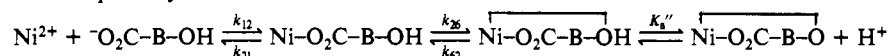


## Kinetics of Complex Formation between Nickel(II) and Salicylate Derivatives

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The kinetics of the reaction of  $\text{Ni}(\text{OH}_2)_6^{2+}$  with salicylic acid, 5-chlorosalicylic acid, and 3,5-dinitrosalicylic acid have been studied in the general pH range of 5.5-7 at 25 °C in 0.3 M  $\text{NaClO}_4$ . The disagreement between previous studies on these systems is shown to be caused by the use of an incomplete rate law by earlier workers. For the first two systems the dominant reaction pathway is



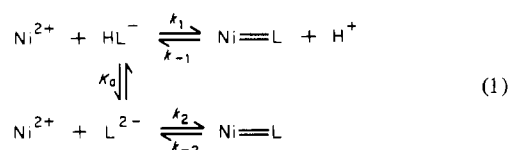
The results for salicylate, for example, give  $k_{12}k_{26}/(k_{21} + k_{26}) = (2.5 \pm 0.5) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  and  $K_a'' = (6 \pm 1) \times 10^{-7} \text{ M}$ . The greater acidity of 3,5-dinitrosalicylate produces a more complex rate law for which either of two limiting cases gives an internally consistent interpretation.

The reaction of nickel(II) with salicylate and its derivatives has been the subject of several kinetic studies.<sup>1-4</sup> Unfortunately, these studies have given widely variable results as can be seen from the summary in Table I. For example, the 20-fold difference in rate constants found for the dianions of salicylate<sup>1</sup> and 5-nitrosalicylate<sup>2</sup> is difficult to reconcile with a dissociative ion-pair mechanism for substitution on nickel(II).<sup>5</sup> Furthermore, Mentasti and co-workers<sup>3,4</sup> found it necessary to propose hydrolyzed nickel(II) ( $\text{NiOH}^+$ ) as a reactive species, while the previous studies<sup>1,2</sup> at much higher pH did not require  $\text{NiOH}^+$ . Mentasti and co-workers found quite small rate constants for the reaction of nickel(II) with salicylate anions, but aluminum(III) seems to react at a normal rate with these species.<sup>6,7</sup>

With the hope that these anomalies might have a rational explanation, a stopped-flow study has been undertaken of the reaction of nickel(II) with several salicylate derivatives. The systems have been studied over as wide as possible a range of pH and nickel(II) concentration consistent with maintaining a useful transmittance change, a homogeneous solution, and a reasonable ionic strength.

## Results and Discussion

The results of the stopped-flow kinetic study of nickel(II) with salicylate are given in Table II. The simple scheme that is commonly used to account for such results has the form



where  $\text{HL}^-$  and  $\text{L}^{2-}$  represent the salicylate anion and dianion respectively, and  $\text{Ni}=\text{L}$  represents the chelated product. Under the pseudo-first-order conditions of  $[\text{Ni}^{2+}] \gg [\text{HL}^- + \text{L}^{2-}]$  the first-order rate constant is given by

$$k_{\text{exptl}} = (k_1[\text{H}^+] + k_2K_a) \left\{ \frac{[\text{Ni}^{2+}]}{K_a + [\text{H}^+]} + \frac{1}{K_aK_f} \right\} \quad (2)$$

where  $K_f = [\text{Ni}=\text{L}]/[\text{Ni}^{2+}][\text{L}^{2-}]$ . Since  $[\text{H}^+] \gg K_a$  under the experimental conditions, then eq 2 predicts that a plot of  $k_{\text{exptl}}/([\text{Ni}^{2+}][\text{H}^+]^{-1} + (K_aK_f)^{-1})^{-1}$  vs.  $[\text{H}^+]$  should be linear. This function is plotted in Figure 1 and clearly deviates from lin-

Table I. Summary of Previous Kinetic Results for Nickel(II)-Salicylate Systems

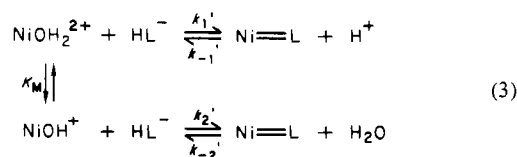
ligand	pH range	reacn	$k$ , $\text{M}^{-1} \text{ s}^{-1}$ <sup>a</sup>	ref
salicylate	7.8-8.2	$\text{Ni}^{2+} + \text{L}^{2-}$	$5.3 \times 10^3$	1
		$\text{Ni}^{2+} + \text{HL}^-$	$4.7 \times 10^3$	1 <sup>b</sup>
	6.02-7.2	$\text{Ni}^{2+} + \text{HL}^-$	70	3
		$\text{NiOH}^+ + \text{HL}^-$	$6.3 \times 10^4$	3
5-nitrosalicylate	7.5-8.0	$\text{Ni}^{2+} + \text{L}^{2-}$	$1.02 \times 10^5$	2 <sup>c</sup>
		$\text{Ni}^{2+} + \text{HL}^-$	80	4
	6-7.2	$\text{NiOH}^+ + \text{HL}^-$	$5.1 \times 10^4$	4

<sup>a</sup> Rate constants at 25 °C. <sup>b</sup> The data have been reanalyzed with  $\text{HL}^-$  as reactant, so that  $\tau^{-1} = k_f[\text{M} + \text{HL}^-] + k_r[\text{H}^+]/K_aK_f$ , where  $K_a$  and  $K_f$  are defined in eq 1 and values are taken from ref 3. The plot of  $\tau^{-1}/[\text{H}^+]$  vs.  $[\text{M} + \text{HL}^-]/[\text{H}^+]$  is linear with the slope given above. The inadequacy of this analysis is discussed in the text.

