. It was shown earlier[1] that

$$K_{eq} = \frac{\alpha^2}{((1-\alpha)/2)(R - 0.5 - \alpha/2)} \tag{5}$$

where $R = [M]_T/[D]_T$. Calculation of $K_{eq}$ via eq 5 at 540 and 400 nm at six α values gave $K_1/K_2 = 0.30$ with a standard deviation of 0.10. This can be compared with the ratios for **1** in 50% aqueous dioxane of 1.2 by potentiometric titration[9] and 0.6 by a spectrophotometric method.[10]

Figure 2 shows a plot of α as a function of the molar ratio *R* for $[D]_T = 2.0 \times 10^{-5}$ M. The continuous line was calculated with the mean value of $K_{eq}$ after eq 5 was solved for α. Significant features of the plot to be noted for later reference are that, at equilibrium, 67% of the dye is present as MD in a 10-fold excess of nickel(II) and 94% is present as MD in a 100-fold excess.

A similar determination was carried out in a pH 8.18 Tris buffer. This amine forms at least two complexes with Ni(II)[11]

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**Table I.** Fraction of the Dye Present as the 1:1 Complex after Initial Chelation and at Equilibrium

| $[dye]_0$, mM | $[Ni]_0$, mM | α initial | α equilibrium |
|---|---|---|---|
| | A. pH 7.1 MES (M = $Ni^{2+}$) | | |
| 0.02 | 0.2 | 0.02, 0.06 | 0.67 |
| 0.02 | 0.4 | 0.10 | 0.78 |
| 0.02 | 1.0 | 0.10 | 0.89 |
| 0.02 | 2.0 | 0.32 | 0.94 |
| 0.01 | 1.0 | 0.24, 0.24 | |
| | B. pH 5.8 MES (M = $Ni^{2+}$) | | |
| 0.02 | 0.2 | 0.11 | 0.67 |
| 0.02 | 0.4 | 0.14 | 0.78 |
| 0.02 | 1.0 | 0.26 | 0.89 |
| 0.02 | 2.0 | 0.49 | 0.94 |
| 0.01 | 1.0 | 0.37 | |
| | C. pH 8.2 Tris (M = $\sum MB_i$) | | |
| 0.02 | 0.2 | 0.57 | 0.78 |
| 0.02 | 0.4 | 0.64 | 0.87 |
| 0.02 | 1.0 | 0.81 | |
| 0.02 | 2.0 | 0.83 | 0.97 |
| 0.01 | 1.0 | 0.89 | |

($MB_i$) and probably forms ternary complexes with MD ($MDB_j$), so that the measured equilibrium constant $K_{eq}'$ is a more complex composite than $K_{eq}$ and is defined by eq 6. The mean experi-

$$K_{eq}' = \frac{(\sum[MDB_j])^2}{[MD_2](\sum[MB_i])} \quad (6)$$

mental value for determinations at two wavelengths and seven α values was 0.63 with a standard deviation of 0.23. At equilibrium in the Tris buffer, 78% and 97% of the dye should be present in complexes having 1:1 dye:nickel stoichiometry in 10- and 100-fold excesses of Ni(II), respectively.

The absorption curves of the two complexes in Figure 1 show that the absorptivity per mole of dye in MD is higher than that of $MD_2$ at 540 nm and lower at 400 nm. The absorbance ratio at these two wavelengths provides a more sensitive measure of the composition of a mixture of the two complexes than does the absolute absorbance at either single wavelength. Calibration curves of measured $A_{540}$:$A_{400}$ ratios as a function of equilibrium α values were smooth with little scatter and provided a means for determining the initial product composition of the rapid chelation.

**Initial Products of Chelation.** Absorption curves of the initial products of the rapid chelation at various stoichiometric $R$ ratios showed the presence of mixtures of MD and $MD_2$ containing more of the 1:2 complex than expected for thermodynamic control of the product mixture. Initial compositions were determined from the absorbance ratios at 540 and 400 nm and are compared with equilibrium compositions in Table I. Slow equilibration of the initial mixtures gave time-dependent families of absorption curves with isosbestic points identical with those of mixtures of MD and $MD_2$. In a pH 7.0 MES buffer with $[D]_0$ = 0.02 mM and $[Ni]_0$ = 0.2 mM, the first-order rate constant for reequilibration of the initial mixture of complexes was $4 \times 10^{-5}$ $s^{-1}$.

