

TABLE I: Reaction Network for the Thiocyanate-Iodate Reaction

no.	reaction
M1	$\text{IO}_3^- + \text{SCN}^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{I}^- + \text{HCN} + \text{H}^+$
M2	$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$
M3	$\text{I}_2 + \text{CN}^- \rightarrow \text{ICN} + \text{I}^-$
M4	$3\text{I}_2 + \text{SCN}^- + 4\text{H}_2\text{O} \rightarrow 6\text{I}^- + \text{SO}_4^{2-} + \text{HCN} + 7\text{H}^+$
M5	$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$
M6	$\text{ICN} + \text{H}^+ + \text{I}^- \rightleftharpoons \text{I}_2 + \text{HCN}$
M7	$6\text{IO}_3^- + 5\text{SCN}^- + 2\text{H}_2\text{O} \rightarrow 3\text{I}_2 + 5\text{SO}_4^{2-} + 4\text{HCN} + \text{CN}^-$
M8	$7\text{IO}_3^- + 5\text{SCN}^- + 2\text{H}^+ \rightarrow \text{I}_2 + 5\text{ICN} + 5\text{SO}_4^{2-} + \text{H}_2\text{O}$
M9	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$

**Reaction Network.** Nine reactions may be identified as relevant in acidic mixtures of iodate and thiocyanate (Table I).

**Reaction M1:** This is the stoichiometry of the reaction when thiocyanate is in excess over iodate. Its rate of reaction depends strongly on pH.

**Reaction M2:** The well-known Dushman reaction is a standard reaction in volumetric analysis.<sup>17</sup> Its rate is proportional to  $[\text{H}^+]^2$ . In excess iodate conditions, after production of iodide in reaction M1, we would expect this reaction to take over and produce iodine.

**Reaction M3:** This is a very rapid reaction which should instantaneously consume all iodine produced in (M2) for as long as there is cyanide in solution (from (M1)).

**Reaction M4:** The oxidation of thiocyanate by iodine has been studied by several workers.<sup>2-5</sup> It is a very slow autoinhibitory reaction.

**Reaction M5:** The iodine-iodide reaction is a rapid equilibrium.<sup>18</sup>

**Reaction M6:** In high acid, ICN can regenerate  $\text{I}_2$  and HCN.<sup>16</sup> This is possible because HCN is such a weak acid.

**Reaction M7:** This reaction (R3) is significant only in high acid conditions, since the cyanide ion's affinity for acid is weaker than its affinity for iodine. The reaction as written may appear incomplete, since we still have  $\text{CN}^-$  and  $\text{I}_2$  among the products. However, since the medium is highly acidic, the  $\text{CN}^-$  ions quickly combine with  $\text{H}^+$  ions of the medium to form HCN. If excess ICN has been formed, reaction M6 can regenerate iodine.

**Reaction M8:** This reaction (R2) can be viewed as a composite of (M1), (M2), and (M3). It has a short induction period and is also catalyzed by acid.

(17) Reference 14, p 374.

(18) Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554.

(19) Briot, G. T.; Smith, R. H. *Aust. J. Chem.* **1973**, *26*, 1863.

Reaction M9: The dissociation of HCN is a rapid equilibrium with  $\text{p}K_a = 9.3$ .

## Discussion

The nine reactions we have identified can explain the oligooscillatory behavior observed. In excess thiocyanate conditions (Figure 1), reaction M1 produces iodide ions before the iodate is totally consumed. Thus, for some time there is competition between  $\text{SCN}^-$  and  $\text{I}^-$  for  $\text{IO}_3^-$  (reactions M1 and M2), and iodine is produced by (M2). Competition ends when the iodate ions have been depleted. At this point, the solution now has iodine, thiocyanate, and reaction products of reaction M1. Reaction M4 now controls the observed depletion of iodine. Although reaction M4 is reported to be slow and autoinhibitory, this behavior is less pronounced when  $[\text{SCN}^-]_0 > [\text{I}_2]_0$ . In fact, when thiocyanate is in sufficient (about 10-fold) excess over iodine, the reaction is quite fast, and pseudo-first-order kinetics can be observed.<sup>18</sup> Reaction M3 is significant only after  $\text{SCN}^-$  is oxidized and the sulfur-carbon bond has been cleaved. Reaction M5 is necessary to achieve an accurate depiction of the iodine species present.

