

one-electron transfer in a single activated state. Two-electron transfer is commonly proposed for periodate oxidation of organic substrates,<sup>19</sup> for iodide,<sup>20</sup> and for one pathway in the Fe(II)<sup>3</sup> reactions. The transfer of electrons from two chromium(III) ions to I(VII) precludes the formation of a high-energy free-radical I(VI). The formation of I(VI) is probably avoided, in the whole course of this reaction, if Cr(IV) is oxidized in a single step by I(VII) to Cr(VI).

Oxidation of chromium(III) by periodate, based on the validity of the above mechanism, is in accord with the hypothesis that periodate is an inner-sphere oxidant. In this reaction the bridging ligand is supplied by the reductant. An outer-sphere mechanism, on the other hand, may be ruled out on two accounts: (i) the second-order dependence on [Cr(III)] and (ii) the difference in the reactivity between hydroxo- and aquochromium(III) ions. Outer-sphere reactions are generally

of the first order in each reactant, and hydroxo and aquo species of a given complex react with comparable rates with a common reactant by an outer-sphere mechanism.<sup>21</sup>

An alternative reaction pathway is to propose that mixed inner- and outer-sphere mechanisms are operative. The inner-sphere electron transfer will be from chromium(III) in [Cr-(OH)-L]<sup>+</sup> to I(VII) and a concurrent outer-sphere electron transfer from a second chromium(III) ion.

In conclusion the chromium(III)-periodate reaction exhibited an unusual second-order dependence on [Cr(III)]. The reaction does not contradict the hypothesis that periodate is an inner-sphere oxidant as, at least, one electron is transferred via an inner-sphere pathway to I(VII). Hydroxochromium(III) ion is the first entering chromium(III) as it is capable of bridging the two reactants via its coordinated hydroxide ligand.

Registry No. Cr<sup>3+</sup>, 16065-83-1; IO<sub>4</sub><sup>-</sup>, 15056-35-6.

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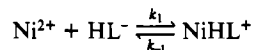
Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

## Complexation Kinetics and Equilibria of Nickel(II) with Vanillomandelic, Mandelic, and Thiolactic Acid Ligands

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The complexation reactions of Ni<sup>2+</sup> with the monovalent bidentate ligands vanillomandelic, mandelic, and thiolactic acids were studied at 25 °C and ionic strength 0.5 M (KNO<sub>3</sub>) by temperature-jump and stopped-flow methods. The formation rate constants determined for the reaction



were  $(3.64 \pm 0.39) \times 10^3$ ,  $(4.93 \pm 0.56) \times 10^3$ , and  $(7.66 \pm 0.52) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  for vanillomandelic acid, mandelic acid, and thiolactic acid, respectively. Stability constants for the formation of the metal mono complexes were determined by utilizing the Bjerrum titration technique. The values obtained for  $K_{\text{NiHL}} = [\text{NiHL}^+]/[\text{Ni}^{2+}][\text{HL}^-]$  were  $32.93 \pm 8.66$  (Ni<sup>2+</sup>-vanillomandelic acid),  $45.46 \pm 8.07$  (Ni<sup>2+</sup>-mandelic acid), and  $56.58 \pm 10.63 \text{ M}^{-1}$  (Ni<sup>2+</sup>-thiolactic acid). The kinetics of complex formation is discussed in terms of two different rate-determining steps, sterically controlled substitution and internal hydrogen bonding, as the results do not support the more usual dissociative substitution mechanism on nickel(II).

### Introduction

In the field of solution kinetics, Ni<sup>2+</sup> is one of the more extensively investigated transition-metal ions. The attention paid to nickel(II) is due not only to general interest in the kinetics of metal-complexation reactions, but also to the fact that the rate constants for nickelous ion substitution fall within a convenient time range. Few surprises have resulted from these studies; usually the formation of a mono complex follows the multistep Eigen mechanism,<sup>1</sup> in which an incoming ligand replaces one or more coordinated water molecules depending on its denticity. The overall rate is not determined by ligand characteristics but by the rate of loss of the first water molecule from the inner-sphere coordination shell.

