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Kinetics of the Formation Reactions between Nickel(II) and *N,N'*-Bis(2-picolyl)ethylenediamine and *N,N'*-Dibenzylethylenediamine

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The kinetics of the formation reactions between nickel(II) and *N,N'*-bis(2-picolyl)ethylenediamine and *N,N'*-dibenzylethylenediamine have been studied over the pH ranges of 9.2–4.2 and 8.5–7.0, respectively, at 25° and $\mu = 0.1\ M$. In both cases, the reactions were first order in nickel(II) and in ligand. For *N,N'*-dibenzylethylenediamine, $k_{\mathrm{Ni}}{}^{\mathrm{L}} = 3.1 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{\mathrm{Ni}}{}^{\mathrm{HL}} = 22.5\ M^{-1}\ \mathrm{sec}^{-1}$. Steric factors, due to the relative inaccessibility of the dentate sites, are observed, as well as slight internal conjugate base effects. For *N,N'*-bispicolylethylenediamine, $k_{\mathrm{Ni}}{}^{\mathrm{L}} = 1.8 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$, $k_{\mathrm{Ni}}{}^{\mathrm{HL}} = 2.6 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_{\mathrm{Ni}}{}^{\mathrm{H_2L}} = 1.2 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$. A mechanism is established involving an initial and rate determining bond formation to a pyridine nitrogen. Steric factors for the two types of dentate sites in the ligand are used to establish this. An internal conjugate base effect is also seen. Comparison of the data to the data of other systems involving both aromatic nitrogen donors and substituted ethylenediamines is made.

Introduction

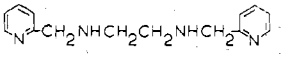
The formation and dissociation of nickel complexes has received much attention resulting in a rather detailed mechanistic picture of their reactions. The general dissociative mechanism postulated by Eigen[1] has been well tested for Ni(II)[2] and shown to explain most complex formation reactions on the basis of metal–water loss and also on the basis of being ligand independent. However, recent work has shown that the ligand may affect the formation rate in several ways.

The size and structure of the ligand determines how accessible the donor sites are and, thus, a factor for steric hindrance should be included in predicting a rate normally based on outer-sphere diffusion and rate of water loss. Thus, in forming Ni(II) complexes, alkylamines react slightly slower than ammonia,[3] *N*-alkyl-substituted ethylenediamines react slower than ethylenediamine (en),[4] and *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED) react at anomalously slow rates.[5] In fact, steric hindrance may slow down chelate ring closure to the point where it is rate determining.[2,6,7]

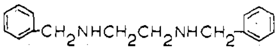
The basicity of the incoming ligand, if over a threshold value for a given metal, has been shown to accelerate bond formation through an internal conjugate base (ICB) mechanism.[8] Thus unprotonated en, diethylenetriamine (dien), and triethylenetetramine (trien) react faster than expected due to an ICB effect, an ICB effect has been found superimposed on steric factors for N-substituted ethylenediamines,[4] and coordinated ligands can enhance the ICB effect.[9] Finally, the rate of metal water loss is not a constant but varies with the groups coordinated to the metal.[10]

The study of nitrogen dentate ligands containing both aromatic and aliphatic sites has been very scant. Recently, the kinetics of formation of bis(2-pyridylmethyl)amine, DPA, with both cobalt and nickel was reported,[11] yet details of the mechanism of formation were not considered. Simarily, the rate constant for the formation of 2-aminomethylpyridinenickel(II) has been measured[12] but not discussed in detail. This work was done in an attempt to interpret the reaction of nickel with ligands possessing both aromatic and aliphatic nitrogen donors in a detailed fashion in light of some of the subtle effects of complex formation.

The compounds chosen for study were *N,N'*-bis(2-picolyl)ethylenediamine (BPEDA) and *N,N'*-dibenzylethylenediamine (DBEDA).



BPEDA



DBEDA

The experimentally measured formation reaction for both ligands to give a 1:1 complex with nickel is shown in eq 1.

$$\mathrm{Ni(H_2O)_6}^{2+} + \mathrm{H}_x\mathrm{LN}_y{}^{x+} \rightleftarrows \mathrm{Ni(H_2O)}_{6-y}\mathrm{LN}_y{}^{2+} + y\mathrm{H_2O} + x\mathrm{H}^{x+} \qquad (1)$$

The experimental results can be interpreted in terms of an initial and rate-determining bond formation to the pyridine residue of BPEDA. Both steric effects for attack at the various nitrogens and an ICB effect are present. Good correlation with previous studies is found.

Experimental Section

Reagents. BPEDA was prepared from anhydrous ethylenediamine[13] and pyridine-2-carboxaldehyde. The resulting imine was hydrogenated using a 10% Pd–C catalyst according to Gruenwedel.[14] The viscous yellow liquid was vacuum distilled at 24 mm and the product boiling at 140–145° was collected. This was converted to the tetrahydrochloride and recrystallized from MeOH–ether (4:1). Colorless crystals which melted at 208–209° were formed. The product was found to be air sensitive and was stored in a vacuum desiccator under N_2. *Anal.* Calcd for

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$C_{14}H_{18}N_4 \cdot 4HCl$: N, 14.43; H, 5.67; C, 43.52. Found: N, 14.28; H, 5.51; C, 42.63.