<sup>c</sup> There is an inconsistency in these results since the reverse rate constant of  $\sim 0.2 \text{ s}^{-1}$  disagrees with the value of  $4.2 \text{ s}^{-1}$  calculated from the forward rate constant and the equilibrium constant.

earity in the high- $[\text{H}^+]$  region. If the nonlinear region is disregarded, then the intercept gives  $k_2K_a \approx 0.8 \times 10^{-5} \text{ s}^{-1}$ , and with  $K_a = 5 \times 10^{-14} \text{ M}$ , then  $k_2 \approx 1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This value is about  $10^3$  times larger than expected for a dianion reacting with  $\text{Ni}(\text{OH}_2)_6^{2+}$ ; for example,  $\text{H}_3\text{COPO}_3^{2-}$  has a rate constant of  $2.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>5</sup> The very large value of  $k_2$  is not consistent with the normal reactivity of  $\text{Ni}(\text{OH}_2)_6^{2+}$ , and the scheme in eq 1 must be abandoned both on this basis and because of the nonlinearity of Figure 1.

Mentasti and co-workers<sup>2,3</sup> have proposed that hydrolyzed nickel(II) ( $(\text{H}_2\text{O})_5\text{NiOH}^+$ ) is a reactive species in these systems. Then the reaction scheme is given by eq 3.



For this scheme the pseudo-first-order rate constant has the form

$$k_{\text{exptl}} = (k_1'[\text{H}^+] + k_2'K_M) \left\{ \frac{[\text{Ni}^{2+}][\text{H}^+]}{(K_M + [\text{H}^+])(K_a + [\text{H}^+])} + \frac{1}{K_aK_f} \right\} \quad (4)$$

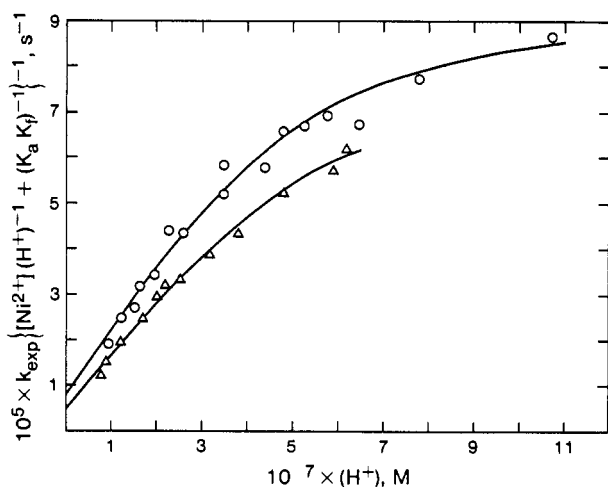
Since  $K_M$  ( $3.8 \times 10^{-10} \text{ M}$ )<sup>8</sup> and  $K_a$  ( $5 \times 10^{-14} \text{ M}$ )<sup>3</sup> are much

- (1) Williams, J. C.; Petrucci, S. J. *Am. Chem. Soc.* 1973, 95, 7619.
- (2) Hague, D. N.; Kinley, K. J. *Chem. Soc., Dalton Trans.* 1974, 249.
- (3) Mentasti, E.; Pelizzetti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* 1979, 18, 2007.
- (4) Mentasti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* 1980, 19, 3525.
- (5) Wilkins, R. G. *Acc. Chem. Res.* 1970, 3, 408; *Pure Appl. Chem.* 1973, 33, 583.
- (6) Secco, F.; Venturini, M. *Inorg. Chem.* 1975, 14, 1978.
- (7) Perlmutter-Hayman, B.; Tapuhi, E. *Inorg. Chem.* 1977, 16, 2742.

- (8) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976; Chapter 10. Hohl and Geier used a stopped-flow method to eliminate polymerization problems and obtained  $K_M = 1 \times 10^{-11} \text{ M}$ : Hohl, H.; Geier, G. *Chimia* 1971, 25, 401.

**Table II.** Kinetic Data for the Reaction of Nickel(II) with Salicylic Acid (25 °C,  $\mu = 0.30$  M (NaClO<sub>4</sub>))