Table I shows that, in the noncomplexing MES buffer,[1,12] the initial product in a 10-fold excess of Ni(II) is almost exclusively the 1:2 complex. If $MD_2$ is formed via MD in a competitive consecutive reaction (eq 1 and 2) in excess metal ion, then $k_{MD_2} >> k_{MD}$. At molar ratios where $MD_2$ is the sole product, the stoichiometry involves two dyes per metal ion and the rate-determining step is the formation of MD; i.e., MD is scavenged by D as soon as it forms. Under these conditions, $k_{obsd} = 2k_{MD}'$, where $k_{MD}' = k_{MD}[M]$.

**Kinetics of Chelation.** Stopped-flow measurements were monitored at wavelengths corresponding to one of the isosbestic points in the absorption curves of MD and $MD_2$ (460 and 548 nm with zwitterionic buffers and 480 and 548 nm with Tris buffers). The runs followed first-order kinetics through at least 3 half-lives, and the pseudo-first-order rate constants were the same at the two wavelengths. Plots of $k_{obsd}$ vs. $[Ni]_T$ were linear up to 1 mM and could be extrapolated to the origin, showing the absence of a measurable back-reaction. At higher nickel concentrations, the plot developed curvature.

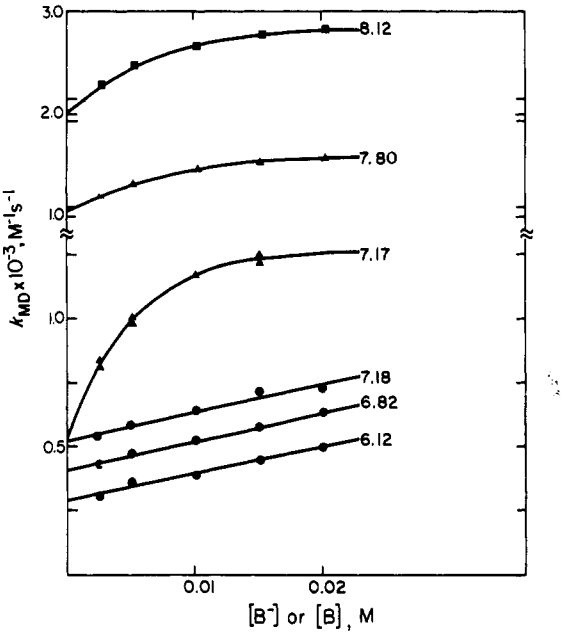


**Figure 3.** Plot of the formation rate constant for MD as a function of the concentration of buffer base in MES (●), HEPES (▲), and Tris (■) buffers. The pH value are indicated.

Most of the runs in this study were made with the initial conditions of $[dye]_0$ = 0.02 mM and $[Ni]_0$ = 0.2 mM so that $MD_2$ was the initial product and $k_{obsd} = 2k_{MD}'$. The ionic strength was constant at 0.04 M. There is no detectable accumulation of an intermediate under these conditions.

**Effect of pH and Buffers.** Measurements were made in MES, HEPES, and Tris buffers over the pH range 5.7–8.2. In this range the pyridinium ion of the ligand is completely dissociated and the hydrazone proton is negligibly dissociated. In this pH range the chelation has a pH-independent rate and is subject to specific- and general-base catalysis so that

$$k_{MD}\ (M^{-1}\ s^{-1}) = k_0 + k_{OH}[OH^-] + k_B[B] \quad (7)$$

Figure 3 shows some typical plots of the second-order rate constant $k_{MD}$ as a function of the concentration of the buffer base. The linear plots of constant slope for the MES buffers at several pH values are evidence for general-base catalysis by this buffer. The mean value of the third-order catalytic constant $k_B$ from four pH values with this buffer is $1.1 \times 10^4$ $M^{-2}$ $s^{-1}$ with a standard deviation of $0.1 \times 10^4$ $M^{-2}$ $s^{-1}$.

The nonlinear plots of $k_{MD}$ vs. $[B^-]$ with HEPES buffers suggest that specific interactions with this buffer obscure any base catalysis. The absorption curve of dye **2** in a pH 6.89 HEPES buffer ($[B^-]$ = 0.01 M) in the absence of Ni(II) had a significantly higher absorptivity than the curve for a MES buffer of the same pH and $[B^-]$. The interaction is apparently between the buffer and the dye and not with the metal ion. Similar evidence for a specific dye–buffer interaction between the buffers derived from piperazine and a cyano keto azo dye ligand was noted earlier.[2] The curves of Figure 3 for the HEPES buffers could not be modeled in terms of a simple complexation between dye and buffer with a single equilibrium constant.