DBEDA was obtained from the Aldrich Chemical Co. and recrystallized as a dihydrochloride from hot absolute MeOH. Solutions of DBEDA were standardized by potentiometric titrations, while those of BPEDA were standardized from mole ratio plots at 560 nm using a standard nickel solution.

All other chemicals were reagent grade and were used without further purification. All solutions were prepared with deionized distilled water. Solutions of $NiCl_2$ were prepared and standardized using EDTA titrations. Boric acid–sodium borate with varying amounts of mannitol provided a buffer from pH 9 to 4.2. The ionic strength was maintained constant with $NaClO_4$.

Equilibrium and Kinetic Measurements. All pH measurements were made on a Beckman Model 110 Research pH meter with an NaCl reference electrode. Data from potentiometric titrations were obtained by mixing known amounts of DBEDA·2HCl in a four-neck round-bottom flask immersed in a constant-temperature bath regulated at 25.0 ± 0.1°. The ionic strength was set at 0.1 *M* and the solution titrated using carbonate-free NaOH.

All absorbance measurements were recorded on a Cary Model 14 spectrophotometer. Values of the molar absorptivity of absorbing species at pertinent wavelengths are as follows: at 235 nm, $\epsilon_{\mathrm{NiDBEDA}}$ 778, $\epsilon_{\mathrm{DBEDA}}$ 278, $\epsilon_{\mathrm{HDBEDA}}$ 149, $\epsilon_{\mathrm{H_2DBEDA}}$ 84.2; at 300 nm, $\epsilon_{\mathrm{NiBPEDA}}$ 173. The absorbance of BPEDA varied with pH at 300 nm. No attempt to calculate individual molar absorptivities was made.

Kinetic runs were made on an American Instrument Co. stopped-flow apparatus attached to a Shimadzu QV 50 spectrophotometer. Spectral changes from the latter were displayed on a Tektronix Type 549 storage oscilloscope and recorded on Polaroid film. The change in per cent transmittance was measured at 300 nm for the reaction of Ni(II) with BPEDA and data were obtained over the pH range of 9.2–4.2. The reaction of Ni(II) with DBEDA was followed at 235 nm over a pH range of 8.5–7.0. For kinetic runs below pH 8.25, both reactant solutions were adjusted to the desired pH and mixed and the pH values of the products were obtained. For kinetic runs above pH 8.26, sodium perchlorate was added to the nickel solution and the pH adjusted to 8.2. No spectral evidence of $Ni(OH)_2$ was found. Buffer was added to the ligand solution and the pH adjusted to the desired value. In this manner it was possible to obtain kinetic data up to pH 9.2 since, upon mixing the reactant solutions, proton equilibria were established much faster than formation equilibria which, in turn, are much faster than hydroxide precipitation. Buffer capacity was checked by adjusting both reactant solutions to the desired pH, mixing, and measuring the pH of the products. All data were obtained at 25.0 ± 0.1° and $\mu = 0.1\ M$.

Results

Protonation Constants of DBEDA. The proton association constants of DBEDA, defined by eq 2, were obtained

$$K_{\mathrm{H}_n\mathrm{L}} = \frac{[\mathrm{H}_n\mathrm{L}^{n+}]}{[\mathrm{H}_{n-1}\mathrm{L}^{(n-1)+}]\,a_{\mathrm{H}^+}} \tag{2}$$

using the method of Schwarzenbach,[15] described by Jonassen and Westerman.[16] Data were taken from the titration curve in the areas where the ratio of moles of base to moles of ligand was 0.5 and 1.5. All possible combinations of these points were used, as previously described,[16] to obtain the values of $K_{\mathrm{H_2L}}$ and K_{HL} which are listed in Table I.

The values of $K_{\mathrm{H_2L}}$ and K_{HL} for DBEDA are slightly higher than those of BPEDA,[14,17] presumably showing the difference between a benzene ring compared to a pyridyl group in affecting the aliphatic nitrogen basicity. Values for both ligands are considerably less than those for *N,N'*-diethylethylenediamine ($\log K_{\mathrm{HL}} = 10.10$, $\log K_{\mathrm{H_2L}} = 7.32$)[4] showing the inductive effect of the aromatic ring.

Table I. Protonation Association Constants for DBEDA and BPEDA at $\mu = 0.1\ M$ and at 25°

Ligand	Log $K_{\mathrm{H_4L}}$	Log $K_{\mathrm{H_3L}}$	Log $K_{\mathrm{H_2L}}$	Log K_{HL}	Ref
DBEDA			6.02 ± 0.03	8.85 ± 0.02	*a*
BPEDA	1.8	2.0	5.47	8.28	*b*
BPEDA	1.62	1.81	5.45	8.23	*c*

[a] This work. [b] Reference 14. [c] Reference 17.