Deviations from this "normal" substitution, in which the rate constants obtained are lower than those predicted by the Eigen mechanism, have been attributed to processes involving rate-determining chelate ring closure (sterically controlled substitution),<sup>2,3</sup> steric hindrance,<sup>4,5</sup> protonated ligands,<sup>3,6</sup> and,

in some instances, ligands in which the reactive site is blocked due to internal hydrogen bonding.<sup>6,7</sup>

Abnormally low rate constants have been obtained for Ni<sup>2+</sup> complexation reactions with the monovalent bidentate chelates

(2) Kowalak, A.; Kustin, K.; Pasternack, R. F.; Petrucci, S. *J. Am. Chem. Soc.* **1967**, *89*, 3126.

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(4) Turan, T. S. *Inorg. Chem.* **1974**, *13*, 1584.

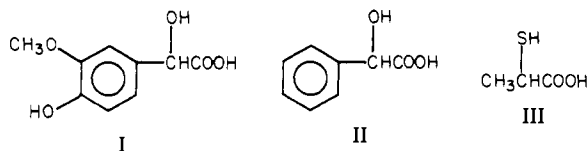
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glycolic,<sup>8</sup> lactic,<sup>9</sup> and salicylic<sup>7,10</sup> acids, where coordination occurs at the COO<sup>-</sup> and OH groups. The lower reaction rates for these complexes have been explained in terms of rate-determining ring closure<sup>8-10</sup> and more recently for the Ni<sup>2+</sup>-salicylate mono complex reaction, by internal H bonding.<sup>7</sup> For more information about the formation kinetics of such complexes, the present investigation of nickel complexation was carried out with vanillomandelic (I), mandelic (II), and thiolactic (III) acids. With vanillomandelic and mandelic acids,



bidendate Ni<sup>2+</sup> chelation occurs through coordination of the carboxylic and  $\alpha$ -hydroxyl groups. The effect of replacing the hydroxy group by the more acidic thiol group was studied in the Ni<sup>2+</sup>-thiolactic acid complexation reaction.

All temperature-jump and stopped-flow experiments were performed at low pHs (3–4.5) to avoid possible interference from the NiOH<sup>+</sup> species. Equilibrium experiments were carried out with the Bjerrum technique<sup>11</sup> since stability constants for the formation of the complexes studied were not available.

### Experimental Section

Inorganic chemicals such as Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and KNO<sub>3</sub> were obtained from the Fisher Scientific Co. and used without further purification. Doubly distilled water was used in all solution preparations. EDTA titrations were carried out to determine the Ni<sup>2+</sup> concentration in the stock solutions.

The organic chemicals vanillomandelic, mandelic, and thiolactic acids were from Sigma Chemicals Co., J. T. Baker Chemicals Co., and Aldrich Chemicals Co., respectively. Methyl orange and methyl red from Eastman Industries were used as indicators. The concentrations of the ligand stock solutions were determined by potentiometric titration with sodium hydroxide reagent standardized with 0.1 N potassium hydrogen phthalate. In the test solutions, metal concentrations were generally kept in excess of the ligand to avoid the formation of higher order species (i.e., Ni(HL)<sub>2</sub>); however, a number of runs where [metal]<sub>0</sub> < [ligand]<sub>0</sub> were made to check for any anomalies. The pH of the test solutions was adjusted with dropwise addition of NaOH or HNO<sub>3</sub>. Ionic strength was maintained at 0.5 M with KNO<sub>3</sub>. pH readings, taken on a Radiometer TTA3 pH meter or on an Orion Research Digital Ionalyzer, Model 801A, were converted to H<sup>+</sup> concentrations by dividing the measured hydrogen activity by  $\gamma_{\pm} = 0.692$  obtained from the Davies<sup>12</sup> equation.

Spectral analysis was carried out on a Beckman Model-25 spectrophotometer. Kinetics experiments were performed at 25.0 ± 0.1 °C with temperature-jump and stopped-flow apparatus previously described.<sup>13,14</sup> Data was collected either as photographs of stored oscilloscope traces or recorded digitally on Texas Instruments 733 ASR terminal magnetic cassette tapes by a Biomation 610 B transient recorder equipped with a Datacap Model B103 interface. Rate constant determinations were performed through the use of a PDP-10 computer system and a Charles River Data System MP 211 computer.

Bjerrum titrations were done by using a 100-mL capped double-walled cell. Solutions were thermostated at 25 ± 0.1 °C by circulating constant-temperature water through the double wall. All titrations were done under argon.