In excess iodate conditions (Figure 2), reaction also commences with (M1) and (M2). The difference now is that thiocyanate is depleted instead of iodate. The drop in  $[\text{I}_2]$  next observed results from reaction M3. The further rise in iodine concentration at the end of the reaction is caused by (M6), which depletes ICN and yields the stoichiometric amount of iodine in highly acidic environments. Oxidation of thiocyanate goes through several intermediates<sup>11</sup> before formation of  $\text{CN}^-$ , which will then consume the iodine formed by (M2). When iodate is in excess, the overall oxidation of thiocyanate, which produces iodide, is controlled by the  $[\text{H}^+]$  dependence of (M2). If  $[\text{H}^+]$  is sufficiently high, iodine is produced rapidly enough to accumulate; lower  $[\text{H}^+]$  places (M2) at a kinetic disadvantage compared with (M1) and (M4).

The reaction network we have proposed qualitatively explains the observed oligooscillatory behavior. The mechanisms of reactions M1 and M7 (or M8) have not, however, been fully explored.

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## Effects of Intramolecular Hydrogen Bonding on the Rates of Complex Formation of $\text{Co}^{2+}$ and $\text{Zn}^{2+}$ with Substituted Salicylic Acids

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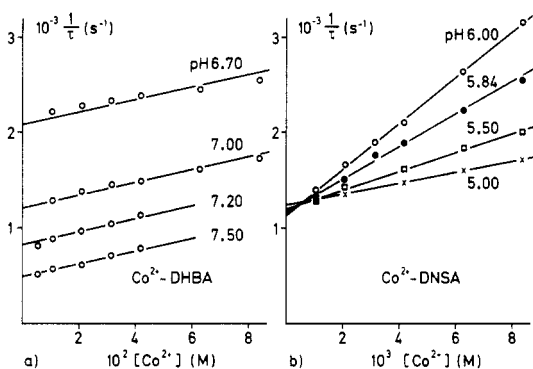
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The kinetics of the complex formation of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  with two substituted salicylates have been investigated and compared to those of  $\text{Ni}^{2+}$  (reported previously). The rate constants for the unprotonated salicylates are consistent with a rate-determining first substitution step at the respective aquometal ion. Because of strong intramolecular hydrogen bonding, the monoprotonated ligands are much less reactive (80–4000-fold). The metal ion dependence of the rate constants for these species leads to the conclusion that in the reactions involving  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ring closure is rate determining, whereas in case of the very labile  $\text{Zn}(\text{II})$  the opening of the internal H bond in the initial complex becomes rate determining.

In a previous publication we have reported on the kinetics of complex formation of  $\text{Ni}^{2+}$  with a series of substituted salicylic

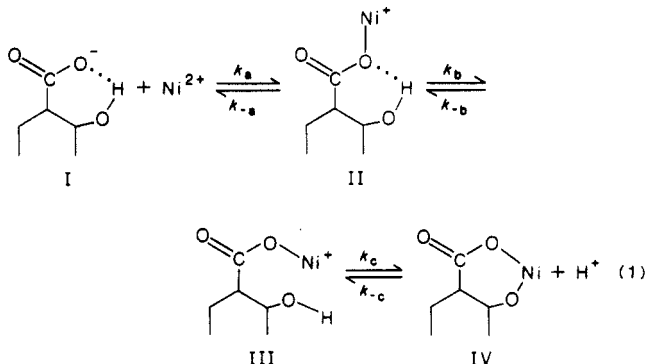
acids.<sup>1</sup> The unprotonated form of 3,5-dinitrosalicylic acid (DNSA) reacts with  $\text{Ni}^{2+}$  with a rate constant ( $k_1 = 3.1 \times 10^4$



**Figure 1.** Plots of  $1/\tau$  vs  $[\text{Co}^{2+}]$  for the reactions of  $\text{Co}^{2+}$  with (a) DHBA and (b) DNSA at various pH values (25 °C,  $I = 0.3$  M).