Stability Constant of NiDBEDA^{2+}. The insolubility of DBEDA prevented more than $5 \times 10^{-2}\ M$ aqueous solutions. At this concentration, spectra of solutions containing excess Ni(II) and DBEDA showed a very slight increase in absorbance in the visible region presumably due to the formation of NiDBEDA^{2+}. In the uv region the complex possessed a much larger molar absorptivity and its composition and stability were studied at 235 nm. Mole ratio plots at pH 9 showed a definite break at Ni:DBEDA = 1:1 but did not permit an accurate evaluation as to whether a break at Ni:DBEDA = 1:2 was present or not. The molar absorptivity of NiDBEDA^{2+} was obtained from the break in the mole ratio plot, and the molar absorptivities of DBEDA, HDBEDA$^+$, and H$_2$DBEDA^{2+} were obtained from absorbance readings of solutions of DBEDA at several pH's. Solutions containing known amounts of Ni(II) and total DBEDA were adjusted to several pH values, thus varying the amount of unprotonated DBEDA. From known values of molar absorptivities, initial concentrations, and the absorbance of these solutions at 235 nm, K_{stab} was calculated by

$$K_{\mathrm{stab}} = \frac{[\mathrm{NiL}]}{([\mathrm{Ni}_{\mathrm{initial}}] - [\mathrm{NiL}])([\mathrm{L}_{\mathrm{initial}}] - [\mathrm{NiL}])} \tag{3}$$

where

$$[\mathrm{NiL}] = \frac{A - \beta_{\mathrm{L}}[\mathrm{L}_{\mathrm{initial}}](\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{HL}}[\mathrm{H}^+]/K_{\mathrm{HL}})}{\epsilon_{\mathrm{NiL}} - \beta_{\mathrm{L}}(\epsilon_{\mathrm{L}} + \epsilon_{\mathrm{HL}}[\mathrm{H}^+]/K_{\mathrm{HL}})}$$

and

$$\beta_{\mathrm{L}} = \frac{[\mathrm{L}]}{[\mathrm{L}_{\mathrm{initial}}] - [\mathrm{NiL}]}$$

The value found was $K_{\mathrm{stab}} = (1.77 \pm 0.41) \times 10^5$.

Kinetic Measurements. The reaction of Ni(II) with both ligands was found to obey the first-order rate equation

$$-\mathrm{d}[\mathrm{Ni}^{2+}]/\mathrm{d}t = k_0[\mathrm{Ni}^{2+}] \tag{4}$$

where k_0 represents the pseudo-first-order rate constant. All reactions were carried out under conditions of at least 10-fold excess ligand so that

$$k_0 = k_{\mathrm{Ni}}^{\mathrm{L_t}}[\mathrm{L_t}] \tag{5}$$

where $[\mathrm{L_t}]$ represents the total concentration of all uncomplexed ligand species. Reactions were plotted to at least 80% completion for BPEDA yielding excellent first-order plots in all cases. Because of the lower stability constant of NiDBEDA^{2+}, the data were plotted both as a pseudo-first-order and as a reversible first-order system. The plots were carried out to 50–70% completion and gave identical rate constants. Thus, reversibility is not important before 70% completion. The data are listed in Table II. Each k_0 is the average of at least two to three runs. The concentration of excess ligand was varied over a 30-fold

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Table II. Experimental Rate Constants for the Reactions of Ni(II) with BPEDA and DBEDA at 25° and μ = 0.1 *M*

pH	k_0, sec^{-1}	10^2[BPEDA], *M*	10^4[Ni^{2+}], *M*	pH	k_0, sec^{-1}	10^3[DBEDA], *M*	10^4[Ni^{2+}], *M*
9.25	16.9	1.01	9.75	8.52	0.233	2.06	1.97
9.00	15.9	1.01	9.75	8.44	0.214	2.06	1.97
8.54	12.7	1.01	9.75	8.28	0.170	2.06	1.97
8.45	12.0	1.01	9.75	8.14	0.152	2.06	1.97
8.44	6.10	0.505	4.91	8.00	0.120	2.06	1.97
8.44	8.95	0.757	4.91	7.94	0.110	2.06	1.97
8.44	12.0	1.01	4.91	7.90	0.0534	1.03	0.985
8.44	15.2	1.26	4.91	7.90	0.0769	1.55	0.985
8.44	18.3	1.52	4.91	7.90	0.104	2.03	0.985
8.26	10.8	1.01	9.75	7.90	0.127	2.58	0.985
8.10	8.98	1.01	9.75	7.90	0.157	3.09	0.985
7.90	7.12	1.01	9.75	7.90	0.184	3.61	0.985
7.60	5.30	1.01	9.75	7.90	0.212	4.12	0.985
7.52	5.01	1.01	9.75	7.74	0.0866	2.06	1.97
6.80	3.15	1.01	9.75	7.62	0.0712	2.06	1.97
6.60	2.96	1.01	9.75	7.20	0.0546	2.06	1.97
6.33	2.46	1.01	9.75	6.95	0.0486	2.06	1.97
5.69	2.02	1.01	9.75				
5.20	1.80	1.01	9.75				
5.00	1.54	1.01	9.75				
4.90	1.45	1.01	9.75				
4.70	1.38	1.01	9.75				
4.20	1.30	1.01	9.75				

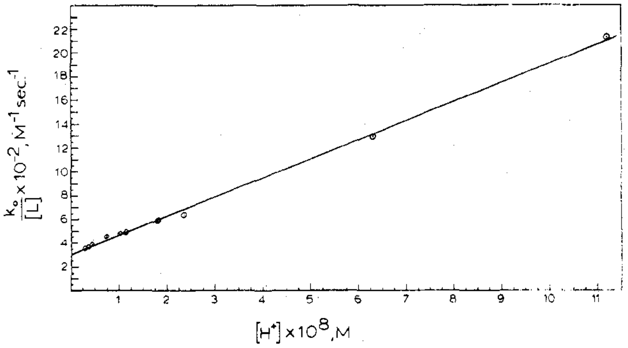

Figure 1. Resolution of the rate constants for the formation of Ni(BPEDA)$^{2+}$ at high pH where $k_{Ni}^{H_2L}$ is unimportant.

range and plots of k_0 against $[L_t]$ at constant pH yielded straight lines. Thus, first-order behavior in both Ni(II) and total ligand was demonstrated for both systems.