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Table I. Equilibrium Data at 25 °C<sup>a</sup>

ligand	pK <sub>a1</sub> <sup>b</sup>	pK <sub>a1</sub> <sup>c</sup>	pK <sub>a2</sub> <sup>c</sup>	K <sub>NiHL</sub> <sup>b,e</sup>	K <sub>NiHL</sub> <sup>d</sup>
vanillomandelic acid	3.39 ± 0.04	3.42 <sup>f</sup>		32.93 ± 8.66	30.43 ± 8.41
mandelic acid	3.35 ± 0.03	3.40 <sup>f</sup>		45.46 ± 8.07	41.24 ± 10.91
thiolactic acid	3.55 ± 0.04	3.54 <sup>g</sup>	10.00 <sup>g</sup>	56.58 ± 10.63	63.55 ± 18.23

<sup>a</sup> Indicator, K<sub>In</sub><sup>h</sup>: methyl orange, 3.47 × 10<sup>-4</sup>;<sup>i</sup> methyl red, 1.00 × 10<sup>-5</sup>.<sup>j</sup> <sup>b</sup> Determined by Bjerrum titration. <sup>c</sup> Published values. <sup>d</sup> Determined from k<sub>1</sub>/k<sub>-1</sub>. <sup>e</sup> K<sub>NiHL</sub> = [NiHL<sup>+</sup>]/[Ni<sup>2+</sup>][HL<sup>-</sup>]. <sup>f</sup> Klingenberg, J. J.; Knecht, D. S.; Harrington, A. F.; Meyer, R. L. *J. Chem. Eng. Data* **1978**, *23*, 327. <sup>g</sup> Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977; Vol. 3. <sup>h</sup> K<sub>In</sub> = [H<sup>+</sup>][In<sup>-</sup>]/[HIn]. <sup>i</sup> Kolthoff, I. M. *J. Phys. Chem.* **1930**, *34*, 1466.

### Results

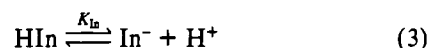
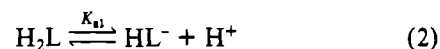
The experimentally determined pK<sub>a</sub> values for the dissociation of the carboxylic proton from the three ligands studied were in good agreement with published results.<sup>15</sup> The stability constants determined by the Bjerrum method for the formation of the nickel mono complexes and the acidity constants are given in Table I.

For the Ni<sup>2+</sup>-vanillomandelic acid and Ni<sup>2+</sup>-mandelic acid systems, the potentiometric titration curves for the metal-ligand solutions showed the loss of a single proton upon complex formation. In the case of the Ni<sup>2+</sup>-thiolactic acid system, however, a second deprotonation (assigned to the thiol group, pK<sub>a2</sub> = 10.00) occurred during complex formation at pHs above 5.00.

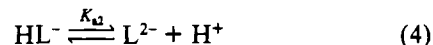
The relaxation results for the three systems (given in Table II) were found to be consistent with the simple scheme



The rapid equilibria involved in this scheme are for the vanillomandelic and mandelic acid systems



For the thiolactic acid system the second deprotonation of the thiol group occurs in the pH range studied, and the reaction



must be included in the overall scheme. In eq 2–4, H<sub>2</sub>L, HL<sup>-</sup>, and L<sup>2-</sup> denote the protonated, singly deprotonated, and fully deprotonated forms of the ligands; HIn and In<sup>-</sup> denote the protonated and deprotonated indicator species.

Initial consideration of a scheme which included the interaction of Ni<sup>2+</sup> with H<sub>2</sub>L to form NiHL<sup>+</sup> resulted in large relative errors (30–50%) for the associated rate constants. As other studies indicate that the fully protonated ligand is relatively unreactive,<sup>3</sup> this pathway was not considered further.

