now appear to be more significant than the SO_2 + $O(^3P)$ + M reaction in leading to the conversion of SO_2 to SO_3 and sulfuric acid aerosol. The point should also be made that based on these results the OH + SO_2 + M reaction would appear to be of major importance in both the troposphere and stratosphere.

Temperature Jump Relaxation Kinetics of the Chelation of Nickel(II) and Cobalt(II) with Some Aromatic Ligands[1]

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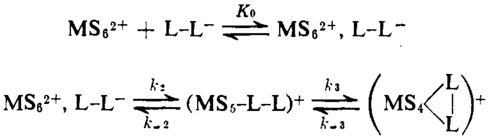
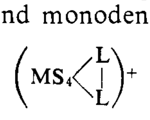
Abstract: The temperature jump relaxation kinetics of Ni^{2+} with anthranilate ion at 25° and salicylate and 5-sulfosalicylate ions at temperatures between 15 and 35° and Co^{2+} with salicylate and 5-sulfosalicylate ions at 20° have been studied and the results reported here. In all cases the forward rate constant k_f appears to be significantly smaller than that required by the "normal" Eigen chelation mechanism in terms of the product $(1/S)K_0k_{ex}$ (with $1/S$ a statistical factor, generally equal to 0.2, K_0 the Fuoss outer-sphere preequilibration constant, and k_{ex} the solvent exchange rate constant determined from nmr measurements). For nickel(II) sulfosalicylate, k_f is the same, within experimental error, as for nickel(II) salicylate. However, because of the extra charge of the sulfonate group and consequently larger K_0, one would expect a much larger rate constant k_f for this ion with respect to the salicylate ion. That this is not the case is suggested by the activation parameters $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ being comparable for both ligands. The preceding is reflected in measurements of complexation rates of Co^{2+} with salicylate and sulfosalicylate ions, the rate constants being within a factor of 2 of each other. A discussion of the statistical reason for this similarity in the rate constants for the salicylate and sulfosalicylate ions is given in terms of charge delocalization with respect to the point of attack at the reaction site. For nickel(II) salicylate comparison between $\Delta H_{ex}^{\ddagger}$ and $\Delta S_{ex}^{\ddagger}$ with the quantities $(\Delta H_f^{\ddagger} - \Delta H_0)$ and $(\Delta S_f^{\ddagger} - \Delta S_0)$ (with ΔH_0 and ΔS_0 the outer-sphere activation parameters) suggests that the source of the deviation from the normal chelation mechanism is entropic.

The kinetics of chelation of ionic complexation reactions has been the subject of many discussions and investigations in the past.[2] One may discuss the equilibrium between a divalent metal cation MS_6^{2+} (with S a solvent molecule) and a monovalent bidentate ligand $(L\text{–}L)^-$ in terms of the Eigen multistep mechanism



$$MS_6^{2+} + L\text{–}L^- \underset{}{\overset{K_0}{\rightleftharpoons}} MS_6^{2+}, L\text{–}L^-$$
$$MS_6^{2+}, L\text{–}L^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (MS_5\text{–}L\text{–}L)^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \left(MS_4\Big\langle\begin{smallmatrix}L\\|\\L\end{smallmatrix}\right)^+ \qquad (1)$$

where $MS_6^{2+}, L\text{–}L^-$ is an outer-sphere ion pair, $(MS_5\text{–}L\text{–}L)^+$ the metal ligand monodentate complex, and



$$\left(MS_4\Big\langle\begin{smallmatrix}L\\|\\L\end{smallmatrix}\right)^+$$

the chelate complex. By applying the rate equations to scheme 1 and imposing a steady state condition on the intermediate, $d(MS_5\text{–}LL)^+/dt = 0$, with the additional requirement of the preequilibration of the first step, one obtains the relations[3,4] in terms of the overall rate constants k_f and k_r.

$$k_f = K_0k_2k_3/(k_3 + k_{-2}) \qquad (2)$$

$$k_r = k_{-2}k_{-3}/(k_3 + k_{-2}) \qquad (3)$$

For an interchange dissociative process (I_d), the second step in the above scheme will have a rate constant k_2 equal to k_{ex} (the one for solvent exchange) within a statistical factor[5,6] $1/S \simeq 0.2$.[5,6] K_0 may be calculated through the Fuoss relation[7]

$$K_0 = (4\pi Na^3/3000)e^be^{-b\varkappa a/(1+\varkappa a)} \qquad (4)$$

where the symbols $b = |z_1z_2|e^2/aDkT$ and $\gamma_{\pm}^2 = e^{-b\varkappa a/(1+\kappa a)}$ are[7] the Bjerrum parameter and the activity coefficient according to Debye and Hückel. k_{ex} is the experimental pseudo-first-order constant for solvent exchange as determined by nmr ^{17}O line broadening.[8]

It is apparent that in the majority of the cases, if $(k_3/k_{-2}) \gg 1$

$$\begin{aligned} k_f &= K_0k_2 = (1/S)K_0k_{ex} \\ k_r &= k_{-2}(k_{-3}/k_3) \end{aligned} \qquad (5)$$

and the closing of the chelate ring is faster than the breaking of the first metal–ligand bond ("normal chelation").

