

Contribution from the Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and Tennessee Technological University, Cookeville, Tennessee 38501

## Ternary Complex Formation between a Tetradentate Nickel(II) Chelate and Additional Donors. A Kinetic and Thermodynamic Study

D. T. FARRAR, J. E. STUEHR,\* A. MORADI-ARAGHI, F. L. URBACH,\* and T. G. CAMPBELL

Received January 30, 1973

Stability constants for the reaction  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+} + \text{L}^{z-} \rightleftharpoons [\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_{2-n}(\text{L})^{2-z} + n\text{H}_2\text{O}$ , where  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$  represents *trans*-diaquo[*N,N'*-bis(2-pyridylmethylene)-1,3-diaminopropane]nickel(II) and L = ammonia, ethylamine, glycine, or *dl*-alanine, have been measured spectrophotometrically. The measured stability constants for ternary complex formation with ammonia ( $K_{\text{st}} = 175$ ) and ethylamine ( $K_{\text{st}} = 58$ ) are considerably smaller than those for glycine ( $K_{\text{st}} = 710$ ) and *dl*-alanine ( $K_{\text{st}} = 820$ ). This result suggests that the  $\alpha$ -amino acids achieve bidentate coordination by the displacement of a terminal chelate arm of the tetradentate ligand or a rearrangement of the tetradentate ligand so that *cis* coordination positions are available. The kinetics of the ternary complex formation with the four entering ligands have been measured by the stopped-flow technique. The addition of ammonia or ethylamine to the complex ion yields a single relaxation time, which is interpreted as the simple displacement of a coordinated water molecule. A fivefold increase in the rate constant for ammonia complexation compared to ethylamine indicates considerable SN2 character for these interactions. The much slower relaxation times observed for glycine or *dl*-alanine addition are interpreted as the chelation step which is hindered by a structural reorganization of the coordination sphere.

### Introduction

Ternary complex formation between a bound metal ion having available coordination positions and an additional ligand species has been implicated in a variety of biological processes.<sup>1-4</sup> For this reason considerable interest has been focused on kinetic studies of this type of interaction with simple metal chelates.<sup>5-16</sup> Kinetic studies of ternary systems have been based largely on nickel(II) chelates<sup>5-8</sup> since their characteristically slower reaction times are more readily measured. These studies have shown that the rate of solvent replacement from the coordination sphere is influenced greatly by the electron-donating effects of coordinated ligands.<sup>5,6</sup>

Recently, ternary complexation with the more labile copper(II)<sup>9-14</sup> and cobalt(II)<sup>15,16</sup> complexes has received attention. Pasternack, *et al.*,<sup>9,10</sup> examined the rates of ternary complex formation between mono(2,2'-bipyridine)copper(II) and a variety of entering ligands. The reaction of various complexed Cu(II) species with pyridine-2-azo-*p*-dimethylaniline (pada) has been reported by Cobb and Hague.<sup>14</sup> The chelation of the bidentate pada was observed to be kinetically hindered when *cis* coordination positions were not available

on the Cu(II) species. Mixed Cu(II) complexes containing serinate and histamine or ethylenediamine have been characterized kinetically by Sharma and Leussing.<sup>11,12</sup> In general, for ternary Cu(II) complexes with two different bidentate ligands, the stability constants for mixed-complex ( $\text{CuLL}'$ ) formation are comparable in magnitude to the constants for the bis species with one ligand ( $\text{CuL}_2$ ), giving rise to a mixture of labile species.

We report here an equilibrium and kinetic study of the ternary interaction between *trans*-diaquo[*N,N'*-bis(2-pyridylmethylene)-1,3-diaminopropane]nickel(II),<sup>17</sup>  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$ , and the four donors, ammonia, ethylamine, glycine, and *dl*-alanine. The chelate system  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$  offers several advantages for a study of ternary complex formation. The stereochemistry of  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$  has been established as a tetragonal six-coordinate complex with an essentially planar arrangement of the tetradentate ligand and two water molecules in axial positions. The substitution of other monodentate donors into the axial sites occurs readily in aqueous solution and does not disturb the planar coordination of the Schiff base ligand. The complex ion is stable toward hydrolysis over the pH range 3-11.<sup>18</sup> Above pH 11, the observed changes in the spectrum of  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$  could arise from a species containing coordinated hydroxide ion or a partially hydrolyzed ligand. Below pH 3,  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$  dissociates to yield free hexaaquanickel(II) by a first-order process with a half-time of 10-30 sec.<sup>18</sup> These times are some 100-fold longer than the kinetic processes reported in this study and present no interference.