The kinetic data were resolved into three rate constants for BPEDA and two rate constants for DBEDA. This is shown in eq 6 where only the first two terms on the right-hand side are present for DBEDA. For BPEDA, in the pH range 9.3-7.5, the concentration of H_2L^{2+} is negligible and eq 6 was rearranged and plotted as shown in Figure 1 to yield k_{Ni}^{HL} = 1.82 × 10^3 M^{-1} sec^{-1} and k_{Ni}^{HL} = 2.63 × 10^2 M^{-1} sec^{-1}. For the pH range 6.8-4.2, where H_2L is important and k_{Ni}^{L} is known, eq 6 was rearranged and plotted as shown in Figure 2 to yield k_{Ni}^{HL} = 2.63 × 10^2 M^{-1} sec^{-1} and $k_{Ni}^{H_2L}$ = 1.15 × 10^2 M^{-1} sec^{-1}.

$$k_0 = k_{Ni}^{L}[L] + k_{Ni}^{HL}[HL^+] + k_{Ni}^{H_2L}[H_2L^{2+}] \qquad (6)$$

Since only two terms would be expected for the Ni(II) reaction with DBEDA, the last term on the right-hand side of eq 6 can be dropped and the equation rearranged and plotted as shown in Figure 3 to yield k_{Ni}^{L} = 3.09 × 10^2 M^{-1} sec^{-1} and k_{Ni}^{HL} = 22.5 M^{-1} sec^{-1}. For both ligands, the overall rate of formation as a function of pH can be calculated from the resolved rate constants and compared to the experimental points. This is shown in Figures 4 and 5. The excellent agreement lends confidence in the resolved values.

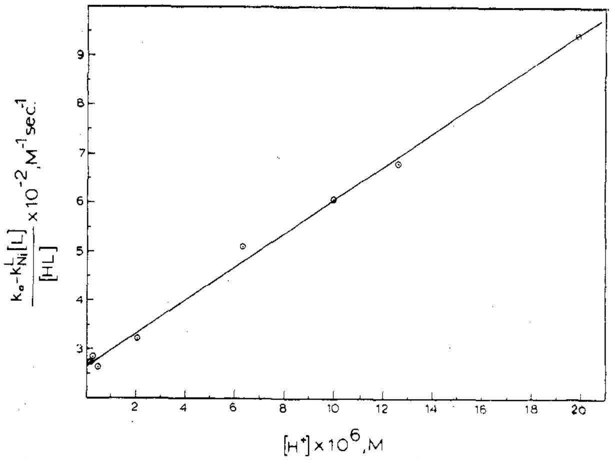

Figure 2. Resolution of rate constants for the formation of Ni(BPEDA)$^{2+}$ at low pH where $k_{Ni}^{H_2L}$ is important and k_{Ni}^{L} is known.

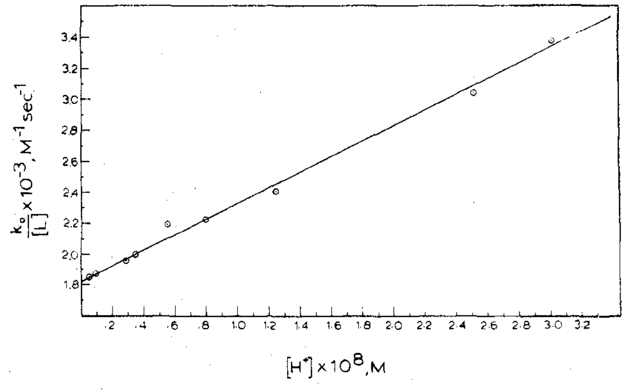

Figure 3. Resolution of the rate constants for the formation of Ni(DBEDA)$^{2+}$.

Discussion

Many previous studies have shown that Ni(II) bonds to polyamines in a stepwise fashion with each bond formation being preceded by the loss of coordinated water from Ni(II).^{2} The initial bond formation is limited by an ion-pair (outer-sphere) complex formation. The scheme is shown in Figure 6 where only a bidentate ligand is shown.

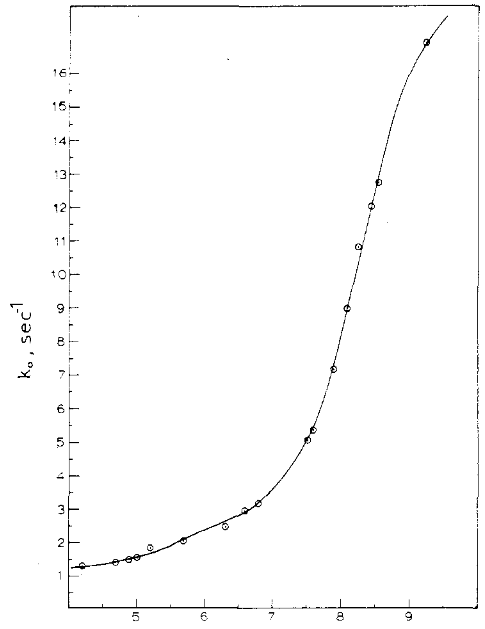

Figure 4. Fit of theoretical curve to experimental rate constants for the formation of $\mathrm{Ni(BPEDA)}^{2+}$. The solid line is the curve predicted by eq 6; circled points are experimentally observed values.