The nonlinear plots for the Tris buffers are a result of the multiple complexation equilibria between the buffer and the Ni(II).[11] To obtain data on the effect of pH outside the buffering range of MES buffers, we were compelled to accept the uncertainty of nonlinear extrapolations for the HEPES and Tris buffers.

(11) Bai, K. S.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1697.
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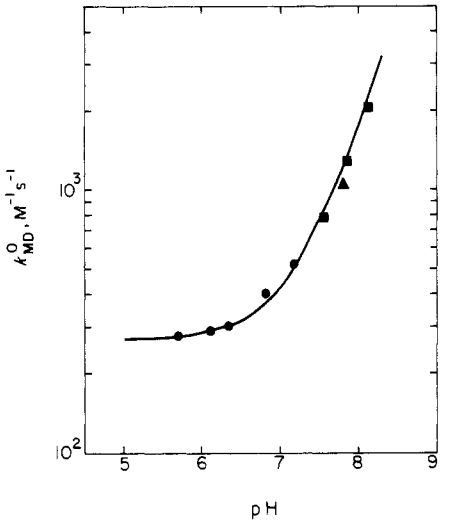


**Figure 4.** Values of $k_{MD}$ extrapolated to zero buffer concentration as a function of pH. The line was calculated from eq 8 with $k_0 = 2.7 \times 10^2$ $M^{-1}$ $s^{-1}$ and $k_{OH} = 1.5 \times 10^9$ $M^{-2}$ $s^{-1}$.

We feel that the precision of the measured rate constants justifies an uncertainty of no more than ±5% in the extrapolated values $k_{MD}^0$ for most of the nonlinear extrapolations. This range of uncertainty is indicated by ticks on the inside of the ordinate axis of Figure 3. The fact that the values from the nonlinear extrapolations fall on the extension of the curve defined by values obtained by linear extrapolation for the MES buffers is a further indication of their accuracy.

Figure 4 shows the plot of extrapolated $k_{MD}^0$ values vs. pH using data from the three buffers. The continuous curve in the plot was calculated via eq 8, where $k_0 = 2.7 \times 10^2$ $M^{-1}$ $s^{-1}$ and $k_{OH} = 1.5 \times 10^9$ $M^{-2}$ $s^{-1}$.

$$k_{MD}^0 = k_0 + k_{OH}[OH^-] \quad (8)$$

**Effect of Ionic Strength.** Measurements of $k_{obsd}$ were made in a pH 8.07 Tris buffer at ionic strengths from 0.001 to 0.08 M. At this pH, the predominant contribution to $k_{obsd}$ is from the pH-dependent term, but a significant contribution is also made by $k_0'$ ($k_0' = k_0[M]$). Plots of log ($k_{obsd} - k_0'$) vs. $I^{1/2}$ were concave upward, indicating failure of the Bjerrum–Brønsted limiting-law relationship over the indicated range of ionic strengths.[13] A plot of log ($k_{obsd} - k_0'$) vs. $(I^{1/2}/(1 + I^{1/2})) - 0.2I$[14] was linear (Figure 5) and gave −2.0 as the product of the ionic charges of the reacting species $Z_M Z_D$. Since complexation of $Ni^{2+}$ with Tris does not alter the charge on the metal ion, I conclude that the dye is reacting as a monoanion in the base-catalyzed reaction.

## Discussion

The kinetic control of the complexes formed in the nickel–β-PAN system is similar to that found with α-PAN dyes.[1] The slow equilibration of the initial to the equilibrium product mixture points out the importance of determining formation constants of the complexes by methods that ensure that the measurements are made on the system at equilibrium. The remarkable finding in this study is that an excess of the 1:2 complex can form competitively at high initial excesses of Ni(II) (Table I). The simplest pathway for formation of the excess $MD_2$ is through the competitive consecutive reactions given by eq 1 and 2 whereby $MD_2$ forms via MD as an intermediate in a rapid competitive reaction. The parallel feature of the reaction scheme allays misgivings about "overshooting" an equilibrium.