The relaxation expression for eq 1 is

$$\frac{1}{\tau} = k_1 \left( \frac{[\text{Ni}^{2+}]}{\alpha} + [\text{HL}^-] \right) + k_{-1} \quad (5)$$

where

$$\alpha = 1 + \frac{K_{a2}}{[\text{H}^+]} + \frac{[\text{H}^+]}{K_{a1}} - \frac{\beta[\text{HL}^-]}{K_{a1}} + \frac{\beta[\text{L}^{2-}]}{[\text{H}^+]} \quad (6)$$

- (15) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1977; Vol. 3.

$$\beta = \frac{[\text{H}^+]/K_{a1}}{1 + \frac{[\text{HL}^-]}{K_{a1}} + \frac{[\text{In}^-]}{K_{\text{In}} + [\text{H}^+]}} \quad (7)$$

for the vanillomandelic and mandelic acid systems and

$$\beta = \frac{1 + \frac{2[\text{H}^+]}{K_{a1}}}{1 + \frac{2[\text{HL}^-]}{K_{a1}} + \frac{[\text{In}^-]}{K_{\text{In}} + [\text{H}^+]}} \quad (8)$$

for the thiolactic acid system, and the square brackets designate the equilibrium concentrations of the different species.

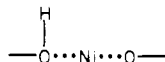
Plots of  $1/\tau$  vs.  $([\text{Ni}^{2+}]/\alpha + [\text{HL}^-])$  resulted in straight lines with slopes of  $k_1$  and intercepts of  $k_{-1}$ . These plots for the  $\text{Ni}^{2+}$ -vanillomandelic acid,  $\text{Ni}^{2+}$ -mandelic acid, and  $\text{Ni}^{2+}$ -thiolactic acid complexes are shown in Figures 1–3. The  $k_1$  and  $k_{-1}$  values are given in Table III.

As a check of the validity of the stability constants determined by the Bjerrum method, an iterative method was carried out where the stability constant value calculated from the ratio  $k_1/k_{-1}$  was used in the determination of a new set of equilibrium concentrations. This procedure was continued until the stability constant calculated from  $k_1/k_{-1}$  coincided with that used to determine the equilibrium concentrations. The results from these calculations are given in Table I.

### Discussion

The mono complex formation constants calculated by using the iterative procedure are in good agreement with those determined by the Bjerrum method. These values, which cover the range 30.43–63.55  $\text{M}^{-1}$ , are greater than the stability constants for simple nickel-monocarboxylic acid complexes (i.e., 1–10  $\text{M}^{-1}$ )<sup>15</sup> and are consistent with literature values for other nickel- $\alpha$ -hydroxycarboxylic acid complexes.<sup>15</sup> Greater stability would be expected when chelation of the metal ion involves coordination at the  $\alpha$ -hydroxy or  $\alpha$ -thiol groups as well as at the carboxylic groups.

Both the titration and kinetics analyses indicate that bidentate coordination of  $\text{Ni}^{2+}$  by vanillomandelic and mandelic acids occurs without the loss of the second proton from the  $\alpha$ -hydroxyl group. Though this type of chelation is somewhat atypical, retention of the proton of a coordinating hydroxyl moiety has been known to occur for a number of nickel complexes.<sup>6,8,9,16</sup> Moreover, the existence of a stable complex with



coordination has been shown from recent X-ray crystallographic studies.<sup>17</sup>

For the  $\text{Ni}^{2+}$ -thiolactic acid complex, displacement of the thiol proton can occur at higher pHs due to the greater acidity of the SH group. However, under the present experimental conditions of very low pH, formation of the  $\text{NiL}$  species is negligible.

For metal ion complexation that proceeds by a "normal" dissociative mechanism,<sup>1</sup> the forward rate constant,  $k_1$ , is equal to the product of the ion-pair formation constant,  $K_{\text{ip}}$ , and the water-exchange rate constant for the particular metal ion,  $k_0$ . For a 2:1 electrolyte,  $K_{\text{ip}}$  has been calculated from the Eigen-Fuoss<sup>18</sup> equation to be 2  $\text{M}^{-1}$ . For the nickelous ion,  $k_0$  is about  $3 \times 10^4 \text{ s}^{-1}$ ,<sup>3</sup> thus, for Ni(II) substitution, a value

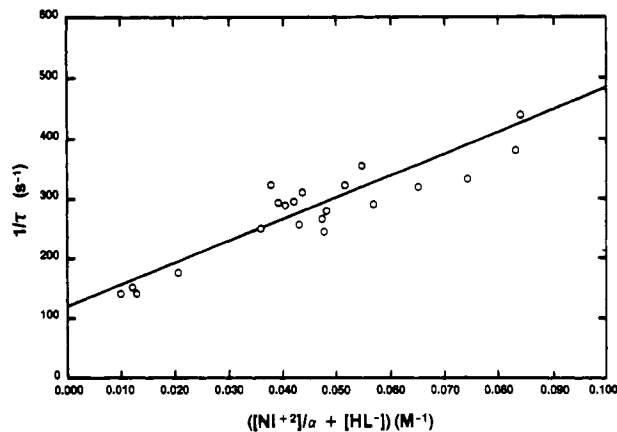


Figure 1. Plot of  $1/\tau_{\text{obsd}}$  vs.  $([\text{Ni}^{2+}]/\alpha + [\text{HL}^-])$  for  $\text{Ni}^{2+}$ -vanillomandelic acid complexation. (The  $\text{HL}^-$  term designates the complexing form of the ligand.) The straight line was obtained by least-squares data analysis.