### Experimental Section

**Materials.** The preparation of  $\text{Ni}(\text{pya}_2\text{tn})\text{Cl}_2 \cdot \text{H}_2\text{O}$  was described previously.<sup>17</sup> Other chemicals used in this study were reagent grade or equivalent. All solutions were prepared with degassed, triply distilled water, and were made 0.1 M in  $\text{KNO}_3$ . The concentrations of the ammonia and ethylamine solutions were determined by standard titrimetric procedures.

**Instrumentation.** The pH of all solutions was adjusted by the addition of KOH and  $\text{HNO}_3$  solutions. A Sargent digital pH meter, with a combination electrode calibrated against certified buffers, was used for pH measurements. All work reported in this paper was carried out in the pH range 8.6-11. Spectra of the reactant and

(17) T. G. Campbell and F. L. Urbach, *Inorg. Chem.*, **12**, 1836, 1840 (1973).

(18) F. L. Urbach, J. E. Stuehr, and D. T. Farrar, unpublished results, 1969.

\* To whom correspondence should be addressed at Case Western Reserve University.

- (1) B. L. Vallee, *Compr. Biochem.*, **1962**, *12*, 165 (1964).
- (2) A. S. Mildvan, *Advan. Chem. Ser.*, No. 100, 390 (1971).
- (3) H. Sigel and D. B. McCormick, *Accounts Chem. Res.*, **3**, 201 (1970).
- (4) E. T. Kaiser and B. L. Kaiser, *Accounts Chem. Res.*, **5**, 219 (1972).
- (5) R. K. Steinhaus and D. W. Margerum, *J. Amer. Chem. Soc.*, **88**, 441 (1966).
- (6) D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967).
- (7) H. Hoffman and E. Yeager, *Ber. Bunsenges. Phys. Chem.*, **74**, 641 (1970).
- (8) M. A. Cobb and D. N. Hague, *Trans. Faraday Soc.*, **68**, 932 (1972).
- (9) R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, **92**, 6146 (1970).
- (10) R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, **11**, 276 (1972).
- (11) V. S. Sharma and D. L. Leussing, *J. Chem. Soc. D*, 1278 (1970).
- (12) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 138 (1972).
- (13) H. Hauer, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, **93**, 4173 (1971).
- (14) M. A. Cobb and D. N. Hague, *J. Chem. Soc. D*, 192 (1971).
- (15) R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, **11**, 420 (1972).
- (16) J. P. Jones and D. W. Margerum, *Inorg. Chem.*, **8**, 1486 (1969).

Table I. Stability Constants<sup>a</sup> for
$$[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+} + \text{L}^{z-} \rightleftharpoons [\text{Ni}(\text{pya}_2\text{tn})\text{L}(\text{H}_2\text{O})_{2-n}]^{2-z} + n\text{H}_2\text{O}$$

L	pK <sub>a</sub>	K <sub>st</sub>	No. of determinations
Ammonia <sup>b</sup>	9.46	175 ± 50	13
Ethylamine <sup>c</sup>	10.67	58 ± 10	13
Glycine <sup>d</sup>	9.62	710 ± 100	10
Alanine <sup>e</sup>	9.86	820 ± 40	7

<sup>a</sup> At 25° and *I* = 0.1. <sup>b</sup> *M*<sup>0</sup> = 0.01–0.05 *M*, *L*<sup>0</sup> = 0.01–0.05 *M*, pH 9–11, 550 nm. <sup>c</sup> *M*<sup>0</sup> = 0.01–0.05 *M*, *L*<sup>0</sup> = 0.01–0.8 *M*, pH 10.3–10.8, 500 nm. <sup>d</sup> *M*<sup>0</sup> = 0.01–0.05 *M*, *L*<sup>0</sup> = 0.01–0.05 *M*, pH 8.7–9.0, 550 nm. <sup>e</sup> *M*<sup>0</sup> = 0.002–0.03 *M*, *L*<sup>0</sup> = 0.002–0.03 *M*, pH 10.5, 550 nm.

product solutions were measured with a Cary Model 14 recording spectrophotometer or a Beckman-Gilford spectrophotometer to ascertain optimum wavelengths for the kinetic studies and to measure the stability constants. The kinetic measurements at 25° were made with a Gibson-Durrum stopped-flow spectrophotometer under close-to-equilibrium conditions. Stopped-flow measurements at 500 or 550 nm were made for each reaction at a number of concentrations of *M*<sup>0</sup> and *L*<sup>0</sup>. The initial pH of each reactant solution was adjusted to the 10–11 range and the pH of the final solution was measured. The transmittance changes accompanying each reaction were displayed upon the screen of a storage oscilloscope and then photographed and enlarged. Logarithmic graphs of the changes in absorbance (or, for small effects, transmittance) were used to determine relaxation times. Only the close-to-equilibrium portions of the kinetic curves gave a linear plot. A computer program was written to solve the simultaneous equations necessary to calculate concentrations of the various species.