$10^2 [\text{Ni}^{2+}]$ , M	pH	$k_{\text{exptl}}$ , s <sup>-1</sup>	$k_{\text{calcd}}$ , s <sup>-1</sup>
2.00	6.29	66.6	60.3
	6.38	59.7	54.2
	6.49	47.0	47.0
	6.64	34.0	38.1
	6.86	26.3	27.4
2.50	6.99	19.8	22.4
	6.24	66.3	65.0
	6.32	63.0	59.5
	6.46	57.3	50.2
	6.59	43.7	42.2
	6.79	33.7	31.7
	6.91	27.7	26.6
3.00	7.02	22.4	22.6
	6.19	77.8	69.7
	6.25	72.5	65.6
	6.28	69.3	63.5
	6.29	66.6	62.8
	6.40	55.3	55.3
	6.40	53.1	55.3
	6.56	42.9	45.2
	6.59	43.7	43.4
	6.71	36.4	36.8
	6.75	36.5	34.8
4.20	6.96	23.6	26.0
	6.96	25.7	26.0
	6.19	65.5	72.8
	6.28	61.1	66.5
	6.36	58.0	61.0
	6.46	53.5	54.3
	6.64	47.9	43.6
	6.65	48.0	43.0
	6.81	41.5	35.0
	6.82	31.9	34.6
	6.93	35.0	30.1
4.50	6.98	33.1	28.2
	7.02	26.3	26.9
	5.97	82.3	88.4
	6.11	74.7	79.0
	6.21	70.3	72.1
	6.37	58.8	61.1
	6.46	50.3	55.1
	6.56	45.3	48.9
	6.62	43.4	45.4

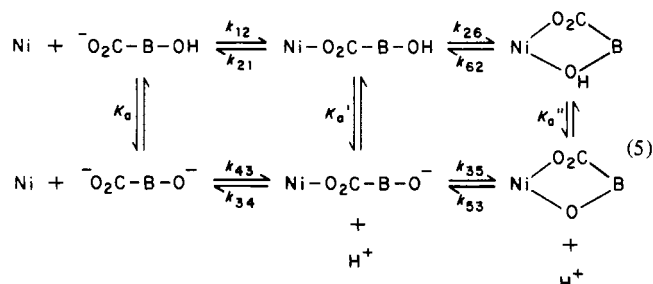
**Figure 1.** Variation of  $k_{\text{exptl}}\{[\text{Ni}^{2+}][\text{H}^+]^{-1} + (K_a K_f)^{-1}\}$  with  $[\text{H}^+]$  for the complexing of nickel(II) by salicylic acid (O) and 5-chlorosalicylic acid ( $\Delta$ ). For clarity only part of the data is shown; lines are eye guides only.

smaller than  $[\text{H}^+]$ , then eq 4 also predicts that the plot in Figure 1 should be linear. If, again, the nonlinearity of Figure 1 is disregarded, then it is possible to calculate that  $k_2' \approx 2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . This value seems more normal for substitution on nickel(II), but there is no precedent for the reactivity of a monodentate ligand with  $(\text{H}_2\text{O})_5\text{NiOH}^+$ . However, it has

been suggested that  $\text{NiOH}^+$  could be more reactive toward hydrogen-bonded ligands.<sup>9</sup> It seems peculiar that this species was not required to explain the earlier results at higher pH (Table I).

The above arguments against the reaction schemes in eq 1 and 3 still might be regarded as dangerously subjective. However, the fact remains that neither of these schemes explains the curvature in Figure 1. In other words, they are not consistent with the experimental rate law. Experience indicates that such problems may be overcome by a more detailed examination of the chelation process.<sup>5,10,11</sup>

A reaction scheme that will be shown to be consistent with the results is given by eq 5 (where  $\text{B} \equiv \text{C}_6\text{H}_4$ ). If a steady state



is assumed for the monodentate intermediates, then it can be shown that

$$k_{\text{exptl}} = \frac{(k_{12}[\text{H}^+] + k_{43}K_a)(k_{26}[\text{H}^+] + k_{35}K_a')}{(k_{21} + k_{26})[\text{H}^+] + (k_{34} + k_{35})K_a'} \times \left\{ \frac{[\text{Ni}^{2+}]}{(K_a + [\text{H}^+])} + \frac{K_a''}{K_a K_f (K_a'' + [\text{H}^+])} \right\} \quad (6)$$

where  $K_f = [\text{NiO}_2\text{C-B-O}^-]/[\text{Ni}^{2+}][\text{O}_2\text{C-B-O}^-] \text{ M}^{-1}$ . It will be convenient to make the substitution  $k_{34}K_a' = (k_{21}/k_{12})k_{43}K_a$  and rearrange the denominator of eq 6 to obtain

$$k_{\text{exptl}} = \frac{(k_{12}[\text{H}^+] + k_{43}K_a)(k_{26}[\text{H}^+] + k_{35}K_a')}{\frac{k_{21}}{k_{12}}(k_{12}[\text{H}^+] + k_{43}K_a) + (k_{26}[\text{H}^+] + k_{35}K_a')} \times \left\{ \frac{[\text{Ni}^{2+}]}{(K_a + [\text{H}^+])} + \frac{K_a''}{K_a K_f (K_a'' + [\text{H}^+])} \right\} \quad (7)$$

This equation can be simplified by using previous results on the substitution reactivity of  $\text{Ni}(\text{OH}_2)_6^{2+}$ <sup>5,10</sup> and the fact that (salicylato)pentaamminecobalt(III) has a  $\text{p}K_a \approx 10$ .<sup>12</sup> This value should be analogous to  $K_a'$  in eq 5, and a consideration of the charges of cobalt(III) and nickel(II) indicates that  $K_a' < 10^{-10} \text{ M}$ . It is expected that  $k_{35} \approx k_{26} \approx 3 \times 10^4 \text{ s}^{-1}$ , the water exchange on nickel(II),<sup>13</sup> and since  $[\text{H}^+] \gg K_a'$ , then  $k_{26}[\text{H}^+] \gg k_{35}K_a'$ . The dissociative ion-pair mechanism leads to the prediction that  $k_{43}$  is 3–4 times larger than  $k_{12}$ , but  $[\text{H}^+]$  is more than  $10^6$  times larger than  $K_a$ , so that  $k_{12}[\text{H}^+] \gg k_{43}K_a$  for our experimental conditions. Then eq 7 simplifies to

$$k_{\text{exptl}} = \frac{k_{26}}{k_{21} + k_{26}} (k_{12}[\text{H}^+]) \left\{ \frac{[\text{Ni}^{2+}]}{[\text{H}^+]} + \frac{K_a''}{K_a K_f (K_a'' + [\text{H}^+])} \right\} \quad (8)$$