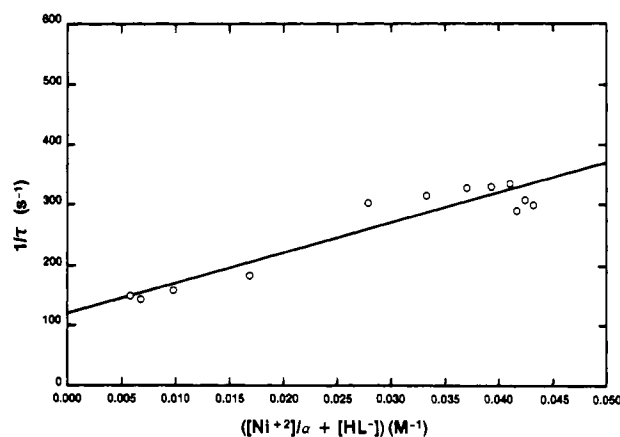


Figure 2. Plot of  $1/\tau_{\text{obsd}}$  vs.  $([\text{Ni}^{2+}]/\alpha + [\text{HL}^-])$  for  $\text{Ni}^{2+}$ -mandelic acid complexation. (The  $\text{HL}^-$  term designates the complexing form of the ligand.) The straight line was obtained by least-squares data analysis.

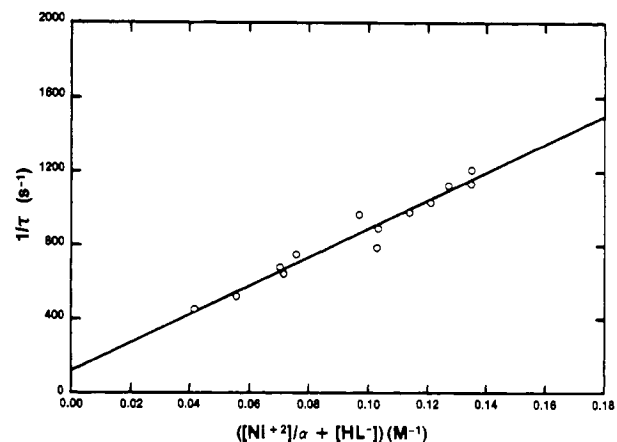


Figure 3. Plot of  $1/\tau_{\text{obsd}}$  vs.  $([\text{Ni}^{2+}]/\alpha + [\text{HL}^-])$  for  $\text{Ni}^{2+}$ -thiolactic acid complexation. (The  $\text{HL}^-$  term designates the complexing form of the ligand.) The straight line was obtained by least-squares data analysis.

around  $6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_1$  is expected.

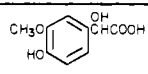
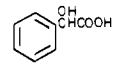
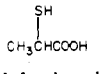
The forward rate constant values obtained in this study for nickel complexation with vanillomandelic, mandelic, and thiolactic acids are 8–16 times smaller than the  $k_1$  predicted for normal dissociative substitution. There are two mechanisms which can explain these low complexation rate constants. One is the sterically controlled substitution mechanism in which the rate-determining step is chelate ring closure.<sup>2,3</sup> The

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(17) Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *1*, 113.