## Results

**Stability Constants.** The stability constants, *K*<sub>st</sub>, of the ternary complexes (abbreviation ML) formed between [Ni(py<sub>a</sub><sub>2</sub>tn)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (*M*) and glycine, ammonia, ethylamine, and alanine (*L*) were determined spectrophotometrically by a method similar to that described by McConnell and Davidson<sup>19</sup>

$$\frac{M^0 L^0}{\Delta A F} = \left( \frac{M^0 + L^0 - \overline{ML}}{F} \right) \frac{1}{l \Delta \epsilon} + \frac{1}{l \Delta \epsilon K_{st}} \quad (1)$$

in which *M*<sup>0</sup> and *L*<sup>0</sup> are the stoichiometric molarities of [Ni(py<sub>a</sub><sub>2</sub>tn)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> and the ligand, respectively,  $\overline{ML}$  is the equilibrium molarity of the complex,  $\Delta A$  is the change in the absorbance upon ligand addition, *l* is the cuvette length in centimeters, and  $\Delta \epsilon$  is the difference between the molar extinction coefficients of *M* and *ML*. The function *F* is a correction for the ionization of the weak acid and is given by  $(K_a + \overline{H})/K_a$ , where *K*<sub>a</sub> is the ionization constant at *I* = 0.1.

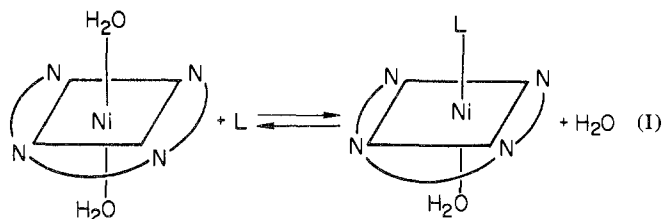
For each of the four systems studied, a number of solutions were prepared, differing in *M*<sup>0</sup> and *L*<sup>0</sup> and having a known, final pH. Absorbances of these solutions were obtained before and after mixing by means of a split compartment cuvette. From eq 1, a plot of  $M^0 L^0 / \Delta A F$  vs.  $(M^0 + L^0 - \overline{ML})/F$  will yield values for  $\Delta \epsilon$  and *K*<sub>st</sub>. The stability constants may be calculated from the intercept of this plot, or alternatively may be calculated from  $\Delta \epsilon$ , since  $\overline{ML} = \Delta A / l \Delta \epsilon$ . Since  $\overline{ML}$  is not known initially, successive approximations must be made until the value becomes constant for each solution. Convergence to constant values was typically achieved within 20 iterations using a Univac 1108 computer. (Between 7 and 12 points were used for each system.) Table I summarizes the measured stability constants. Values ranged from 58 and 175 for ethylamine and ammonia to 710–820 for the potentially bidentate ligands glycine and *dl*-alanine.

(19) H. McConnell and N. Davidson, *J. Amer. Chem. Soc.*, **72**, 3164 (1950).