- (9) Perlmutter-Hayman, B.; Shinar, R. *Inorg. Chem.* **1977**, *16*, 2643.  
 (10) Voss, R. H.; Jordan, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 6926.  
 (11) Cavasino, F. P. *J. Phys. Chem.* **1965**, *69*, 4380.  
 (12) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.  
 (13) Bechtold, D. B.; Liu, G.; Dodgen, H. W.; Hunt, J. P. *J. Phys. Chem.* **1978**, *82*, 333.

**Table III.** Kinetic Data for the Reaction of Nickel(II) with 5-Chlorosalicylic Acid (25 °C,  $\mu = 0.30$  M (NaClO<sub>4</sub>))

$10^2$ [Ni <sup>2+</sup> ], M	pH	$k_{\text{exptl}}$ , s <sup>-1</sup>	$k_{\text{calcd}}$ , s <sup>-1</sup>
2.00	6.23	26.8	25.7
	6.32	24.9	23.4
	6.50	19.1	19.1
	6.66	16.8	15.7
	6.77	13.7	13.6
	6.92	11.8	11.3
3.00	7.11	8.51	9.11
	6.23	27.1	27.9
	6.33	24.4	25.3
	6.42	22.2	23.1
	6.60	18.4	19.0
	6.69	17.1	17.2
4.00	6.78	14.5	15.6
	7.06	12.5	11.8
	6.21	30.9	30.5
	6.31	27.5	28.0
	6.42	25.4	25.2
	6.55	21.5	22.2
	6.70	19.4	19.2
	6.80	18.1	17.4
6.88	17.1	16.2	

A nonlinear least-squares fit of the data in Table II to eq 8 yields the values  $k_{12}k_{26}(k_{21} + k_{26})^{-1} = (2.49 \pm 0.5) \times 10^2$  M<sup>-1</sup> s<sup>-1</sup>,  $K_a'' = (6.06 \pm 1.0) \times 10^{-7}$  M, and  $K_aK_f = (1.25 \pm 0.35) \times 10^{-6}$ . The last value is in good agreement with that of  $(1.1 \pm 0.4) \times 10^{-6}$  determined by Mentasti et al.<sup>3,14</sup> The adequacy of the fit can be seen by comparison of the calculated and experimental values in Table II.

In order to further assess the validity of the scheme in eq 5, the reaction of nickel(II) with 5-chlorosalicylate has been studied. For this ligand the carboxylate group acid dissociation constant is about 1.5 times larger, and that of the hydroxy group is about 10 times larger than for salicylic acid.<sup>4</sup> However, the approximations used to obtain eq 8 should still apply. As can be seen in Figure 1, 5-chlorosalicylate behaves similarly to salicylate and the results are not consistent with the schemes in eq 1 or 3. However, the data can be fitted to eq 8 as shown by a comparison of the calculated and observed values in Table III. The nonlinear least-squares fit parameters are as follows:  $k_{12}k_{26}(k_{21} + k_{26})^{-1} = (2.14 \pm 0.21) \times 10^2$  M<sup>-1</sup> s<sup>-1</sup>;  $K_a'' = (6.44 \pm 1.3) \times 10^{-7}$  M;  $K_aK_f = (3.07 \pm 0.63) \times 10^{-6}$ . The last value is in satisfactory agreement with that of  $2.3 \times 10^{-6}$  ( $\mu = 0.10$  M) obtained by Mentasti et al.<sup>4</sup>

A more stringent test of the reaction scheme in eq 5 was carried out by a study of the reaction of nickel(II) with 3,5-dinitrosalicylate. This ligand has a much larger acid dissociation constant for the hydroxy group ( $6.31 \times 10^{-8}$  M)<sup>15</sup> than the other systems studied. Thus, it is no longer true that  $[H^+] \gg K_a$ .

Taylor and Chaudhuri<sup>15</sup> recently studied the equilibria in the nickel(II)-3,5-dinitrosalicylate system and found a formation constant of  $1.12 \times 10^4$  M<sup>-1</sup> for NiL<sup>16</sup> and  $1.78$  M<sup>-1</sup> for NiHL<sup>+</sup>.<sup>16</sup> These values can be combined with the ligand  $K_a$  to calculate  $K_a'' = (1.12 \times 10^4)(6.31 \times 10^{-8})/1.78 = 4.0 \times 10^{-4}$  M. Although the formation constant for NiHL<sup>+</sup> may refer to outer-sphere complex formation, it at least places a lower limit on the inner-sphere value. Therefore, it is reasonable to conclude that  $K_a'' \geq 4 \times 10^{-4}$  M, and  $K_a'' \gg [H^+]$