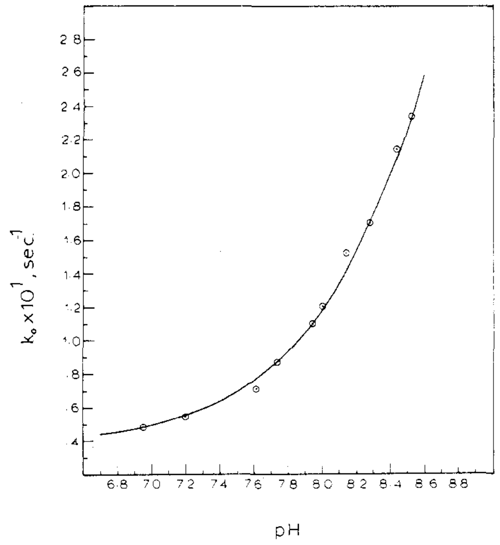

Figure 5. Fit of theoretical curve to experimental rate constants for the formation of $\mathrm{Ni(DBEDA)}^{2+}$. The solid line is the curve predicted by eq 6, excluding the term $k_{\mathrm{Ni}}{}^{\mathrm{H_2L}}[\mathrm{H_2L}^{2+}]$; circled points are experimentally observed values.

It is assumed that the polyamines in this study follow a similar stepwise-type mechanism. The main points of interest are the point of initial bonding in BPEDA and location of the rate-determining step for both ligands.

Reaction of Ni(II) with DBEDA. The reaction of Ni(II) with DBEDA is relatively simple since initial bond formation must be to an aliphatic nitrogen. The possibility exists that ring closure is rate determining; however, studies on other substituted ethylenediamines[4] have shown that this is true only for ligands more highly substituted than *N,N'*-diethylethylenediamine (*N,N'*-(Et)$_2$en). Since DBEDA contains secondary nitrogens like *N,N'*-(Et)$_2$en and since molecular models show the benzene ring is far enough removed so as not to interfere with bonding, it is safe to assume that, as in the case of *N,N'*-(Et)$_2$en, initial bonding

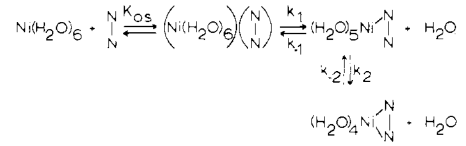

Figure 6. Proposed reaction mechanism for Ni(II) reacting with BPEDA and DBEDA. Only two nitrogens are shown since pH data indicate that the rate-determining step must be either the first or second nickel–nitrogen bond formation. Protonated species are omitted for clarity but would follow the same mechanism with proton equilibria being established rapidly compared to any of the steps in Figure 6.

of DBEDA, and not ring closure, is rate determining.

From Figure 6, when initial bond formation is rate determining, eq 7 holds,[2] where K_{os} is the diffusion-

$$k_{\mathrm{Ni}}{}^{\mathrm{L}} = K_{\mathrm{os}}k_1 \qquad (7)$$

controlled equilibrium constant for the formation of an outer-sphere complex. It is possible to estimate $k_{\mathrm{Ni}}{}^{\mathrm{L}}$ and $k_{\mathrm{Ni}}{}^{\mathrm{HL}}$ from calculated values of K_{os} and known values of $k^{\mathrm{Ni-H_2O}}$. To calculate K_{os} ($Z_2 = 0$ for $k_{\mathrm{Ni}}{}^{\mathrm{L}}$ and $Z_2 = 1$ for $k_{\mathrm{Ni}}{}^{\mathrm{HL}}$, etc.), we used the equation[2]

$$K_{\mathrm{os}} = \frac{4}{3}\pi a^3 N_{\mathrm{A}} \times 10^{-3} \times \exp\left[-\left(\frac{Z_1Z_2e_0^2}{a'DkT} - \frac{Z_1Z_2e_0^2\kappa}{DkT(1+\kappa a')}\right)\right] \qquad (8)$$

where

$$\kappa = \left(\frac{8\pi N_{\mathrm{A}}e_0^2\mu}{1000DkT}\right)^{1/2} \qquad (9)$$

The terms have been previously defined.[2] Molecular models were used to estimate a value of $a = 4 \times 10^{-8}$ cm which yielded a value of $K_{\mathrm{os}} = 0.16$. Using $k^{\mathrm{Ni-H_2O}} = 2.7 \times 10^4$ sec^{-1} [18] and a statistical factor of 2 gives $k_{\mathrm{Ni}}{}^{\mathrm{L}} = 8.7 \times 10^3$ M^{-1} sec^{-1} from eq 7. The same treatment can be applied to the monoprotonated species. Here, $Z_1 = 2, Z_2 = 1$, and $a' = 8 \times 10^{-8}$ cm which yield $K_{\mathrm{os}} = 0.062$. Equation 7 with no statistical factor gives $k_{\mathrm{Ni}}{}^{\mathrm{HL}} = 1.7 \times 10^3$ M^{-1} sec^{-1}. The calculated and experimental values for this and other systems appear in Table III.