(18) (a) Eigen, M. Z. *Phys. Chem. (Frankfurt)* **1954**, *1*, 176. (b) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

Table II. Relaxation Data<sup>a</sup> for Ni<sup>2+</sup> Complexation with Vanillic, Mandelic, and Thiolactic Acids at 25 °C and  $\mu = 0.5$  M

ligand	pH	$10^2 \times [Ni^{2+}]_0,^b$ M	$10^2 \times [HL^-]_0,^b$ M	$10^2 \times 1/\tau, s^{-1}$
 vanillic acid	3.51	5.00	1.00	2.57
	3.51	5.00	0.80	2.95
	3.50	5.00	0.60	2.89
	3.49	5.00	0.50	2.95
	3.50	5.00	1.20	3.11
	3.50	4.00	1.20	2.50
	3.52	2.00	1.20	1.77
	3.51	1.00	1.20	1.41
	3.51	0.90	1.20	1.52
	3.51	0.60	1.20	1.42
	3.51	6.00	1.20	3.22
	3.48	9.00	1.20	4.78
	3.81	6.00	1.20	3.55
	3.76	4.00	1.20	3.22
	4.25	5.00	1.20	2.45
	4.19	4.00	1.20	2.93
	4.21	5.00	0.50	2.66
4.21	7.00	1.20	3.20	
4.26	8.00	1.20	3.33	
4.21	9.00	1.20	3.81	
4.51	5.00	1.20	2.79	
4.52	6.00	1.20	2.91	
4.50	9.00	1.20	4.39	
 mandelic acid	3.01	5.00	2.80	3.28
	2.99	5.00	1.00	3.02
	3.00	6.00	1.00	3.15
	3.24	6.00	1.00	3.07
	3.19	5.00	2.00	3.30
	3.20	5.00	3.00	3.34
	3.51	5.00	1.00	2.89
	3.51	5.00	2.00	2.99
	3.53	3.00	0.05	1.83 <sup>c</sup>
	3.51	1.00	0.50	1.58 <sup>c</sup>
 thiolactic acid	3.54	1.00	0.10	1.45 <sup>c</sup>
	3.50	1.00	0.05	1.48 <sup>c</sup>
	3.53	10.00	8.00	7.86
	3.48	10.00	5.00	11.17
	3.50	10.00	9.00	9.59
	3.56	8.00	8.00	7.45
	3.82	10.00	6.00	9.78
	3.73	10.00	4.00	12.10
	3.70	8.00	4.00	8.87
	3.94	6.00	4.00	6.79
3.98	10.00	4.00	11.30	
4.00	8.00	2.00	10.36	
3.95	5.00	2.00	6.45	
3.99	4.00	2.00	5.20	
3.98	4.00	4.00	4.51	

<sup>a</sup> The values of  $\tau$  were obtained by averaging at least five experimental values. The deviations were less than 10% in these averaged relaxation times. <sup>b</sup> The subscript refers to total stoichiometric concentration. <sup>c</sup> Stopped-flow experiments.




Table III. Rate Constant Results for Nickel Complexation with Vanillic, Mandelic, and Thiolactic Acids

ligand	$10^{-3}k_1, M^{-1} s^{-1}$	$10^{-2}k_{-1}, s^{-1}$
vanillic acid	$3.64 \pm 0.39$	$1.19 \pm 0.19$
mandelic acid	$4.93 \pm 0.56$	$1.19 \pm 0.18$
thiolactic acid	$7.66 \pm 0.52$	$1.21 \pm 0.25$

second mechanism is characterized by internal hydrogen bonding, which blocks the site of metal ion attack.<sup>6,7</sup> In Table IV, rate constant values are given for a number of metal-ligand systems in which one or both of these mechanisms may play a role.

Comparison of the  $k_1$  values given in Table IV shows that, except for the Ni<sup>2+</sup>-lactate<sup>9</sup> and Ni<sup>2+</sup>-glycolate<sup>8</sup> complexes, the Ni<sup>2+</sup>-complex formation rate constants with the  $\alpha$ -hydroxy

Table IV. Formation Rate Constants for the Reactions of Metal Ions with a Number of Monovalent Bidentate Ligands at 25 °C