$\text{M}^{-1} \text{s}^{-1}$ ) which is approximately as expected for a rate-determining first substitution step at  $\text{Ni}^{2+}(\text{aq})$ . The rate constants  $k_1$  (upper limits only) which have been evaluated for the unprotonated forms of the more basic ligands 2,6-dihydroxybenzoic acid (DHBA) and 2-mercaptobenzoic acid (thiosalicylic acid, TSA) too are consistent with such a mechanism, and so is, approximately, the value of the rate constant ( $k_2 = 9.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) for the reaction of  $\text{Ni}^{2+}$  with the monoprotonated form of TSA.<sup>1</sup> Monoprotonated TSA is known to exhibit only weak intramolecular hydrogen bonding.<sup>2</sup>

By contrast, the monoprotonated species of DNSA and DHBA, which form strong intramolecular hydrogen bonds,<sup>1,2</sup> react with  $\text{Ni}^{2+}$  much slower (by factors of ca. 30 and ca. 150, respectively) than expected for the type of mechanism mentioned above. Clearly, the first binding step cannot be rate determining in these processes. To rationalize the observations, a reaction mechanism of the following type was considered,<sup>1</sup>



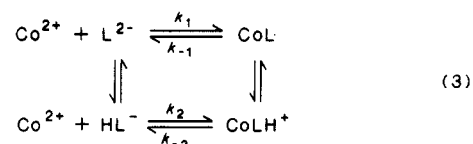
with the intermediates II and III as steady states. Since the overall rate constant of this pathway was not affected by changes in the buffer concentration, it can be ruled out that proton loss is rate determining. Thus either the opening of the intramolecular H bond ( $k_b$ ) or the closing of the chelate ring ( $k_c$ ) must be rate determining in the forward direction. A distinction between these two cases cannot be made from the  $\text{Ni}^{2+}$  data alone.

In order to gain further insight into the reaction mechanism we have extended such kinetic studies to include the metal ions  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ . The experimental procedures and conditions were exactly as described before,<sup>1</sup> i.e., 25 °C, ionic strength 0.3 M ( $\text{NaClO}_4$ ),  $3 \times 10^{-3}$  M cacodylate buffer. The kinetic measurements were carried out by means of the temperature-jump relaxation technique with spectrophotometric detection ( $\lambda = 332$  nm, DHBA, or 390 nm, DNSA). Metal ion concentrations were always 10–700-fold higher than ligand concentrations. Except for a fast initial change in absorbance ( $<10 \mu\text{s}$ , heating time 3  $\mu\text{s}$ ) due to protolytic equilibrations and the temperature dependence of the ligands' extinction coefficients,<sup>2</sup> only one single-exponential relaxation was always observed, with a time constant  $\tau$  which varies from 300  $\mu\text{s}$  to 2 ms in the reactions with  $\text{Co}^{2+}$ . Results for the reactions of  $\text{Co}^{2+}$  with DNSA and DHBA are

shown in Figure 1 in the form of plots of the reciprocal relaxation time,  $1/\tau$ , vs the metal ion concentration. Each value of  $\tau$  given is the mean of at least four individual measurements. With  $\text{Co}^{2+} + \text{DNSA}$ , additional experiments were carried out at pH 4.56. In order to achieve sufficiently large amplitudes, high metal ion concentrations, e.g.,  $9 \times 10^{-3}$ – $54 \times 10^{-3}$  M, are required at this low pH (results not included in Figure 1b). At a given pH relationships of the type

$$1/\tau = k_f[\text{Co}^{2+}] + k_d \quad (2)$$

are observed for both systems. This behavior is consistent with a reaction scheme of the form



where  $\text{L}^{2-}$  represents a ligand species in which the carboxylate group and a hydroxy group are deprotonated. The protolytic steps may be considered as rapid preequilibria compared to the complex formation steps. Indeed, varying the concentration of buffer (cacodylate) did not affect the observed time constant  $\tau$ . Then<sup>1</sup>

$$k_f = k_1 K_{A2} / [\text{H}^+] + k_2 \quad (4)$$

with  $K_{A2} = [\text{H}^+][\text{L}^{2-}] / [\text{HL}^-] \ll [\text{H}^+]$ ,<sup>1</sup> and

$$k_d = k_{-1} + k_{-2}[\text{H}^+] / K_c \quad (5)$$

where  $K_c = [\text{H}^+][\text{CoL}] / [\text{CoLH}^+] \gg [\text{H}^+]$ .<sup>1,3</sup>