Both calculated values are seen to be greater than the corresponding experimental ones. Previous studies have attributed a decrease in formation rate to steric effects.[3-5] In fact, even methylamine reacts slower than ammonia.[3] Thus, *N*-benzyl and *N*-ethyl substituents on the aliphatic nitrogens where initial bond formation occurs certainly should have a pronounced effect on the formation rate. The relative effect of these groups can be estimated as proposed by Rorabacher[5] by calculating an organic substituent function where k_0 is a reference constant,

$$E_{\mathrm{s}} = \log(k/k_0) \qquad (10)$$

equal to the calculated formation constant from eq 7. Values of E_{s} for DBEDA, HDBEDA^+, and other related ligands are listed in Table III. For unprotonated DBEDA, there is the possibility of rate enhancement due to an ICB effect[8] since p$K_{\mathrm{HL}} > 8$. The difference in E_{s} values for DBEDA and HDBEDA^+ reflects this and corresponds to a modest ICB effect of about 3. This is in satisfactory agreement with the magnitude of other ICB effects relative to the corresponding ligand pK values.[5,8]

Reaction of Ni(II) with BPEDA. The reaction of Ni(II)

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Table III. Experimental and Predicted Formation Rate Constants and Calculated Steric Factors for the Reaction of Ni(II) with Various Ligands[h]

Ligand	$k_{\mathrm{Ni}}{}^{\mathrm{L}}$, M^{-1} sec^{-1} Exptl	$k_{\mathrm{Ni}}{}^{\mathrm{L}}$, M^{-1} sec^{-1} Calcd	E_s	Ref
DBEDA	3.09×10^2	8.7×10^3	−1.4	*a*
HDBEDA$^+$	22.5	1.7×10^3	−1.9	*a*
BPEDA	1.82×10^3	8.7×10^3	−0.7	*a*
HBPEDA$^+$	2.63×10^2	4.4×10^3	−1.2	*a*
H_2BPEDA^{2+}	1.15×10^2	1.7×10^3	−1.2	*a*
Pyridine	4×10^3	4.3×10^3	−0.03	*c*
Bipyridine	1.6×10^3	8.7×10^3	−0.7	*c*
Terpyridine[b]	1.4×10^3	8.7×10^3	−0.8	*c*
1,10-Phenanthroline	3.2×10^3	8.7×10^3	−0.4	*c*
N,N-(Et)$_2$en	9.7×10^3	8×10^3	+0.1	*d*
H(*N,N*-(Et)$_2$en)$^+$	8.0	2×10^3	−2.3	*d*
Methylamine	1.31×10^3	4.5×10^3	−0.5	*e*
Dimethylamine	3.32×10^2	4.5×10^3	−1.1	*e*
2-Aminomethylpyridine (AMP)	8.6×10^3	4.3×10^3	+0.3	*f*
HAMP$^+$	35	1.7×10^3	−1.7	*f*
Di(2-picolyl)amine (DPA)	5.8×10^3	8.7×10^3	−0.2	*g*
HDPA$^+$	3.4×10^2	3.3×10^3	−1.0	*g*
Ethylamine	8.65×10^2	4.5×10^3	−0.7	*e*

[a] This work. [b] Predicted value calculated assuming attack at only end nitrogens. [c] R. M. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 5, 622 (1966). [d] Reference 4. [e] Reference 3. [f] Reference 12. [g] Reference 11. [h] Predicted constants were calculated from eq 7 and 8 and E_s values from eq 9.

with BPEDA involves several possibilities. The initial bond formation may be to a pyridine nitrogen as the rate-determining step, the initial bond formation may be to a pyridine nitrogen but ring closure to an adjacent aliphatic nitrogen may be rate determining, or initial bond formation may be to an aliphatic nitrogen and may also be rate-determining. Initial bond formation to an aliphatic nitrogen with ring closure to either a second aliphatic nitrogen or a pyridine nitrogen as rate determining can be ruled out for the same reasons that apply to DBEDA.

The pathway assuming initial, rate-determining bond formation to an aliphatic nitrogen, similar to that for DBEDA, will be considered first. If this is correct, then similar E_s values for HDBEDA$^+$ and HBPEDA$^+$ should be obtained. The values of K_{os} would be identical for both ligands and eq 10 gives $E_s = -0.8$ for HBPEDA. Since no ICB effect is possible for either monoprotonated ligand, comparison of this value with that for HDBEDA, $E_s = -1.9$, shows that initial bond formation to an aliphatic nitrogen is not possible. The experimental rate for BPEDA is simply too fast. Thus, initial bond formation must be at the terminal pyridine nitrogen sites. Either this step or subsequent ring closure is rate determining.