metal ion	ligand	$k_1, M^{-1} s^{-1}$	$k_{-1}, s^{-1}$	ref
Ni <sup>2+</sup>	vanillic acid	$3.64 \times 10^3$	$1.19 \times 10^2$	this work
	mandelic acid	$4.93 \times 10^3$	$1.19 \times 10^2$	this work
	thiolactic acid	$7.66 \times 10^3$	$1.21 \times 10^2$	this work
		$5.26 \times 10^3$	0.35	10
	salicylic acid	$7 \times 10^4$	$5 \times 10^7$ <sup>a</sup>	7
		$4.71 \times 10^3$	~0	10
	sulfosalicylic acid	$2.32 \times 10^3$	9.3	10
	anthranilic acid	$2.6 \times 10^4$	$1.7 \times 10^2$	9
		$2.6 \times 10^4$	$2.6 \times 10^2$	8
	glycolic acid			
Co <sup>2+</sup>	salicylic acid	$1.3 \times 10^5$ (20 °C)	~0	10
	sulfosalicylic acid	$2.67 \times 10^5$ (20 °C)	~0	10
VO <sup>2+</sup>	vanillic acid	$1.13 \times 10^3$	$2.54 \times 10^5$ <sup>a</sup>	19
	mandelic acid	$1.09 \times 10^3$	$1.78 \times 10^5$ <sup>a</sup>	19
	thiolactic acid	$6.76 \times 10^2$	$3.78 \times 10^4$ <sup>a</sup>	19
Al <sup>3+</sup>	salicylic acid	$9.1 \times 10^{-1}$	$7.8 \times 10^{-1}$ <sup>a</sup>	20
Fe <sup>3+</sup>	salicylic acid	3.0		21

<sup>a</sup> M<sup>-1</sup> s<sup>-1</sup>.

carboxylic, sulfosalicylic, and salicylic acids are almost the same in value ( $(3.64-5.26) \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>). Since the kinetics experiments for the Ni<sup>2+</sup>-lactate and Ni<sup>2+</sup>-glycolate systems were done under conditions of excess ligand to metal, the comparatively higher rates may be due to a contribution from the bis complex formation reaction to the overall rate.

In a reanalysis of the Ni(II)-salicylic acid system first studied by Williams and Petrucci,<sup>10</sup> Mentasti et al.<sup>7</sup> calculated a complexation rate constant of 70 M<sup>-1</sup> s<sup>-1</sup>. This very low  $k_1$  value resulted from analysis of a scheme which included the interaction of the NiOH<sup>+</sup> species. In the present study, high acidity was maintained in order to avoid reactions involving NiOH<sup>+</sup>. The formation rate constants obtained in this study are comparable to the  $k_1$  values determined earlier by Williams and Petrucci<sup>10</sup> for nickel-salicylic acid complexation.

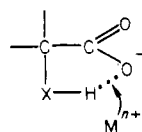
For metal-ligand complexation reactions that may involve sterically controlled substitution,<sup>2,3</sup> no decrease in the overall rate is expected if the rate constant for the ring closure step ( $k_0$ ) is much greater than the rate constant for the formation of the ion pair from the monobonded intermediate complex ( $k_{-0}$ ). In the present study, abnormally slow rates were observed for the 1:1 complexation reactions of vanillic, mandelic, and thiolactic acids with Ni(II). For the vanadyl complexes<sup>19</sup> of these ligands, normal formation rate constants were obtained. Analogously, for the salicylic acid metal ion mono complexes, low rate constants with Co(II)<sup>10</sup> and Ni(II)<sup>10</sup> and normal rate constants with Al(III)<sup>20</sup> and Fe(III)<sup>21</sup> were

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observed. If chelate ring closure is involved in the formation of these metal-ligand complexes, then the observed rate constant results indicate that  $k_0' \lesssim k_0$  for the Ni(II) and Co(II) complexes, while, for the Al(III), Fe(III), and V(IV) complexation reactions,  $k_0' \gg k_0$ .

The internal hydrogen-bond<sup>6,7</sup> mechanism is also applicable to the aforementioned metal ion complexation reactions. In this mechanism metal ion attack at the reactive site of the ligand is blocked by a proton hydrogen-bonded to the site. An example for  $\alpha$ -substituted carboxylic acids is



X = S, O, or NH<sub>2</sub>  
 M<sup>n+</sup> = metal ion  
 n = 2, 3  
 ... = hydrogen bond

With such a mechanism, ligand reactivity can vary from metal ion to metal ion if the rate of substitution is dependent on the ability of the metal ion to displace the proton blocking the reactive site. Thus, the normal complexation rate constants observed for Al(III), Fe(III), and V(IV) may be due to their greater ability relative to Co(II) and Ni(II) to break hydrogen bonds.