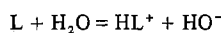
Table II. Kinetic Data

<i>M</i> <sup>0</sup> , <i>M</i>	<i>L</i> <sup>0</sup> , <i>M</i>	pH	1/ $\tau$ , sec <sup>-1</sup>	$\frac{\overline{M}}{1 + \beta} + \overline{L}$
(1) Ni(py <sub>a</sub> <sub>2</sub> tn) <sup>2+</sup> -Ammonia				
0.0750	0.1551	10.48	533	0.0817
0.0500	0.1034	10.54	468	0.0578
0.0500	0.1008	10.22	365	0.0520
0.0500	0.0504	10.07	233	0.0280
0.0500	0.0495	10.12	301	0.0280
0.0500	0.0495	9.82	257	0.0280
0.0500	0.0248	9.97	185	0.0333
0.0500	0.0124	9.84	187	0.0396
0.0375	0.0371	10.12	223	0.0235
0.0250	0.0252	10.24	213	0.0184
0.0250	0.0248	10.40	255	0.0183
0.0125	0.0159	10.55	269	0.0130
0.0125	0.0126	10.31	196	0.0117
0.0125	0.0124	10.44	148	0.0117
0.00625	0.00619	10.49	136	0.00716
(2) Ni(py <sub>a</sub> <sub>2</sub> tn) <sup>2+</sup> -Ethylamine				
0.0477	0.1445	10.46	101	0.0525
0.0477	0.1215	10.36	97.6	0.0452
0.0477	0.0983	10.31	79.0	0.0416
0.0477	0.0983	9.74	92.0	0.0405
0.0477	0.0492	10.46	74.5	0.0393
0.0239	0.0246	10.39	67.4	0.0229
0.0239	0.0231	10.31	56.8	0.0227
0.0119	0.0116	10.44	42.3	0.0124
(3) Ni(py <sub>a</sub> <sub>2</sub> tn) <sup>2+</sup> -Glycine				
0.0500	0.0500	9.38	39.0	0.0168
0.0375	0.0375	9.42	33.5	0.0141
0.0250	0.0250	9.67	29.1	0.0106
0.0125	0.0125	9.88	25.6	0.00687
0.00500	0.05000	10.20	22.5	0.00381
0.00250	0.00250	10.19	15.7	0.00236
0.00125	0.00125	10.31	13.2	0.00142
0.00125	0.000625	10.25	13.0	0.00117
0.00125	0.000313	10.28	15.0	0.00108
(4) Ni(py <sub>a</sub> <sub>2</sub> tn) <sup>2+</sup> -Alanine				
0.0500	0.0500	10.20	55.0	0.0143
0.0500	0.0500	9.87	46.8	0.0148
0.0250	0.0250	10.48	47.2	0.00952
0.0200	0.0188	10.80	43.9	0.00828
0.0125	0.0125	10.01	40.3	0.00645
0.00500	0.00600	10.76	34.7	0.00391
0.00250	0.00300	10.66	24.0	0.00243
0.00200	0.00250	10.77	26.9	0.00216

**Kinetics.** For each system studied, a single concentration- and pH-dependent relaxation time was observed, Table II. Half-times ranged from 2–15 msec for the ammonia and ethylamine systems to considerably longer times for glycine and *dl*-alanine (13–53 msec).<sup>20</sup> Shortest times (2–10 msec) were found for the ammonia reaction. The shortest of these approached the resolution of the stopped-flow instrument, accounting for the considerable scatter apparent in Figure 1. All data were consistent with the addition of a donor ligand to the chelate system, *i.e.*



(20) In some instances a much slower, second kinetic process was observed, with a transmittance change in a direction opposite to that found for reaction I. This effect was considerably smaller (<1% transmittance change) than that of the first step and was not studied in detail.



The expression for the relaxation time for (I) is given by

$$\frac{1}{\tau} = k_f \left[ \frac{\bar{M}}{1 + \beta} + \bar{L} \right] + k_r \quad (2)$$

The bars designate equilibrium concentrations of the indicated species, and  $\beta$ , a correction term for the rapid proton transfer, is  $K_w/[K_a(HL + OH)]$ . The forward and reverse rate constants are given by  $k_f$  and  $k_r$ , respectively. Where mechanism I applies, a plot of  $1/\tau$  vs. the concentration function of eq 2 yields values for  $k_f$  and  $k_r$  from the slope and intercept, respectively (Figure 1).

In a consideration of other mechanisms consistent with the data, an obvious alternative is mechanism II, in which the chelate system reacts with the protonated ligand. How-



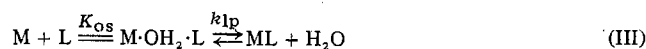
ever, the experimental data for the four systems did not correlate at all with the relaxation time expression for mechanism II. The data either scattered randomly or (for glycine) yielded a graph of negative slope. The data were also not consistent with a dual pathway mechanism involving both (I) and (II).

We also considered the possibility that two ligand molecules were adding to the chelate system and that we were in fact observing the second addition. This possibility is based on the fact that crystalline bis adducts,  $[Ni(py_2tn)(donor)_2]X_2$ , can be isolated from solutions containing an excess of the donor species. Using the spectral data for each system, we attempted to find a pair of stability constants consistent with bis-adduct formation. No consistent values of two stability constants could be found for any of the four systems; it can therefore be concluded that the observed relaxation effect is the first addition to yield a 1:1 complex. The fact that the ratio of forward and reverse rate constants returned the spectroscopic stability constants lends further weight to this conclusion.

The detailed interpretation of the results differs for the monodentate ligands as compared with the potentially bidentate ligands. As a consequence, the results for ammonia and ethylamine will be discussed separately from those for glycine and alanine.