For  $\text{Co}^{2+}$ -DHBA, the slopes of the plots of  $1/\tau$  vs  $[\text{Co}^{2+}]$  (Figure 1a) do not exhibit a significant variation with pH. The straight lines shown have equal slopes and have been placed such that they give a good fit to the experimental data (uncertainties in  $\tau$  are  $\leq \pm 5\%$ ). The near-constancy of the slopes indicates that the complex formation occurs almost exclusively by reaction with  $\text{HL}^-$  and gives  $k_f = k_2 = 6.6 (\pm 0.9) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

The experimental data for  $\text{Co}^{2+} + \text{DNSA}$  indicate that both pathways contribute to the overall reaction. Introducing eq 4 and 5 (and simple equilibrium relationships) into the expression for  $1/\tau$  (eq 2) yields

$$\frac{1}{\tau} = (k_1 K_{A2} + k_2 [\text{H}^+]) \left( \frac{[\text{Co}^{2+}]}{[\text{H}^+]} + \frac{1}{K_{A2} K_{ML}} \right) \quad (6)$$

where  $K_{ML} = [\text{CoL}] / [\text{Co}^{2+}][\text{L}^{2-}] = k_1 / k_{-1}$ .

Values of  $k_1$ ,  $k_2$ , and  $K_{ML}$  were evaluated from eq 6 by a computer-programmed least-squares fit using all 26 experiments:  $k_1 = 2.3 (\pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_2 = 7.1 (\pm 0.8) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $K_{ML} = 2.1 (\pm 0.15) \times 10^3 \text{ M}^{-1}$ . The quality of the fit is demonstrated by a comparison of the observed and calculated values of  $\tau$ , Table I. The experimental errors in  $\tau$  are highest at low pH and low  $\text{Co}^{2+}$  concentrations (small relaxation amplitudes).<sup>4</sup>

Analogous experiments were carried out for the system  $\text{Zn}^{2+} + \text{DNSA}$  ( $[\text{Zn}^{2+}] = 1 \times 10^{-3}$ – $7 \times 10^{-2}$  M,  $[\text{DNSA}] = 1 \times 10^{-4}$  M, pH 5.0–6.0,  $\lambda = 390$  nm). Again only one time constant was observed in all experiments. The kinetics, however, appear to be more complicated than in the reactions with  $\text{Co}^{2+}$ : The measured time constant ( $\tau = 11$ – $54 \mu\text{s}$ ) depends now also on the concentration of buffer ( $2 \times 10^{-3}$ – $10 \times 10^{-3}$  M cacodylate), and under

(3) Chopra, S.; Jordan, R. B. *Inorg. Chem.* **1983**, *22*, 1708.

(4) A referee has pointed out (and we had noticed before) that a better fit can be obtained if the condition  $K_c \gg [\text{H}^+]$  (line after eq 5) is abandoned. The last term of eq 6 has then to be multiplied by  $K_c / (K_c + [\text{H}^+])$ . Using this equation, a best fit is obtained with  $K_c = 1.6 \times 10^3 \text{ M}$ ,  $k_1 = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_2 = 2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , and  $K_{ML} = 1.9 \times 10^3 \text{ M}^{-1}$ . We consider this improvement of the fit to be fortuitous since all other evidence indicates that  $K_c$  is much larger than  $1.6 \times 10^3$ . The results of our equilibrium studies for  $\text{Ni}^{2+}$ -DNSA and  $\text{Co}^{2+}$ -DNSA (ref 1 and this paper) indicate  $K_c \geq 1 \times 10^4 \text{ M}$ , and Chopra and Jordan (ref 3, p 1710) have concluded that  $K_c \geq 4 \times 10^4 \text{ M}$  for  $\text{Ni}^{2+}$ -DNSA. A similar value should be expected for  $\text{Co}^{2+}$ -DNSA.