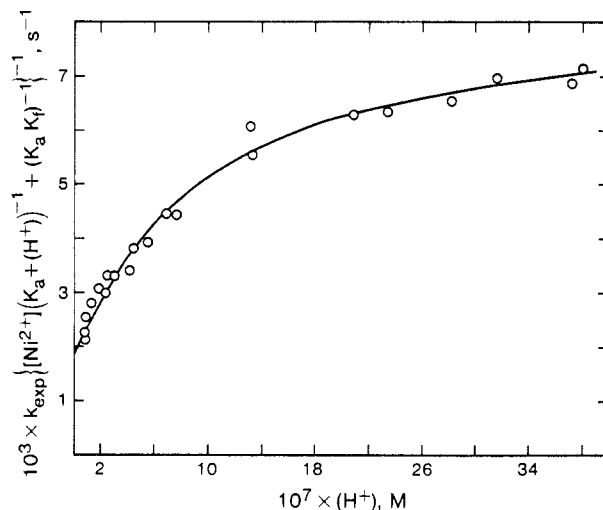
(14) The protonated species need not be in conflict with the results of ref 3 and 4. The species constitutes less than 7% of the total ligand, although it may be 50% of the complexed ligand for pH 6-7. Spectrophotometric detection monitors the phenolic hydrogen ionization, so that the protonated species would not be detectable spectrophotometrically.

(15) Chaudhuri, P.; Taylor, R. S. *Anal. Chim. Acta* **1975**, *78*, 451.

(16) Here L and HL refer to the dianion and monoanion of 3,5-dinitrosalicylate, respectively.

**Table IV.** Kinetic Data for the Reaction of Nickel(II) with 3,5-Dinitrosalicylic Acid (25 °C,  $\mu = 0.30$  M (NaClO<sub>4</sub>))

$10^{-3}$ [Ni <sup>2+</sup> ], M	pH	$k_{\text{exptl}}$ , s <sup>-1</sup>	$k_{\text{calcd}}$ , s <sup>-1</sup>
3.075	6.16	24.5	24.5
	6.26	25.3	26.3
	6.38	26.7	28.8
	6.52	33.3	32.0
	6.72	41.8	37.4
	6.88	48.2	42.3
5.027	7.06	56.1	48.4
	5.43	18.9	19.3
	5.50	20.7	20.3
	5.68	23.5	23.5
	5.88	30.7	28.0
	6.15	36.6	36.0
5.086	6.26	38.7	39.8
	6.36	44.6	43.4
	6.62	53.8	54.4
	6.76	57.0	61.3
	6.91	72.2	69.4
	7.08	80.7	79.2
7.570	6.11	46.3	48.5
	6.28	54.8	57.5
	6.39	62.7	63.8
	6.53	74.2	72.7
	6.72	86.6	86.3
	6.87	89.7	98.2
10.05	7.02	104.4	111.1
	5.42	28.8	28.3
	5.55	32.0	32.8
	5.65	36.6	36.9
	5.87	47.2	47.6
	6.15	66.6	65.0
6.35	81.0	79.8	
6.46	98.2	88.9	
6.60	110.9	101.5	
6.91	114.9	133.7	



**Figure 2.** Variation of  $F_{\text{exptl}} = k_{\text{exptl}}[\text{Ni}^{2+}](K_a + [\text{H}^+])^{-1} + (K_aK_f)^{-1}$  with  $[\text{H}^+]$  for the complexing of nickel(II) by 3,5-dinitrosalicylic acid. For clarity only about half of the data is shown. The curve represents the best fit of all the data to eq 10.

for  $\text{pH} > 5$ . If this condition is applied to eq 7, then a convenient experimental function,  $F_{\text{exptl}}$ , can be defined so that

$$\begin{aligned}
 F_{\text{exptl}} &= k_{\text{exptl}} \left\{ \frac{[\text{Ni}^{2+}]}{K_a + [\text{H}^+]} + \frac{1}{K_aK_f} \right\}^{-1} \\
 &= \frac{(k_{12}[\text{H}^+] + k_{43}K_a)(k_{26}[\text{H}^+] + k_{35}K_a')}{k_{21}(k_{12}[\text{H}^+] + k_{43}K_a) + (k_{26}[\text{H}^+] + k_{35}K_a')}
 \end{aligned}
 \tag{9}$$

The kinetic results are given in Table IV, and the variation of  $F_{\text{exptl}}$  with  $[H^+]$  is shown in Figure 2. The results can be fitted to the equation

$$F_{\text{exptl}} = (A[H^+] + B)/([H^+] + C) \quad (10)$$

The adequacy of the fit can be judged from the curve in Figure 2 and from the observed and calculated  $k_{\text{exptl}}$  values in Table IV.