## Discussion

**Monodentate Ligands.** For ammonia and ethylamine, the forward rate constants from Figure 1 are 7000 and 1500  $M^{-1} \text{ sec}^{-1}$ , respectively (see Table III). In both instances the ratio of slope to intercept,  $k_f/k_r$ , is numerically equal to the measured stability constant as given in Table I. Consequently, there is little doubt that a coordinated water molecule is being displaced by these ligands, with no further complications. The usual formulation of the Eigen-Tamm mechanism for complex formation *via* an outer-sphere complex intermediate may be represented by



where  $K_{os}$  is the outer-sphere complex association constant and  $k_{lp}$ , the ligand penetration rate constant, is the rate constant for the rate-determining step. The latter is related to the overall measured forward rate constant by  $k_f = K_{os}k_{lp}$ . The value of  $K_{os}$  depends on interacting charge types as well as statistical corrections. For the interaction between the divalent complex ion  $[Ni(py_2tn)(H_2O)_2]^{2+}$  and a neutral ligand,  $K_{os}$  is estimated to be  $0.17 M^{-1}$ . This value includes a statistical factor of  $1/3$  to account for the fact that only two of the six metal ion positions are available for coordina-

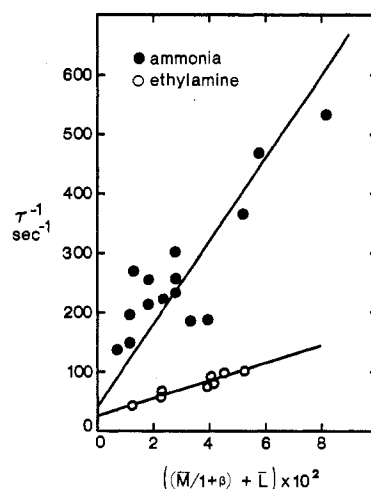


Figure 1. Concentration dependence of the relaxation time for the reaction of  $[Ni(py_2tn)(H_2O)_2]^{2+}$  with ethylamine and ammonia at  $25^\circ$  and  $I = 0.1$ . The solid lines are drawn with ratio of slope to intercept equal to the measured stability constant.

Table III. Summary of Results

Ligand	$K_{st}, M^{-1}$	$K_{12}, M^{-1}$	$10^{-3}k_f, M^{-1} \text{ sec}^{-1}$	$k_r, \text{ sec}^{-1}$	$10^{-4}k_{lp}, \text{ sec}^{-1}$	$k_{23}, \text{ sec}^{-1}$
Glycine	710	150	5.7	8		38
Alanine	820	150	8.9	11		59
Ammonia	175		7.0	40	4	
Ethylamine	58		1.5	26	0.9	

<sup>a</sup> For mechanism IV. <sup>b</sup> Calculated from  $k_{lp} = k_f/K_{os}S$  where  $K_{os} = 0.5$  and  $S$  (statistical factor) =  $1/3$  for  $[Ni(py_2tn)(H_2O)_2]^{2+}$ .

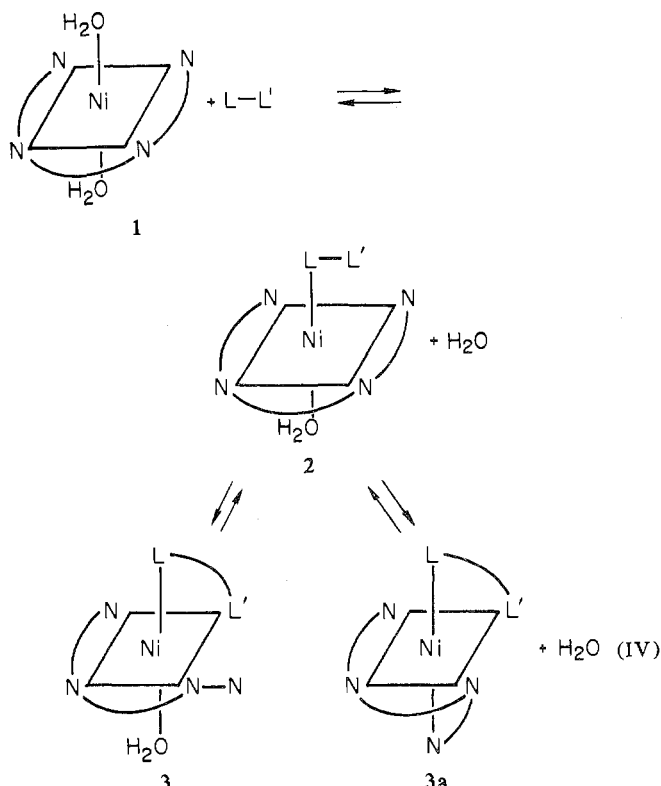
tion. With this value, one estimates  $k_{lp}$  to be  $4 \times 10^4$  and  $0.9 \times 10^4 \text{ sec}^{-1}$  for ammonia and ethylamine, respectively. These two values of  $k_{lp}$  are clearly different (see Figure 1) by a factor of almost 5. The presence of the chelate system in the  $Ni(py_2tn)^{2+}$  complex will change the inherent exchange rate for the remaining solvent molecules as compared to hexaaquonickel(II).<sup>5,6,21,22</sup> Nmr studies have shown that the exchange rates increase dramatically when nonaromatic nitrogen bases constitute part of the inner coordination sphere<sup>21</sup> and that the increase is much smaller for aromatic nitrogen-containing systems.<sup>22</sup> It is not possible therefore to state which of the two ligand penetration rate constants we obtain is the "normal" value. One possible explanation for the fivefold difference is that complexation reaction I has considerable SN2 character; that is, the presence of the chelate system has changed not only the rate but also the nature of the displacement of the axial waters. Similar differences were noted by Sharma and Leussing<sup>12</sup> for ternary complexes with the copper-serinate system. An explanation in terms of a conventional SN1 mechanism is not easily made.