Location of the rate-determining step may be ascertained from a consideration of Figure 6. Assuming that (i) outer-sphere complex formation and dissociation rates are faster than subsequent steps and (ii) the steady-state condition may be applied for the intermediates, eq 11 holds.

$$k_{\mathrm{Ni}}{}^{\mathrm{L}} = \frac{k_{\mathrm{os}}k_1k_2}{k_{-1} + k_2} \qquad (11)$$

The position of the rate-determining step depends upon the magnitude of k_{-1} and k_2. The dissociation of Ni(py)$^{2+}$, py = pyridine, has been experimentally measured as 38 sec^{-1} [19] and may be used to approximate k_{-1}. The value of k_2 may be estimated from a study of Ni(trien)$^{2+}$ formation.[20] Initial bond formation has been shown to be rate determining for Ni(trien)$^{2+}$. An estimate of k_2 has been made for trien which involves rotation of a carbon-carbon or a carbon-nitrogen bond in order to swing a second nitrogen into a bonding position. This is followed by Ni(II) water loss. The ligands BPEDA and trien differ little in terms of rotation of a second nitrogen into a bonding position. Thus, $k_2 \approx 200$ sec^{-1}.[21] Further evidence on the magnitude of k_2 may be obtained from the estimate $k_2 = 900$ sec^{-1} for tetrameen[2] which is even more highly substituted than BPEDA and trien. Equation 11 then reduces to eq 7 with initial bond formation as the rate-determining step.

The presence of an ICB effect for BPEDA may be found by calculating E_s for BPEDA and subsequent comparison to E_s for HBPEDA$^+$. Since initial bond formation is to a pyridine nitrogen in both cases, steric factors will be identical. Equation 8 gives $K_{os} = 0.16$ for BPEDA using $a = 4 \times 10^{-8}$ cm, while $K_{os} = 0.081$ for HBPEDA$^+$ using $a = 4 \times 10^{-8}$ cm and $a' = 10 \times 10^{-8}$ cm. These values in eq 7 along with $k^{\mathrm{Ni-H_2O}} = 2.7 \times 10^4$ sec^{-1} and a statistical factor of 2 yield $k_{\mathrm{Ni}}{}^{\mathrm{L}} = 8.7 \times 10^3$ and $k_{\mathrm{Ni}}{}^{\mathrm{HL}} = 4.4 \times 10^3$. Values of E_s may be calculated from eq 10 and are listed in Table III. As with DBEDA, the difference between the two values show a slight ICB effect of about 3. Again, in view of p$K_{\mathrm{HL}} = 8.3$, this value is reasonable.

The reaction of Ni(II) with H_2BPEDA^{2+} must also involve initial bond formation to a pyridine nitrogen since both protons occupy aliphatic nitrogen sites. Further, initial bonding must be rate determining since the only other free nitrogen is 9 atoms removed and would result in the formation of a highly unstable 11-member ring. The value of K_{os} can be calculated from eq 8 using $Z_1 = Z_2 = 2$, $a = 4 \times 10^{-8}$ cm, and $a' = 9 \times 10^{-8}$ cm which gives $K_{os} = 0.032$. This value along with $k^{\mathrm{Ni-H_2O}} = 2.7 \times 10^4$ sec^{-1} in eq 7 gives $k_{\mathrm{Ni}}{}^{\mathrm{H_2L}} = 1.7 \times 10^3$ M^{-1} sec^{-1}. The value of E_s for H_2BPEDA^{2+} and HBPEDA$^+$ should be equal since both involve pyridine nitrogens and neither can have an ICB effect. Equation 10 gives E_s for H_2BPEDA^{2+} as −1.2 which is in excellent agreement with $E_s = -1.2$ for HBPEDA$^+$ and lends further support for initial bonding at the pyridine nitrogens.

Comparison of Steric Effects on Other Systems. It is of interest to compare E_s values obtained from BPEDA and DBEDA with those found for other N-substituted ethylenediamines. These are listed in Table III. Comparing the monoprotonated species H(*N,N*'-(Et)$_2$en)$^+$ shows a value similar to HDBEDA$^+$. This is not unexpected since the aromatic ring of DBEDA is one carbon removed from the nitrogen donor and is planar. The larger value of E_s for H(*N,N*'-(Et)$_2$en)$^+$ is somewhat surprising. The value of E_s for monoprotonated HBPEDA$^+$ should be less than that of HDBEDA$^+$ since the substituents on the pyridine ring are tied back in the aromatic ring. The two E_s values illustrate this.

An interesting trend is seen in comparing E_s values for pyridine, bipyridine, terpyridine, 1,10-phenanthroline, HBPEDA$^+$, and dimethylamine. As expected, the smallest steric effect is seen for pyridine; however, it is far smaller than would be expected from comparison to dimethylamine. E_s jumps significantly for bipyridine, terpyridine, phenanthroline, and HBPEDA. Bipyridine and terpyridine, assuming attack at only the two end nitrogens of terpyridine,

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[19] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).

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

[21] The value of $k_2 \approx 200$ sec^{-1} does not include any nickel-water loss enhancement due to coordinated nitrogens. Present data[10] indicate that coordinated aromatic nitrogens do not enhance nickel-water loss.

show similar values and $HBPEDA^+$ shows a slightly larger value, due presumably to the rest of the molecule as a substituent in the 2 position of the pyridine ring. Phenanthroline shows a rather low value in view of the fact that the second ring cannot rotate out of the way during initial bonding as is the case with the others. This may suggest some type of accelerating effect due to the close proximity of the second nitrogen during initial bonding.