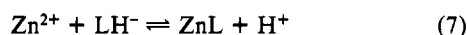
(1) Diebler, H.; Secco, F.; Venturini, M. *J. Phys. Chem.* **1987**, *91*, 5106.

(2) Diebler, H.; Secco, F.; Venturini, M. *J. Phys. Chem.* **1984**, *88*, 4229.

TABLE I: Co<sup>2+</sup> + DNSA System: Experimental and Calculated Values of  $\tau$ 

pH	10 <sup>3</sup> [Co <sup>2+</sup> ]	$\tau_{\text{exptl}}$ , ms	$\tau_{\text{calcd}}$ , ms	
6.00	8.36	0.316	0.308	
	6.27	0.379	0.368	
	4.18	0.476	0.457	
	3.14	0.529	0.520	
	2.09	0.602	0.603	
	1.05	0.718	0.718	
5.84	8.36	0.393	0.381	
	6.27	0.449	0.443	
	4.18	0.529	0.531	
	3.14	0.569	0.589	
	2.09	0.667	0.661	
	1.05	0.753	0.753	
5.50	8.36	0.498	0.524	
	6.27	0.545	0.578	
	4.18	0.620	0.644	
	2.09	0.699	0.727	
	1.05	0.770	0.777	
	5.00	8.36	0.588	0.596
5.00	6.27	0.622	0.621	
	4.18	0.670	0.647	
	2.09	0.728	0.676	
	1.05	0.768	0.692	
	4.56	53.5	0.332	0.352
	35.7	0.387	0.390	
17.8	0.432	0.438		
8.92	0.558	0.467		

most conditions  $\tau$  increases with increasing metal ion concentration. Complex formation reactions of Zn<sup>2+</sup> proceed much faster than those of Ni<sup>2+</sup> and Co<sup>2+</sup>,<sup>5</sup> and apparently the protonation/deprotonation steps (scheme 3) are no longer rapid preequilibria compared to the reaction steps with Zn<sup>2+</sup>. Only one reaction effect is observed since L<sup>2-</sup> and ZnLH<sup>+</sup> may to a good approximation be considered as steady states under our conditions. Thus we are left with the overall reaction



which may proceed by two pathways, via L<sup>2-</sup> or via ZnLH<sup>+</sup> (scheme 3). Which [Zn<sup>2+</sup>]  $\gg$  [DNSA] and the steady-state approximations for [L<sup>2-</sup>] and [ZnLH<sup>+</sup>], the reciprocal relaxation time is now given by

$$\frac{1}{\tau} = \frac{k_1 k_d^L [\text{Zn}^{2+}] + k_{-1} k_p^L}{k_1 [\text{Zn}^{2+}] + k_p^L} + \frac{k_2 k_d^C [\text{Zn}^{2+}] + k_{-2} k_p^C}{k_d^C + k_{-2}} \quad (8)$$

where  $k_p^L$  and  $k_d^L$  are the rate constants for the protonation and deprotonation of the ligand (uncatalyzed and buffer-catalyzed, i.e.,  $k_p^L = k_p[\text{H}^+] + k'_p[\text{CacH}]$ ,  $k_d^L = k_s + k'_s[\text{cac}^-]$ , where  $\text{H}^+ + \text{L}^{2-} \rightleftharpoons \text{LH}^-$  ( $k_p, k_s$ ) and  $\text{cacH} + \text{L}^{2-} \rightleftharpoons \text{cac}^- + \text{LH}^-$  ( $k'_p, k'_s$ )) and  $k_p^C$  and  $k_d^C$  are the rate constants for protonation and deprotonation of the complex. The rate constants  $k_p^L$  and  $k_d^L$  (i.e.,  $k_p, k_s, k'_p$ , and  $k'_s$ ) have been determined experimentally,<sup>2</sup> whereas values for  $k_p^C$  and  $k_d^C$  can only be estimated. Then the rate constants  $k_1, k_{-1}, k_2$ , and  $k_{-2}$  may be evaluated (from 31 experiments) by a fitting procedure based on eq 8. The evaluation clearly showed that  $k_d^C \gg k_{-2}$ . This condition allows a simplification of the expression for  $1/\tau$  and (with equilibrium relationships) a reduction in the number of parameters which have to be fitted (now 3):