A simple comparison shows that eq 9 reduces to the form of eq 10 in either of two limiting cases. If  $k_{43}K_a \gg k_{12}[H^+]$ , then, after rearrangement and substitution for  $K_a' = (k_{21}/k_{12})(k_{43}/k_{34})K_a$ , it is found that  $A = k_{43}K_a$ ,  $(AC/B) - 1 = k_{34}/k_{35}$ , and  $A^2/(AC - B) = (k_{12}/k_{21})k_{26}$ . A nonlinear least-squares fit of the data gives  $k_{43} = (1.34 \pm 0.07) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{35}/k_{34} = 0.245 \pm 0.02$ , and  $(k_{12}/k_{21})k_{26} = (1.07 \pm 0.12) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

On the other hand, if  $k_{35}K_a' \gg k_{26}[H^+]$ , then  $A = (k_{43}/k_{34})k_{35}K_a$ ,  $(AC/B) - 1 = k_{35}/k_{34}$ , and  $A^2/(AC - B) = k_{12}$ . A nonlinear least-squares fit of the data gives  $k_{43} = (3.26 \pm 0.26) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{35}/k_{34} = 4.09 \pm 0.29$ , and  $k_{12} = (1.07 \pm 0.12) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

A choice between these two cases might be made on the basis of the consistency of the values with a dissociative ion-pair mechanism,<sup>5</sup> in which case  $k_{12}$  and  $k_{43}$  should be similar to values for other mono- and dianions, respectively. The reactions of the carboxylate dianions of several malonate derivatives<sup>11,17</sup> and phthalate<sup>18</sup> have values in the range of  $(7-23) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The carboxylate monoanions of picolinate,<sup>10</sup> fumarate,<sup>10</sup> and monohydrogen phthalate<sup>18</sup> complex nickel(II) with rate constants of  $3.6 \times 10^4$ ,  $3.9 \times 10^4$ , and  $3.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. Therefore, normal behavior of 3,5-dinitrosalicylate would give  $k_{43} \approx 10 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{12} \approx 3.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

For the first limiting case of eq 9 ( $k_{43}K_a \gg k_{12}[H^+]$ ) the value of  $k_{43}$  ( $13 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) appears normal. However, from the experimental conditions of  $[H^+] \leq 4 \times 10^{-6} \text{ M}$  and the value of  $k_{43}K_a$  it is possible to calculate an upper limit of  $k_{12} \ll 2.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  to satisfy the condition for this case. In turn this limit can be used with the value of  $(k_{12}/k_{21})k_{26}$  to calculate that  $k_{26}/k_{21} \geq 5$ . The value of  $k_{12}$  is at least 16 times smaller than the "normal" carboxylate values given above. The  $k_{26}/k_{21}$  ratio also seems unusual when compared to  $k_{35}/k_{34} = 0.25$ . A simple dissociative mechanism would predict  $k_{26} \approx k_{35}$ , and  $k_{21} > k_{34}$  from the relative basicity of the ligands so that  $k_{35}/k_{34}$  would be greater than  $k_{26}/k_{21}$ . The small  $k_{12}$  could be due to hydrogen bonding in the monoanion, and hydrogen bonding to coordinated water might decrease  $k_{21}$  and/or increase  $k_{26}$ .

The second limiting case gives an almost normal value for  $k_{12}$  ( $1.07 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ), but the value of  $k_{43}$  ( $3.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) is smaller than expected for a dianion. It is difficult to see why this dianion should be 7 times less reactive than the phthalate dianion. The condition that  $k_{35}K_a' \gg k_{26}[H^+]$  can be written as  $k_{21}/k_{26} \gg [H^+]k_{12}(k_{34}/k_{35})/k_{43}K_a \approx 6$  or  $k_{26}/k_{21} < 0.17$ . This ratio has the expected relationship to  $k_{35}/k_{34}$  (4.05) if simple ligand basicity factors make  $k_{21} > k_{34}$  and  $k_{26} \approx k_{35}$ .

It seems reasonable to expect  $k_{12}$  to be similar for the three systems studied here. Unfortunately, only  $k_{12}k_{26}/(k_{21} + k_{26})$  could be determined for salicylate and 5-chlorosalicylate, but the  $k_{26}/k_{21}$  limits from the 3,5-dinitrosalicylate system can be used to estimate  $k_{12}$  for the other two ligands. If  $k_{26}/k_{21} > 5$ , as in the first limiting case of eq 9, and an average value of  $k_{12}k_{26}/(k_{21} + k_{26}) \approx 2.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  is used, then  $k_{12} <$

$(2.3 \times 10^2)(1 + 1/5) = 2.8 \times 10^2$ . This is consistent with the upper limit of  $2.3 \times 10^3$  estimated for this case. For the second case  $k_{26}/k_{21} < 0.17$  so that  $k_{12} > (2.3 \times 10^2)(1 + 1/0.17) = 1.6 \times 10^3$ . This lower limit is consistent with the value of  $1.07 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_{12}$  in the second case. In other words, the results from the two cases are internally consistent and do not differentiate the two possibilities.

These ambiguities in the interpretation could be settled if previous work had shown that salicylate monoanions have either normal or abnormal reactivity with other metal ions. If intramolecular hydrogen bonding is an important kinetic feature of these ligands, then one might expect it to be manifested with other hydrated metal ions. Studies with  $\text{Al}(\text{OH}_2)_6^{3+6,7}$  and  $(\text{H}_2\text{O})_5\text{FeOH}^{2+19}$  have been interpreted to indicate that salicylate monoanions have a normal reactivity for a dissociative ion-pair mechanism, and it is generally suggested that some metal ions are more effective in breaking the hydrogen bond. However, all of these studies have been analyzed in terms of a reaction scheme analogous to eq 3, and the present results indicate that this analysis may be misleading.