I modeled the reaction sequence (eq 1 and 2) on a computer for the condition of $[dye]_0 = 0.02$ mM and $[Ni]_0 = 2$ mM to ascertain the relative values of the two rate constants required to give the initial α value for this condition given in Table I. I found that $\alpha = 0.3$ when $k_{MD_2}/k_{MD} \simeq 300$. Such a high ratio is unexpected from conventional considerations. It is expected that $k_{MD_2}$ should be smaller than $k_{MD}$ because of a statistical factor of 2 and because of the reduced charge on the metal ion in the MD complex. A calculation of the outer-sphere formation constant $K_{os}$, based on an electrostatic model,[15] indicates that, at an ionic strength of 0.04 M, reduction of the charge on nickel from +2 to +1 should reduce $K_{os}$ from 2.7 to 0.7 $M^{-1}$. An ion separation of 0.4 nm was assumed for the calculation. We must thus account for a rate enhancement of $\sim 2 \times 4 \times 300$ to account for the competitive formation of $MD_2$ by eq 1 and 2. Arguments given earlier for the α-PAN dyes indicate that such a large rate enhancement cannot be accounted for entirely by an increase in the water-exchange rate in the inner sphere of the metal ion in the MD complex.[1] Following the proposal by Margerum and coworkers,[16,17] I have concluded that the enhanced value of $k_{MD_2}$ results from an exalted value of $K_{os}$ whereby the first dye complexed serves as a template for rapid addition of a second dye through a stacking interaction of the planar aromatic moieties.

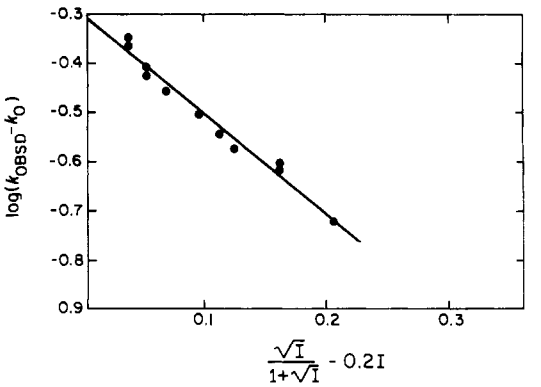


**Figure 5.** Effect of ionic strength on the pseudo-first-order rate constant for the base-catalyzed formation of MD in pH 8.07 Tris buffer.

Alternative explanations fall short of explaining the facile competitive formation of $MD_2$. An argument based on the assumption that $k_{MD_2}$ has a "normal" value and $MD_2$ forms competitively because $k_{MD}$ is abnormally small fails to explain why the same factors that make $k_{MD}$ small do not apply with equal force to $k_{MD_2}$. In addition, the rate constant for formation of MD by the base-catalyzed path is unusually large, and yet excess $MD_2$ can still form competitively by this route. Again, it could be supposed that because ring closure appears to be rate-limiting in the pH-independent path, competitive formation of $MD_2$ begins by rapid capture of a second dye ligand by the unidentate intermediate A (eq 9). Since A is present in a very low concentration, this proposal would require an abnormally high rate in the forward direction, an abnormally low rate in the reverse direction, or an unprecedented catalysis of ring closure from intermediate B. Although the involvement of B cannot be ruled out, invoking its existence adds little to our understanding.

$$\underset{A}{M\text{-}L\text{-}L\text{-}L} + L\text{-}L\text{-}L \rightleftarrows \underset{B}{L\text{-}L\text{-}L\text{-}M\text{-}L\text{-}L\text{-}L} \quad (9)$$

The pH dependence of the extrapolated $k_{MD}^0$ values and the role of the tautomeric forms of **2** were considered in terms of Scheme I. The azonaphthol tautomer (HL) is depicted as having an intramolecular hydrogen bond, although experimental evidence for this is lacking. CPK space-filling models show severe crowding of the naphthol OH and the lone pair of the β-nitrogen that hinders formation of a planar six-membered assembly involving the hydrogen bridge. NMR data show that the tautomers are interconverted rapidly.[5] The scheme does not consider all the possible