**Bidentate Ligands.** For the complexation reactions with glycine and alanine, several interesting features were noted. First, the half-times were considerably longer (13–53 msec) compared to ammonia and ethylamine. Second, in most instances the transmittance changes accompanying the reaction were quite large (2–20% changes in transmittance). Third, as noted earlier, the stability constants are much larger (710 and 820  $M^{-1}$ , respectively) than those for ammonia and ethylamine. These observations suggest that the

(21) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).

(22) M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

potentially bidentate ligands are forming a chelate ring with the Ni(II) ion. Chelation of the amino acid ligand can occur only if one of the pyridine donors of the  $\text{pya}_2\text{tn}$  ligand is displaced or if the tetradentate ligand rearranges to a structure which leaves cis positions available on the complex ion. Our data cannot distinguish between possibilities. Finally, the plots of  $1/\tau$  vs. the concentration function for these systems are nonlinear (Figure 2). The initial steep portions of the graphs bend at high concentrations, apparently approaching a plateau. All of these observations are consistent with the stepwise formation of a chelate according to (IV), where  $\text{L-L}' = \text{NH}_2\text{CHR}\text{COO}^-$ .



There are two relaxation times associated with (IV): one ( $\tau_1$ ) associated with the complexation step 1-2 via either the amino or the acetate group on the amino acid and a slower one ( $\tau_2$ ) for the step 2-3 or 2-3a. The two times are given by

$$\frac{1}{\tau_1} = k_{12} \left[ \frac{\bar{M}}{1 + \beta} + \bar{L} \right] + k_{21} \quad (3)$$

and

$$\frac{1}{\tau_2} = \frac{K_{12}k_{23} \left[ \frac{\bar{M}}{1 + \beta} + \bar{L} \right]}{1 + K_{12} \left[ \frac{\bar{M}}{1 + \beta} + \bar{L} \right]} + k_{32} = \frac{k_{2f} \left[ \frac{\bar{M}}{1 + \beta} + \bar{L} \right]}{1 + K_{12} \left[ \frac{\bar{M}}{1 + \beta} + \bar{L} \right]} + k_{2r}$$

where  $k_{2f}$  equals  $K_{12}k_{23}$  and  $K_{12}$  is the equilibrium constant for step 1-2 of mechanism IV.

The relaxation time ( $\tau_1$ ) for the first group attaching to the nickel chelate will be faster than the one we observed for the amino acids. If the  $\text{NH}_2$  group complexes first, the relaxation time will be comparable to that observed for  $\text{NH}_3$

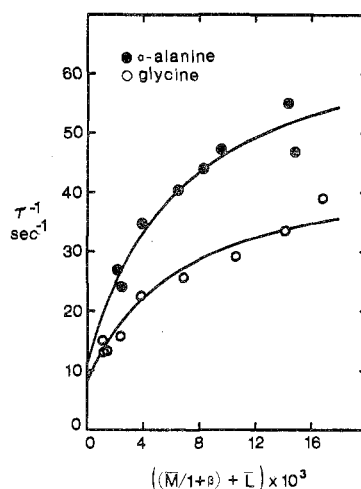


Figure 2. Concentration dependence of the relaxation time for the reaction of  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})_2]^{2+}$  with glycine and  $\alpha$ -alanine at  $25^\circ$  and  $I = 0.1$ . The solid curves were calculated from eq 4.

or ethylamine. If acetate complexes first, the relaxation time will be shorter still, since the dissociation rate constant for penta-aquanickel acetate<sup>23</sup> is quite large:  $5 \times 10^3 \text{ sec}^{-1}$ . As a consequence, the relaxation time for hexaaquanickel(II) and acetate can be no longer than  $200 \mu\text{sec}$  and becomes shorter with increasing concentration. Although we were able to measure an equilibrium spectral difference when acetate was mixed with the chelate system, the same solutions in the stopped-flow instrument showed no kinetic effect corresponding to this spectral change. This indicates a reaction that takes place much faster than  $10^{-3} \text{ sec}$ . Unfortunately we cannot distinguish between the two kinetic possibilities.