The most recent study of the gallium(III)-salicylate and -5-chlorosalicylate systems<sup>20</sup> has shown spectrophotometric evidence for protonated gallium complexes  $\text{GaHL}^{2+}$  analogous to the  $\text{NiHL}^+$  proposed here. It is noteworthy that gallium(III) seems to have anomalously low rate constants with the ligand anion  $\text{HL}^-$ . Secco et al.<sup>20</sup> have ascribed the low rate constants and their variation with ligand basicity to an  $\text{S}_{\text{N}}2_{\text{ip}}$  mechanism. The results could be explained by a reaction scheme analogous to that proposed here (eq 5). If the formation rate constant is approximately given by  $(k_{12}/k_{21})k_{26}$ , then the value could be unexpectedly small because  $(k_{12}/k_{21}) \ll 1$ , and the trend with ligand basicity would be that expected for  $k_{12}/k_{21}$ .

The results of Hague and Kinley<sup>2</sup> on 5-nitrosalicylate may satisfy the condition  $k_{43}K_a > k_{12}[H^+]$  from a consideration of pH range and acidity of the ligand. Then  $k_{\text{exptl}} = k_{43} \times K_a(k_{26}[H^+] + k_{35}K_a')/k_{26}[H^+] + (k_{34} + k_{35})K_a'^{-1}$ , and if  $k_{26}[H^+] > (k_{34} + k_{35})K_a'$  or more probably  $k_{34} \approx k_{35}$ , then the calculated rate constant is  $\sim k_{43}$ . The value obtained by Hague and Kinley,  $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , is in agreement with the value of  $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  obtained here for one of the limiting cases with 3,5-dinitrosalicylate.

It is more difficult to assess the results of Williams and Petrucci<sup>1</sup> because of ambiguities in the publication. The discussion of ion-pair effects implies that  $\text{HL}^-$  is the reactant, and the rate law is written as if  $\text{L}^{2-}$  is the reactant, but otherwise the data treatment ( $\alpha \ll 1$ ) requires  $\text{HL}^-$  as the reactant. In addition the salicylate is not fully complexed as assumed by Williams and Petrucci but rather generally about 5% is complexed. The simple analysis in Table I produces a good representation of the data. However, a treatment including indicator coupling, as given by Cavasino,<sup>11</sup> does not give even a smooth variation of relaxation rate with pH at either 20 or 25 °C. Variations of the acid dissociation constants and formation constants over the range of literature values failed to unravel this problem. Therefore it seems pointless to attempt a mechanistic analysis of the data of Williams and Petrucci.<sup>1</sup>

The studies of Mentasti et al.<sup>3,4</sup> were done under conditions similar to those of this work. The previous comments with regard to the inadequacy of eq 2 and 4 apply to the interpretation of Mentasti et al. The failings of these rate laws were not recognized.

The analysis described here shows that it is not necessary to invoke  $(\text{H}_2\text{O})_5\text{NiOH}^+$  to explain the results. This also

(17) Calvaruso, G.; Cavasino, F. P.; DiDio, E. *J. Phys. Chem.* **1976**, *80*, 239.  
 (18) Cavasino, F. P.; DiDio, E.; Locanto, G. *J. Chem. Soc., Dalton Trans.* **1973**, 2419.

(19) Mentasti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 602.  
 (20) Corigli, R.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 2992.

explains why Hague and Kinley did not require hydrolyzed nickel(II) even at pH 8.

Unfortunately, the important question of the kinetic importance of intramolecular hydrogen bonding in salicylate anions remains unresolved. In the case that the monoanion of 3,5-dinitrosalicylate has normal reactivity, one is left with the difficulty of accounting for the low reactivity of the dianion. If the dianion has normal reactivity, then first bond formation and dissociation and subsequently chelate ring closing may be affected by hydrogen bonding in a way to account for the results. However, these are not overwhelming arguments for the kinetic effects of intramolecular hydrogen bonding.

### Experimental Section

**Materials.** Salicylic acid (Matheson Coleman and Bell), 5-chlorosalicylic acid (Eastman), and 3,5-dinitrosalicylic acid (Matheson Coleman and Bell) were recrystallized from water before use. Aqueous nickel(II) perchlorate was prepared from nickel carbonate and standardized as described previously.<sup>10</sup> The buffer Pipes (1,4-piperazinebis(2-ethanesulfonic acid)) (Aldrich) was used as supplied. Solutions for kinetic studies were prepared in doubly distilled deionized water.

**Kinetic Measurements.** A 10-fold or greater molar excess of nickel(II) over ligand was used to ensure pseudo-first-order conditions. The two solutions of nickel(II) plus buffer ( $1.0 \times 10^{-2}$  M) plus sodium perchlorate and ligand plus buffer ( $1.0 \times 10^{-2}$  M) plus sodium

perchlorate were adjusted to the desired pH and ionic strength (0.30 M) before mixing in the stopped-flow system. The recorded pH is that of the mixed solutions collected from the stopped-flow system. The pH before and after mixing generally differed by less than 0.04 unit. In one set of runs with salicylate the buffer concentration was changed to  $5 \times 10^{-3}$  M without detectable effect on the observed rate over the full pH range of the study.

The pH was measured on a Beckman Expandomatic meter using a 2.00 pH unit full-scale expansion. The meter was calibrated against standard buffers before use.