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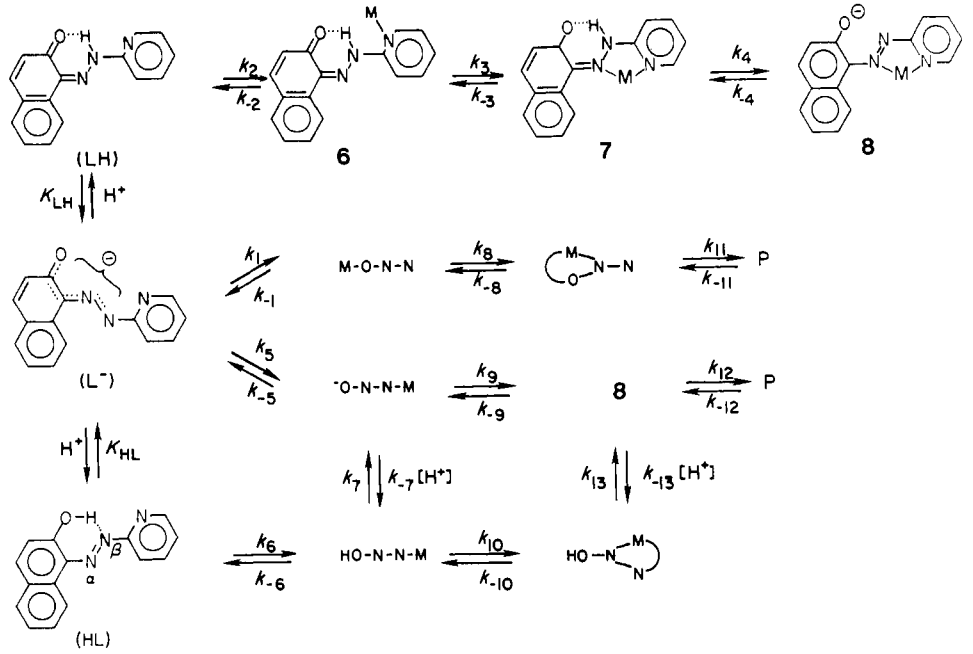
**Scheme I**




proton transfers of all the intermediates. It is sufficiently complete, however, to permit conclusions to be drawn as to which proton transfers need to be considered in establishing mechanistic pathways in the pH range of interest.

The following equilibrium constants are defined:

$$K_{LH} = [LH]/([L^-][H^+])$$

$$K_{HL} = [HL]/([L^-][H^+])$$

$$K_T = [LH]/[HL] = K_{LH}/K_{HL}$$

$$K_{a2} = ([L^-][H^+])/([LH] + [HL]) = 10^{-10.86}$$

$$K_{LH} = K_{a2}^{-1}\left(\frac{K_T}{K_T + 1}\right) \simeq K_{a2}^{-1}$$

$$K_{HL} = K_{a2}^{-1}\left(\frac{1}{1 + K_T}\right) \simeq (K_{a2}K_T)^{-1}$$

The last two equations are true only if $K_T >> 1$. An upper limit for $K_T$ was estimated by assuming that the hydrogen bonding in HL is so weak that the acidity of the naphthol OH is comparable to that of the more acidic OH in (pyridylazo)resorcinol ($pK_a$ = 5.6).[18] With this approximation, $K_T \leq 1 \times 10^{11}/4.0 \times 10^5 \leq 2.5 \times 10^5$.

Reasonable estimates of the rate constants in Scheme I were based on known rate constants for nickel(II) complexes and for proton transfers and on approximations for the $pK_a$ values of acidic ligand groups in the intermediates. I assume that the rate constants for proton recombination with ionized ligand atoms ($k_{-7}$ and $k_{-13}$) will have their diffusion-controlled limits of about $5 \times 10^{10}$ $M^{-1}$ $s^{-1}$.[19] The rate constants for the reverse process (proton transfer from the ligand group in the intermediates to water) were estimated from $pK_a$ values by assuming that complexation by $Ni^{2+}$ would lower the $pK_a$ of the ligand group in the intermediates by about 1 log unit relative to that for the uncomplexed ligand. By this assumption, $k_7 \simeq k_{13} = K_a k_{-7} \simeq (6 \times 10^{-8})(5 \times 10^{10}) = 10^3$ $s^{-1}$. I assumed further that the rate constants for unencumbered ring closure from the intermediates ($k_8$, $k_9$, $k_{10}$, $k_{11}$, and $k_{12}$) will be equal to the nickel–water exchange rates in similar unidentate and bidentate complexes ($10^4$–$10^5$ $s^{-1}$).[20] The rate constants for ligation at the pyridyl nitrogens of the dye ligands ($k_2$, $k_5$, and $k_6$) were assumed to be the same as that for formation of the unidentate Ni(py) complex ($4 \times 10^3$ $M^{-1}$ $s^{-1}$).[21] The rate constant for dissociation of $Ni^{2+}$ from the unidentate pyridine-bound intermediates ($k_{-2}$, $k_{-5}$, and $k_{-6}$) was assumed to be similar to that for the unidentate Ni(py) complex and equal to $k_f/\beta_1 \simeq 4 \times 10^3$ $M^{-1}$ $s^{-1}$/80 $M^{-1}$ = 50 $s^{-1}$.