Comparison of Formation Rates of Ni(II) with BPEDA, TKED, EDDA, and trien. The ligands BPEDA, TKED, EDDA, and trien can all be considered as N-substituted ethylenediamines. The position of the rate-determining step, either initial bond formation or ring closure, depends on the values of k_{-1} and k_2 in eq 11. With the exception of trien, all k_2 values should be about the same since only coordinated nitrogens appear to have a sizable effect on nickel-water loss[10] and since rotational barriers would be similar. Thus, the magnitude of the dissociation constant for the N-substituted dentate group really determines the position of the rate-determining step. The strong nickel-nitrogen bonds, $k^{Ni(py)}$ and k^{NiNH_3}, compared to weak nickel-oxygen bonds, k^{NiOAc} and k^{NiOR}, coupled with the relative inaccessibility of secondary and tertiary nitrogens cause a shift in the rate-determining step from first to second bond formation as k_{-1} increases. BPEDA having $k_{-1} = 38\ \text{sec}^{-1}$ fits the mechanism well.

Comparison of BPEDA with AMP and DPA. The formation reactions of Ni(II) with both free and protonated forms of 2-aminomethylpyridine, AMP, and di(2-picolyl)-amine, DPA, have been measured. Again, assuming no ICB effect to be present in the protonated cases, E_s values can be calculated and are listed in Table III. Since the monoprotonated forms of both ligands involve aliphatic nitrogen protonation, the E_s values reflect steric factors for attack at the aromatic nitrogens. The value for $HDPA^+$ is similar to that for $HBPEDA^+$ as would be expected but that for $HAMP^+$ is abnormally low.

Calculations of E_s for AMP and DPA result in anomously large values. In the case of DPA, pK_{HL} is <8[11] and no ICB effect should be present. Thus, E_s must approximate the steric factor for initial attack at either an aromatic nitrogen or an aliphatic one and can be compared to E_s for $HBPEDA^+$ and $HDPA^+$ approximating an aromatic nitrogen or E_s for $HDBEDA^+$ and $H(N,N'\text{-}(Et)_2en)^+$ approximating a secondary aliphatic nitrogen. Although E_s for DPA is higher than E_s for all the above-mentioned ligands, it clearly is closer to those for $HBPEDA^+$ and $HDPA^+$ than those for $HDBEDA^+$ and $H(N,N'\text{-}(Et)_2en)^+$. On this basis it is likely that, like the Ni(II) attack on BPEDA, initial attack on DPA is also through an aromatic nitrogen.

The situation involving AMP is more complex. E_s could reflect initial attack at an aromatic nitrogen but would also include an ICB effect since pK_{HL} is 8.6.[17] Comparison to E_s for $HAMP^+$ would give an ICB effect of 100 which is unreasonable. Conversely, E_s for AMP could reflect initial attack at the aliphatic nitrogen in which case it could not be compared to E_s for $HAMP^+$ because different dentate sites would be involved although no ICB effect would be present. However, ethylamine should have a similar steric factor but comparison of E_s for $EtNH_2$ and AMP shows them to be a factor of 10 apart. Thus, neither mechanism is supported by the data and a clear picture of the mechanism of Ni(II) formation with AMP cannot be established yet.

Registry No. DBEDA, 140-28-3; BPEDA, 4608-34-8; Ni, 7440-02-0; $HDBEDA^+$, 36223-04-8; $HBPEDA^+$, 36223-05-9; H_2BPEDA^{2+}, 36223-06-0; NiDBEDA, 36202-31-0.

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Proton Magnetic Resonance Study of the Stereochemistry of Four-Coordinate Nickel(II) Complexes. Dihalobis(tertiary phosphine)nickel(II) Complexes

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A series of dihalobis(tertiary phosphine)nickel(II) complexes, NiL_2X_2, has been synthesized. The tertiary phosphine ligands include PR_3, PR_2Ph, and $PRPh_2$ types where R is cyclopropyl or cyclohexyl and Ph is phenyl. These tertiary phosphines and several others were selected to test the relative importance of steric and electronic effects on the planar-tetrahedral structural equilibrium exhibited by NiL_2X_2 type complexes. The thermodynamics and kinetics of this interconversion were determined by proton magnetic resonance and magnetic susceptibility measurements in dichloromethane solution. Results show that steric factors are relatively unimportant in affecting the thermodynamics of the structural equilibrium. Electronic effects, however, are extremely important and are interpreted *via* a metal-phosphorus π-bonding scheme. Kinetic parameters were measured by standard pmr line shape techniques and are reported for trialkyl- and dialkylphenylphosphine complexes for the first time. The activation parameters are similar to other NiL_2X_2 complexes where L = alkyldiphenylphosphine.

Introduction

Tertiary phosphines are among the most extensively investigated ligands in coordination chemistry.[2] Reports have appeared which have presented conflicting evidence for the importance of σ and π bonding between these ligands and transition metals.[3] An understanding of the bonding mode is important because phosphine ligands play a significant role in homogeneous catalysis. A sensitive test

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[1] Lubrizol Fellow, University of Minnesota, 1971-1972.

[2] See for example G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).

[3] (a) L. M. Venanzi, *Chem. Brit.*, 4, 162 (1968); (b) B. B. Chastain, E. A. Rick, R. I. Pruett, and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 3994 (1968); (c) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).