$$\frac{1}{\tau} = \frac{k_1 k_d^L [\text{Zn}^{2+}] + k_{-1} k_p^L}{k_1 [\text{Zn}^{2+}] + k_p^L} + k_2 \left( [\text{Zn}^{2+}] + \frac{k_{-1} [\text{H}^+]}{k_1 K_{A2}} \right) \quad (9)$$

In addition, this modification eliminates the quantities  $k_p^C$  and  $k_d^C$  for which only estimated values are available. A fitting program based upon eq 9 yielded  $k_1 = 5.6 (\pm 1.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,

TABLE II: Zn<sup>2+</sup> + DNSA System: Experimental and Calculated Values of  $\tau$ 

pH	10 <sup>3</sup> [Zn <sup>2+</sup> ]	10 <sup>3</sup> [B] <sub>0</sub> <sup>a</sup>	$\tau_{\text{exptl}}$ , $\mu\text{s}$	$\tau_{\text{calcd}}$ , $\mu\text{s}$
6.00	2.93	2.0	54.3	54.9
	2.93	4.0	44.1	41.5
	2.93	7.0	33.2	30.8
	2.93	10.0	26.8	24.7
	4.88	4.0	52.0	46.3
	0.98	4.0	29.1	25.8
5.50	0.98	4.0	18.6	17.9
	2.93	4.0	32.3	32.3
	4.88	4.0	40.1	41.5
	2.93	2.0	35.1	37.4
	2.93	7.0	26.3	27.0
	2.93	10.0	22.1	23.5
5.00	0.98	4.0	11.5	11.6
	2.93	4.0	20.8	19.9
	4.88	4.0	24.0	25.4
	4.88	4.0	24.1	25.4
	6.83	4.0	28.7	30.4
	9.75	4.0	33.0	36.0
	14.6	4.0	39.9	42.0
	19.5	4.0	43.8	45.7
	24.4	4.0	48.5	47.6
	29.3	4.0	51.0	48.5
	34.1	4.0	50.5	48.5
	39.0	4.0	50.0	48.3
	43.9	4.0	50.0	47.8
	48.8	4.0	47.2	47.2
58.5	4.0	45.7	45.5	
68.3	4.0	44.8	43.7	
2.93	2.0	20.3	20.4	
2.93	7.0	18.9	18.1	
2.93	10.0	16.7	17.0	

<sup>a</sup>Total buffer [cac<sup>-</sup>] + [cacH].

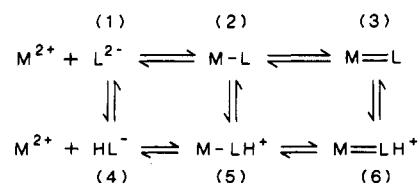
TABLE III: Second-Order Rate Constants (M<sup>-1</sup> s<sup>-1</sup>) for the Reactions of Divalent Metal Ions with Unprotonated ( $k_1$ ) and Monoprotonated ( $k_2$ ) Salicylates (25 °C, I = 0.3 M)

M <sup>2+</sup>	DNSA		DHBA	
	L <sup>2-</sup> $k_1$	HL <sup>-</sup> $k_2$	L <sup>2-</sup> $k_1$	HL <sup>-</sup> $k_2$
Ni <sup>2+</sup> <sup>a</sup>	$3.1 \times 10^4$	380	$< 2 \times 10^7$	65
Co <sup>2+</sup>	$2.3 \times 10^6$	$7.1 \times 10^3$	$< 10^9$	$6.6 \times 10^3$
Zn <sup>2+</sup>	$5.6 \times 10^8$	$1.4 \times 10^5$		

<sup>a</sup>From ref 1.