A graph of  $1/\tau_2$  should begin with a linear portion at low concentrations, with slope  $k_f$  and intercept  $k_r$ , whose ratio equals the measured stability constant. At higher concentrations, the term in the denominator of eq 4 will become significant compared to unity, and the curve will deviate from linearity. This is exactly the behavior displayed in Figure 2 for both glycine and alanine. Analysis of the data by means of the mechanism yields quite similar although not identical results for the two amino acids. The values of  $k_f$  and  $k_r$  are somewhat larger for alanine. The curvature observed is consistent with the same preequilibrium constant for both systems:  $K_{12} = 150 \text{ M}^{-1}$ .

The results obtained with the two amino acids are not therefore comparable to those for the monodentate ligands for which the chelate system remains intact. In fact, there are relatively few systems in the literature to which a detailed comparison can be made. Recently Cobb and Hague<sup>14</sup> have reported the kinetics of ternary complex formation between various  $\text{CuL}$  species with the ligand pada. They noted that when two cis positions remained in the binary  $\text{CuL}$  complex, the pada reacted with a rate constant comparable to that for free  $\text{Cu}^{2+}$ . When, however, only trans positions were available (e.g., in  $\text{Cu}(\text{gly})_2(\text{H}_2\text{O})_2$ ), the rate constants were reduced by some 2 orders of magnitude. Cobb and Hague attributed this slowdown to the rate-determining reorganization of the ligands in the coordination sphere such that two cis positions were generated.

**Registry No.**  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})\text{L}]^{2+}$  (L = ammonia), 39262-40-3;  $[\text{Ni}(\text{pya}_2\text{tn})(\text{H}_2\text{O})\text{L}]^+$  (L = glycine), 37339-50-7;  $[\text{Ni}$

(23) H. Hoffman and E. Yeager, unpublished data, cited in Saline Water Conversion Report, Department of the Interior, U. S. Government Printing Office, Washington, D. C. 1968.

(pya<sub>2</sub>tn)(H<sub>2</sub>O)L]<sup>2+</sup> (L = ethylamine), 39262-41-4; [Ni(py<sub>2</sub>a<sub>2</sub>-tn)(H<sub>2</sub>O)L]<sup>+</sup> (L = alanine (*dl*)), 37339-51-8; [Ni(py<sub>2</sub>a<sub>2</sub>tn)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 39262-42-5.

**Acknowledgment.** This work was supported in part by research grants to J. E. S. from the National Institutes of Health (Grant GM 13116) and Department of the Interior

(OSW Grant 14-1273). D. T. F. wishes acknowledge support from the National Science Foundation as a participant in the NSF College Teachers Summer Research Program. The authors are grateful to Dr. Mark Jones at Vanderbilt University for making his stopped-flow apparatus available for some of the measurements and to Mr. Bruce Boyett for his assistance in collecting some of the data.

Contribution from the Chemistry Department,  
Trinity University, San Antonio, Texas 78284

## Kinetics and Mechanism of the Reactions of Substituted 8-Mercaptoquinoline Complexes of Nickel(II) with Some Alkyl Halides

J. CURTIS SHOUP and JOHN A. BURKE, Jr.\*

Received February 20, 1973

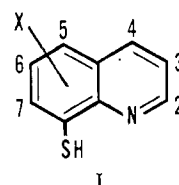
A series of X-8-mercaptoquinoline complexes of nickel(II) (X = 5-chloro, 5-bromo, 6-methoxy, 5-nitro, 7-methyl, 2-methyl) has been synthesized. The rates of reaction of these complexes with benzyl bromide and methyl iodide have been determined as a function of temperature. The enthalpies and entropies of activation for the reactions of these complexes with benzyl bromide are in the ranges 10–16 kcal/mol and –28 to –38 eu, respectively. The rates of reaction of the 5- and 6-substituted complexes with methyl iodide and benzyl bromide were correlated with the substituent by means of the Hammett equation.  $\rho$  was found to be –2.9 for the reactions of these complexes with both of the alkyl halides studied. The results have been interpreted on the basis of a mechanism involving the prior coordination of the alkyl halide to the nickel ion.