In Table IV an increase in  $k_1$  values for the Ni<sup>2+</sup> complexation reactions is observed as the ligand substituent on the carbon adjacent to the carboxylic group is varied from NH<sub>2</sub>

to OH to SH. This trend can be explained in terms of both the internal hydrogen bond mechanism and the SCS mechanism. In the first case the strength of the internal hydrogen bond can be assumed to decrease with the increasing acidity of the substituent group. Consequently, since the acidities of the substituents follow the order SH > OH > NH<sub>2</sub>, Ni(II) complex formation with thiolactic acid might be expected to occur more rapidly than with vanillomandelic and mandelic acids. Similar rate increases with increasing ligand acidity are observed for the Ni(II) complexation reactions<sup>10</sup> with salicylic, sulfosalicylic, and anthranilic acids.

Considering the rate-determining ring closure mechanism, it is conceivable that because of its larger size the thiol group in thiolactic acid may be more favorably positioned for chelate ring closure about the nickelous ion than the corresponding hydroxyl group in vanillomandelic and mandelic acids, and even more so than the amino group in anthranilic acid. Thus, the observed order of reactivity can also be explained in terms of some subtle steric differences between the different ligands.

The complex dissociation constants ( $k_{-1}$ ) given in Table III are of almost exactly the same value for all three ligands. Thus, complex stability is seen to increase with increasing ligand acidity. Though this is an unusual trend for Ni<sup>2+</sup>, it has been observed for a number of Ni<sup>2+</sup>-ligand complexation reactions<sup>6</sup> in which internal hydrogen bonding was postulated to play a part in the kinetics scheme.

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**Registry No.** Vanillomandelic acid, 55-10-7; mandelic acid, 90-64-2; thiolactic acid, 79-42-5; Ni<sup>2+</sup>, 14701-22-5.

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## Temperature-Jump Studies of the Ligand Substitution Reactions of Tetrahedral Cobalt(II) Complexes Solubilized in Reversed Micelles

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The kinetics of ligand substitution of tetrahedral complexes of the Co(II) ion solubilized in reversed micellar systems were studied by means of a temperature-jump method. The investigated reactions are (1)  $\text{CoCl}_4^{2-} + \text{SCN}^- \rightleftharpoons \text{CoCl}_3(\text{SCN})^{2-} + \text{Cl}^-$  in dodecylpyridinium chloride (DPC)/chloroform and (2)  $\text{CoCl}_3(\text{SCN})^{2-} + \text{SCN}^- \rightleftharpoons \text{CoCl}_2(\text{SCN})_2^{2-} + \text{Cl}^-$  in DPC/water/chloroform. In both reactions, the experimental data fit the mechanisms  $\text{CoCl}_3\text{X}^{2-} \rightleftharpoons \text{CoCl}_2\text{X}^- + \text{Cl}^-$ , followed by  $\text{CoCl}_2\text{X}^- + \text{SCN}^- \rightleftharpoons \text{CoCl}_2\text{X}(\text{SCN})^{2-}$ , where X = Cl<sup>-</sup> and SCN<sup>-</sup> for reactions 1 and 2, respectively. The backward rate constants of the second step or the formation of tricoordinate intermediate from  $\text{CoCl}_2\text{X}(\text{SCN})^{2-}$  are obtained to be  $(5.5 \pm 2.0) \times 10^3$  and  $(3.7 \pm 1.0) \times 10^4 \text{ s}^{-1}$  at 20 °C for reactions 1 and 2, respectively. The present results were discussed in comparison with the reported ligand-exchange kinetics of other tetrahedral Co(II) complexes.

Although the mechanism of ligand replacement in an octahedral complex is well established,<sup>1</sup> relatively little is known about substitution reactions of tetrahedral complexes.<sup>2</sup> One of the difficulties in studying the above topic lies in the fact that many complexes which are tetrahedral in crystalline state yield six-coordinate solvated complexes in donor solvents.

Recently we have investigated the structure and reaction of metal complexes solubilized in surfactant aggregates in nonpolar medium (termed as reversed micellar systems).<sup>3-5</sup>

It was revealed that, in the polar interior of a reversed micelle, tetrahedral complexes of the Co(II) ion are stably present even in the presence of cosolubilized water.<sup>5,6</sup> On the basis of this finding, we have decided to study the ligand substitution reactions of tetrahedral Co(II) complexes in the reversed micellar system. The mechanisms of ligand exchange of tetrahedral Co(II) complexes have been investigated so far only in a few examples, all of which were performed in nonpolar solvents.<sup>7-9</sup>

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