$k_{-1} = 1.4 (\pm 0.2) \times 10^5 \text{ s}^{-1}$ , and  $k_2 = 1.4 (\pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . The relaxation times calculated with these values are given in Table II, together with the observed time constants. A survey of the results obtained with DHBA and DNSA is presented in Table III.

The rate constants  $k_1$  and  $k_2$  both refer to bidentate binding processes; i.e., they are apparent constants. The form of the rate law (or of  $1/\tau$ ) does not tell whether the first or the second binding steps are rate determining. Chopra and Jordan<sup>3</sup> have discussed their data in terms of a more extended reaction scheme which includes the monodentate steady-state intermediates (coupled too by fast protolytic equilibration):



As outlined before,<sup>1</sup> this extension does not provide any additional information, and it is easy to see why: If, for instance, the second substitution step is rate determining in the reaction with LH<sup>-</sup> ((5)  $\rightarrow$  (6)), then (4)  $\rightleftharpoons$  (5) is a rapid preequilibrium and one cannot distinguish whether this preequilibrium is established predominantly via (4)  $\rightleftharpoons$  (5) or via (4)  $\rightleftharpoons$  (1)  $\rightleftharpoons$  (2)  $\rightleftharpoons$  (5). Moreover, it may well be that the assumption of a rapid equilibration between

(5) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; Vol. 2. Eigen, M.; Wilkins, R. G. Mechanisms of Inorganic Reactions. *Adv. Chem. Ser.* 1965, 49, 55.

(2) and (5) is not fulfilled: In  $M-LH^+$  the metal ion is bound to the carboxylic group whereas in  $M-L$  it may be bound preferentially to the phenolic  $-O^-$  atom.

Which conclusions can be drawn from the magnitude of the observed rate constants?

The values of  $k_1$  for the reactions with  $DNSA^{2-}$  are in line with those of other ligands of simple structures reacting with these three metal ions;<sup>5</sup> i.e., they are of the magnitude as expected for a rate-determining first substitution step at the aquometal ions. In the case of the strongly basic  $DHBA^{2-}$ , only upper limits of  $k_1$  could be evaluated. Presumably the true values are about the same as those for  $DNSA^{2-}$ .

By contrast, the rate constants  $k_2$  for the reactions with  $HL^-$  of  $DNSA$  and  $DHBA$  are by 2–3 orders of magnitude lower than the corresponding values of  $k_1$ . Electrostatic effects will contribute not more than a factor 5 to these differences. Obviously the first substitution step cannot be rate determining in the reactions with  $HL^-$ . As demonstrated previously, the monoprotonated forms of  $DHBA$  and  $DNSA$  are characterized by strong intramolecular hydrogen bonding.<sup>1,2</sup> The low rates of the reactions  $Ni^{2+} + HL^-$  were rationalized in terms of scheme 1, shown above, with the second step ( $k_b$ ) or the third step ( $k_c$ ) being rate determining.<sup>1</sup> The new data presented here allow a distinction between these two possibilities. The data of Table III reveal that the values of  $k_2$  are much higher in the case of  $Co^{2+}$  than for  $Ni^{2+}$ . A similar difference has been reported also for unsubstituted salicylic acid.<sup>6</sup> If the second step, the opening of the intramolecular H bond, were rate determining, then  $k_2 = (k_a/k_{-a})k_b$ . Now, the stability constant for the binding of  $Co^{2+}$  to a given ligand is usually somewhat lower than that for the binding of  $Ni^{2+}$ ,<sup>7</sup> in accordance with the Irving-Williams rule, and the same is expected for  $k_a/k_{-a}$ . Furthermore, the rate of opening the intramolecular H bond,  $k_b$ , will not depend very much on whether the bound metal ion is  $Co^{2+}$  or  $Ni^{2+}$ . Therefore, if  $k_b$  were rate determining,  $k_2$  should be slightly lower for  $Co^{2+}$  than for  $Ni^{2+}$ , contrary to our observations. If, however, ring closure were rate determining, i.e.,  $k_2 = (k_a k_b / k_{-a} k_{-b}) k_c$ , then the higher values of  $k_2$  in case of  $Co^{2+}$  are easily rationalized by the differences in  $k_c$ . This rate constant for ring closure, i.e., for the second substitution step at the metal center, is much higher in case of  $Co(II)$  than in the case of  $Ni(II)$ .<sup>5</sup>

Our results indicate unambiguously that ring closure is the rate-determining process in the reactions of  $Ni^{2+}$  and  $Co^{2+}$  with the  $HL^-$  species of  $DNSA$  and  $DHBA$ .