A key question is whether the specific-base catalysis can be associated entirely with the ionization of the dye ligand. This is tantamount to asking whether there are terms in $[H^+]$ in the denominator of a general rate expression based on Scheme I that contain rate constants for proton transfer that cannot be neglected at pH 8. I derived such an expression by use of the steady-state approximation for all the intermediates in the scheme, and by insertion of the estimated rate constants given above, I concluded that all terms in $[H^+]$ in the denominator could be neglected at pH 8. The question can be viewed more simply by inquiring whether at pH 8 diffusion-controlled proton transfers that lead to branching in the pathways ($k_{-7}$, $k_{-13}$) can compete with ring closure in the corresponding intermediates. The products $k_{-7}[H^+]$ and $k_{-13}[H^+]$ have values of about $5 \times 10^2$ $s^{-1}$ at pH 8 for diffusion-controlled proton transfer. These values are smaller than the estimated rate constants for unencumbered ring closure.

The analysis leads to the conclusion that the specific-base catalysis involves only the dissociation of the dye ligand. Base-catalyzed chelation proceeds by the $k_1$ and/or the $k_5$ pathways, and the initial ligation is rate-limiting. The total rate of chelation $v_T$ is the sum of the rates via the $L^-$, LH, and HL paths (eq 10).

$$v_T = [M^{2+}](k_{L^-}[L^-] + k_{LH}[LH] + k_{HL}[HL]) \quad (10)$$

$$[L]_T = [L^-](1 + K_{LH}[H^+] + K_{HL}[H^+]) \quad (11)$$

I assume that the ligand proton in the HL tautomer is sufficiently acidic that it will not interfere with ring closure and the $k_6$ step will be rate-limiting for the HL tautomer. There are two possible ways in which slow deprotonation could interfere with ring closure in the chelation of the LH tautomer. The most apparent way occurs at the $k_4$ step, where proton dissociation is required to attain the conformation necessary for the final ring closure. This is the interpretation of Hubbard and Pacheco.[3] An alternative suggestion by Margerum[22] would require deprotonation at the $k_3$ step to make the azo nitrogen atom sufficiently basic to coordinate. The

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(22) Margerum, D. W., personal communication. I am grateful for this suggestion.

basicities of azo nitrogens in similar dyes are lower than that of the pyridyl nitrogen in **2** and **5** by 4–6 log units.[23] If the $k_4$ step is rate-limiting for chelation by LH, the steady-state approximation for intermediates **6** and **7** gives eq 12 for the total rate in terms of the total ligand concentration:

$$\frac{v_T}{[M^{2+}][L]_T} = \left( k_1 + k_5 + \frac{k_2k_3k_4K_{LH}[H^+]}{k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4} + k_6K_{HL}[H^+] \right) \Big/ (1 + K_{LH}[H^+] + K_{HL}[H^+]) \quad (12)$$

Since $K_{LH}[H^+] > (K_{HL}[H^+] + 1)$, eq 12 reduces to

$$\frac{v_T}{[M^{2+}][L]_T} = \frac{k_1 + k_5}{K_{LH}[H^+]} + \frac{k_2k_3k_4}{k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4} + \frac{k_6}{K_T} \quad (13)$$

The rate constants for the ligand species in eq 10 are then given by $k_{L^-} = k_1 + k_5$, $k_{HL} = k_6$, and $k_{LH} = k_2k_3k_4/(k_{-2}k_{-3} + k_{-2}k_4 + k_3k_4)$. If the $k_3$ step is rate-limiting for complexation of the LH tautomer, $k_{LH} = k_2k_3/(k_{-2} + k_3)$.