The optimum wavelengths for observation were determined from preliminary experiments on a Cary 219 spectrophotometer. The wavelengths used were 350, 340, and 360 nm for the salicylate, 5-chlorosalicylate, and 3,5-dinitrosalicylate systems, respectively.

A standard Aminco-Morrow stopped-flow system was used.<sup>10</sup> The transmittance-time curves were stored on a Tracor NS-570 signal averager and then output to a dual-trace oscilloscope for comparison to a synthetic exponential decay curve of variable, known time constant.<sup>21</sup> The recorded rate constants are the average of 5-8 replicate determinations.

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(21) Pinnell, D.; Jordan, R. B. *Inorg. Chem.* 1979, 18, 3191.

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## Electron-Transfer Transitions in Hexachloroferrate(III). Single-Crystal Absorption and MCD Spectra

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Crystals of  $\text{Cs}_2\text{NaYCl}_6$  doped with  $\text{FeCl}_6^{3-}$  in which  $\text{Fe}^{3+}$  occupies sites of exact  $O_h$  symmetry were prepared by the Bridgman technique. Absorption and magnetic circular dichroism (MCD) spectra of  $\text{FeCl}_6^{3-}$  were measured at low temperatures over the region 20 000-45 000  $\text{cm}^{-1}$ . The observed features were attributed to ligand-to-metal electron-transfer transitions. The MCD spectrum is dominated by  $\mathcal{O}$  terms which arise as a joint consequence of the ground-state spin degeneracy and the excited-state spin-orbit splittings. With use of a simple model, spin-orbit coupling effects are treated in detail, and a theoretical simulation of the MCD spectrum is presented that is in semiquantitative agreement with experiment. The energy ordering of the ligand donor orbitals is found to be  $t_{1g} > t_{1u}(\pi + \sigma) > t_{2u} > t_{1u}(\sigma + \pi)$ , and a best fit of the spectrum yields the spin-orbit coupling parameters  $\zeta_{\text{Fe}} = 320 \text{ cm}^{-1}$  and  $\zeta_{\text{Cl}} = 580 \text{ cm}^{-1}$  with about 10%  $\sigma$ - $\pi$  mixing in the  $t_{1u}$  ligand orbitals.

### Introduction

Hexachloro and hexabromo complexes of trivalent 3d transition-metal ions have received very little spectroscopic attention. This is in strong contrast to the corresponding octahedral complexes of rhenium(IV), iridium(IV), ruthenium(IV), molybdenum(IV), and osmium(IV), which have been thoroughly investigated by low-temperature single-crystal absorption and magnetic circular dichroism (MCD) spectroscopy.<sup>1-8</sup> The members of the first transition-metal series are chemically unstable in solution and can best be prepared from the melt. The cubic materials  $\text{Cs}_2\text{NaYCl}_6$  and  $\text{Cs}_2\text{NaInCl}_6$  served as host lattices for studies of the absorption, MCD (d-d transitions), and luminescence properties of  $\text{CrCl}_6^{3-}$ .<sup>9,10</sup> No other reports of absorption spectra of octahedral  $\text{MX}_6^{3-}$  ( $M = 3d$  metal;  $X = \text{Cl}, \text{Br}$ ) are found in the literature. A diffuse powder reflectance spectrum of  $(\text{NH}_4)_4\text{FeCl}_6\cdot\text{SbCl}_6$  in the region of the d-d transitions has been reported.<sup>11</sup>

Ligand-to-metal charge-transfer (CT or electron transfer) transitions were of primary interest in the studies of  $\text{MX}_6^{n-}$  complexes of the second and third transition-metal series. The relative order of donor ligand orbitals was unambiguously established on the basis of the MCD results.<sup>1,3-8</sup> Electron-transfer transitions were also investigated in tetrahedral

- (1) Henning, G. N.; McCaffery, A. J.; Schatz, P. N.; Stephens, P. J. *J. Chem. Phys.* 1968, 48, 5656.
- (2) Jørgensen, C. K. *Prog. Inorg. Chem.* 1970, 12, 101.
- (3) Piepho, S. B.; Lester, T. E.; McCaffery, A. J.; Dickinson, J. R.; Schatz, P. N. *Mol. Phys.* 1970, 19, 781.
- (4) Bird, B. D.; Day, P.; Grant, E. A. *J. Chem. Soc. A* 1970, 100.
- (5) Piepho, S. B.; Dickinson, J. R.; Spencer, J. A.; Schatz, P. N. *Mol. Phys.* 1972, 24, 609.
- (6) Collingwood, J. C.; Schwartz, R. W.; Schatz, P. N.; Patterson, H. H. *Mol. Phys.* 1974, 27, 1291.
- (7) Collingwood, J. C.; Piepho, S. B.; Schwartz, R. W.; Dobosh, P. A.; Dickinson, J. R.; Schatz, P. N. *Mol. Phys.* 1975, 29, 793.
- (8) Collingwood, J. C.; Schatz, P. N.; McCarthy, P. J. *Mol. Phys.* 1975, 30, 469.
- (9) Schwartz, R. W. *Inorg. Chem.* 1976, 15, 2817.
- (10) Güdel, H. U.; Snellgrove, T. R. *Inorg. Chem.* 1978, 17, 1617.
- (11) Yamatera, H.; Kato, A. *Bull. Chem. Soc. Jpn.* 1968, 41, 2220.

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