The evaluation of the kinetics for the reaction  $Zn^{2+} + DNSA$  yielded a value of  $k_1$  which is about 200-fold larger than the one for  $Co^{2+} + DNSA$ . Differences in rate by about a factor 100 have also been reported for the complex formation reactions of several other ligands with these two metal ions.<sup>5</sup> The rate constant  $k_2$ , however, is only 20-fold higher for  $Zn^{2+} + HL^-$  as compared to  $Co^{2+} + HL^-$ , Table I. As discussed before,<sup>1</sup> the reaction with  $HL^-$  includes a pathway in which the ligand's hydrogen bond is closed ( $k_H$ ) and one in which it is open ( $k_o$ ),  $k_2 = k_H + 10^{-3}k_o$ , where the factor  $10^{-3}$  denotes the fraction with the open structure.<sup>2</sup> The reaction with the open form is expected to show normal behavior, the first substitution step being rate determining. For  $Zn^{2+} + HL^-$  (open) the value of  $k_o$  will be near  $1 \times 10^8 M^{-1} s^{-1}$ .<sup>5</sup> Thus the pathway with the "open" ligand contributes heavily to  $k_2$  (contrary to the systems  $Ni^{2+}-DNSA$  and  $Co^{2+}-DNSA$ ), and  $k_H$  is below  $1 \times 10^5 M^{-1} s^{-1}$ ; i.e., it is not much higher than in case of  $Co^{2+}$ . This relatively small variation in  $k_H$  may well be indicative of a change in the rate-determining step (scheme 1): Presumably the rate of the second binding step,  $k_c$ , is so high in the case of  $Zn^{2+}$  that now  $k_c > k_{-b}$ , i.e., the second step of scheme 1, becomes rate determining,  $k_H \approx (k_a/k_{-a})k_b$ . Such a change in the rate-determining step would be expected if  $k_{-b}$  is near  $10^7 s^{-1}$ , since then  $k_c^{Ni}, k_c^{Co} < k_{-b}$ , but  $k_c^{Zn} > k_{-b}$ .

The kinetic data reported here also provide some information on the complex stabilities. The  $[H^+]$  dependence of the apparent stability constant  $k_{app} = k_f/k_d$  enables the determination of individual stability constants; see eq 4 of ref 1. For  $Co^{2+}-DHBA^{2-}$  results  $K_{ML} = [ML]/[M^{2+}][L^{2-}] = k_1/k_{-1} = 6.4 \times 10^6 M^{-1}$  ( $Ni^{2+}-DHBA^{2-} 2.0 \times 10^7$ ). For  $Co^{2+}-DNSA^{2-}$  the computer evaluation (see above) yields directly  $K_{ML} = 2.1 \times 10^3 M^{-1}$  ( $Ni^{2+}-DNSA^{2-}, \approx 6 \times 10^3$ ). Potentiometric titrations (applying a procedure described earlier<sup>8</sup>) and spectrophotometric titrations yielded a somewhat higher value for the stability constant of  $Co^{2+}-DNSA^{2-}$ ,  $K_{ML} = 2.7 (\pm 0.2) \times 10^3 M^{-1}$ . Evidence for the formation of appreciable amounts of protonated complex,  $CoLH^+$ , at pH values  $\geq 5.0$  could not be derived from these studies. The relative stabilities of the  $Ni^{2+}$  and  $Co^{2+}$  complexes confirm what was stated above. Finally, the ratio  $k_1/k_{-1}$  for  $Zn^{2+}-DNSA$  (see above) gives  $K_{ML} = 4 \times 10^3 M^{-1}$ .

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