If $k_6$ has a value close to that for ligation of $Ni^{2+}$ with pyridine ($4 \times 10^3$ $M^{-1}$ $s^{-1}$), $K_T$ would have to be >1 for the $k_6/K_T$ term to equal the experimental value for the pH-independent reaction ($k_0 = 2.7 \times 10^2$ $M^{-1}$ $s^{-1}$). Such a large value of $K_T$ is counter to all experimental evidence, so that chelation via the HL tautomer is not important; its equilibrium concentration is too low. The pH-independent chelation involves the quinone hydrazone tautomer LH, so that $k_0 \equiv k_{LH}$. The rate is lower than that calculated for a rate-limiting initial ligation ($k_2$) because of the impediment to ring closure at the $k_3$ or $k_4$ step. The origin of the general-base catalysis is then the assisted proton removal in one of these ring-closure steps. Thus there is direct experimental evidence for general-base catalysis for a ring closure. General-base catalysis for proton removal in copper(II)–tetraglycine complexes was predicted but not realized experimentally.[24] Pagenkopf and Margerum found general-acid catalysis for protonation of copper(II) triglycine, where proton removal should be general-base catalyzed.[25]

A lower limit on the value of $k_3$ or $k_4$ can be estimated, since a concentration of intermediate **6** or **7** as high as 5% of LH would be detected. Therefore

$$k_{LH}[Ni^{2+}][LH] < k_4(0.05[LH])$$

At the experimental nickel concentration of $2 \times 10^{-4}$ M, where the steady-state approximation holds, $k_{LH}[Ni^{2+}] = 0.1$ $s^{-1}$, so that $0.05k_4 > 0.1$ $s^{-1}$ and $k_4 > 2$ $s^{-1}$. This is a reasonable limit for the slow proton transfer to water. If $k_{-3}$ or $k_{-4}$ has the diffusion-controlled value of about $5 \times 10^{10}$ $M^{-1}$ $s^{-1}$, a limit of $pK_a < 10.4$ is estimated for the appropriate intermediate. This is also a reasonable value for the partially chelated intermediate, where the acidity of a ligand group is enhanced by complexation of other conjugated ligand atoms by a metal cation.

The experimental value of $k_{OH}$ gives an unusually large value for $k_{L^-}$ ($k_{L^-} = k_{OH}K_w/K_{a2} = (1.5 \times 10^9$ $M^{-2}$ $s^{-1})(7.2 \times 10^{-4}$ M) $= 1.1 \times 10^6$ $M^{-1}$ $s^{-1}$). Combining the calculated value of $K_{os}$ (2.7 $M^{-1}$) with the rate constant for water exchange in $Ni^{2+}$ ($3 \times 10^4$ $s^{-1}$) gives a predicted value for $k_{L^-}$ of $8 \times 10^4$ $M^{-1}$ $s^{-1}$. The experimental value is larger by a factor of 30. Coulombic interactions alone do not allow for a much larger value for $K_{os}$ than the one calculated. The Debye length $\kappa^{-1}$ at $I = 0.04$ M is 1.5 nm, which is approximately the distance of separation of the charges on the ligand oxygen and the sulfonate group. The charge on the solubilizing group should be screened, and the dissociated ligand should react as a monoanion, as confirmed by the salt effect upon the rate. The enhanced rate of $L^-$ can be accounted for by assuming an internal-conjugate-base (ICB) mechanism.[26,27] By this mechanism, the ionized oxygen would form a hydrogen bond with a coordinated water to labilize water exchange, and one of the less basic nitrogen atoms would coordinate.

The rate constant for formation of the 1:1 complex from the undissociated β-PAN ligand is smaller than that for the isomeric α-PAN[1] by a factor of 7, whereas the corresponding constant for the dissociated form of β-PAN is larger than that for α-PAN by a factor of 28. The difference in reactivity of the isomeric LH species undoubtedly resides in the lower acidity of β-PAN. The higher reactivity of the $L^-$ form of β-PAN probably results from the greater basicity of the $L^-$ species. There is no obvious difference in steric requirements for the two isomers.

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**Registry No.** $(\beta\text{-PAN})_2Ni$, 34089-40-2; β-PAN, 85-85-8; Ni, 7440-02-0; sodium 2-pyridyldiazotate, 41122-56-9.

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