In investigations on the nature of homogeneous metal catalysis, one approach to the elucidation of these mechanisms involves the study of kinetic alterations arising from metal coordination to one of the organic moieties. A specific system utilizing this approach is the alkylation of coordinated mercaptans where one of the simplest and most completely studied reactions is the alkylation of the nickel complexes of 2-aminoethanethiol.<sup>1,2</sup> The reaction of bis(2-aminoethanethiol)nickel(II) with either methyl iodide or benzyl halides yields the 2:1 thioether complexes.<sup>1,2</sup> More recently, Burke and Brink extended this area by showing that bis(8-mercaptoquinoline)nickel(II), Ni(8-mq)<sub>2</sub>, reacts with alkyl halides under mild conditions.<sup>3</sup> The reaction of Ni(8-mq)<sub>2</sub> with methyl iodide yields bis(5-methyl-8-mercaptoquinoline)nickel(II) iodide as a reaction product. The magnetic moment of 3.18 BM for this dimethylated product reported by Lindoy, *et al.*, is consistent with the spin-free octahedral configuration anticipated if the iodide ions are coordinated to the metal.<sup>4</sup>

The kinetic parameters for the reactions involving 8-mercaptoquinoline and 2-aminoethanethiol as ligands show close similarities suggesting that the reactions proceed *via* the same mechanism. There is evidence, in the case of bis(*N*-alkyl-2-aminoethanethiol)nickel(II), to suggest that a preequilibrium involving the metal ion and the alkyl halide may be considered to polarize the carbon-halogen bond resulting in an enthalpy of activation for the reaction which is lower than anticipated for an SN<sub>2</sub> attack at a saturated carbon atom.<sup>5</sup>

By using the nickel complexes of appropriately substituted 8-mercaptoquinolines it has been possible to study the effect of substituents on the rate of alkylation of coordinated mer-

captans. The nickel complexes of 5-chloro-8-mercaptoquinoline, 5-Cl-8-mq, 5-bromo-8-mercaptoquinoline, 5-Br-8-mq, 5-nitro-8-mercaptoquinoline, 5-NO<sub>2</sub>-8-mq, 6-methoxy-8-mercaptoquinoline, 6-CH<sub>3</sub>O-8-mq, 7-methyl-8-mercaptoquinoline, 7-CH<sub>3</sub>-8-mq, and 2-methyl-8-mercaptoquinoline, 2-CH<sub>3</sub>-8-mq, have been synthesized. The ligands used to prepare these complexes are shown in I. Reaction rates of these complex-



es with benzyl bromide and methyl iodide in chloroform have been determined spectrophotometrically as a function of temperature. For those complexes containing a substituent in the 5 or 6 position, the reaction rates have been correlated with the substituent by means of the Hammett equation.<sup>6</sup> Substituents in the 2 or 7 position are used to provide information regarding steric effects on both the geometry of the complex and the rates of alkylation.

### Experimental Section

**Preparation of the Ligands.** Whenever feasible, the mercaptans were oxidized by dilute hydrogen peroxide to the disulfides. Such a conversion facilitated storage and purification of the ligand. Reduction of the disulfide to the mercaptan was easily accomplished with hypophosphorous acid. The disulfides were prepared according to modified published procedures and are summarized below.

**5-Bromo-8-mercaptoquinoline and 5-Chloro-8-mercaptoquinoline.** The 5-bromo-8-mercaptoquinoline was prepared from 5-bromoquinoline<sup>7</sup> and the 5-chloro-8-mercaptoquinoline was prepared from 5-chloroquinoline.<sup>8</sup> The 5-haloquinolines were readily obtained from

(1) D. H. Busch, J. A. Burke, D. C. Jicka, M. C. Thompson, and M. L. Morris, *Advan. Chem. Ser.*, No. 37, 143 (1963).

(2) E. L. Blinn and D. H. Busch, *Inorg. Chem.*, 7, 820 (1968).

(3) J. A. Burke and E. C. Brink, *Inorg. Chem.*, 8, 386 (1968).

(4) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, 19, 1391 (1966).

(5) E. L. Blinn and D. H. Busch, *J. Amer. Chem. Soc.*, 90, 4280 (1968).

(6) H. H. Jaffe, *Chem. Rev.*, 53, 191 (1953).

(7) J. Bankovskis, D. Zaruma, and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 100 (1963).

(8) J. Bankovskis, Z. U. Misulovira, J. Circule, and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 134 (1962).