Evidence of the converse condition $(k_3/k_{-2}) \ll 1$ has

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[1] This work is part of the thesis of Joseph C. Williams in partial fulfillment of the requirements for the degree of Ph.D., at the Polytechnic Institute of Brooklyn. Support by the IBM Corporation in the form of a graduate fellowship to J. C. W. is acknowledged.

[2] (a) F. Basolo and R. G. Pearson "Mechanism of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 224. (b) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970), and literature references quoted therein.

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[5] C. H. Langford and T. R. Stengle, *Annu. Rev. Phys. Chem.*, **19**, 193 (1968).

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Table I. Stoichiometric Equilibrium Constants[a]

t, °C		Metal ion	K_{HL}, M	K_{H_2L}, M	K_1, M	K_2, M
25	Anthranilic acid[b]	Ni^{2+}	1.13×10^{-5}	7.81×10^{-3}	1.32×10^{2}	2.95×10^{1}
20	Salicylic acid[c]	Ni^{2+}	2.51×10^{-14}	1.05×10^{-3}	8.91×10^{6}	6.31×10^{4}
20		Co^{2+}	2.51×10^{-14}	1.05×10^{-3}	5.25×10^{6}	5.01×10^{4}
20	5-Sulfosalicylic acid[c]	Ni^{2+}	1.12×10^{-12}	2.40×10^{-3}	2.00×10^{6}	7.94×10^{3}
		Co^{2+}	1.12×10^{-12}	2.40×10^{-3}	1.00×10^{6}	3.98×10^{3}
	Indicator	K_{In}, M				
20	Phenol Red[d]	1.26×10^{-8}				

[a] $K_{H_2L} = [H][HL]/[H_2L]$; $K_{HL} = [H][L]/[HL]$; $K_n = [MeL_n]/[MeL_{n-1}][L]$, $n = 1, 2$; $K_{In} = [H][In]/HIn$. [b] P. O. Lumme, *Suom. Kemistilehti B*, **30**, 176 (1957). [c] D. D. Perrin, *Nature* (*London*), **182**, 741 (1958). [d] I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

been reported for Co^{2+} with β-alanine[9] and Cu^{2+} with the enol forms of acetylacetonate[2] (steric substitution). In this case

$$\begin{aligned} k_f &= K_0K_2k_3 \\ k_r &= k_{-3} \end{aligned} \tag{6}$$

and the rate-determining step becomes the closing of the chelate ring.

In previous work, chelating ligands containing binding groups connected by a flexible hydrocarbon chain were used, *e.g.*, amino acids such as glycine,[3] α- and β-alanine,[9] α- and β-aminobutyric acid,[10] etc. Ligands containing a rigid benzene frame such as aromatic amino acids and oxyacids were not used. Some of the latter ligands have great biological importance; further, from a structural point of view, it was of interest to investigate the effect of the nature and position of the ligand in the benzene ring on reactivity with the metal.

For this reason anthranilic and salicylic acids (where the amino group is replaced by an hydroxy group) were used with Ni^{2+} and the latter with Co^{2+}.

The effect of substitution in position 5 of one proton by a sulfonate group was examined by using sulfosalicylic acid with both Ni^{2+} and Co^{2+}.

Comparison of the results for the two ligands salicylic acid and sulfosalicylic acids (and the fact that k_f is comparable for both ligands, despite the -2 charge of sulfosalicylic acid) caused us to decide to perform the temperature-dependence study of the rate constant for the Ni^{2+} salts to resolve this finding.

Experimental Section

Materials. $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (Fisher reagent grade) were used without further purification. Anthranilic acid (Eastman recrystallized, mp 146–147°), salicylic acid (Fisher reagent grade), 5-sulfosalicylic acid (Mallinkrodt, A. R.), and Phenol Red (Matheson Coleman Bell, reagent grade) also were used without further purification. Water was deionized water passed through two ion-exchange, mixed bed Barnstead columns. The electrical conductance monitored during collection was always less than $1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The desired pH of the solution was obtained, after dilution with a 0.1 M KNO_3 solution, by dropwise addition of 1 M HNO_3 or KOH and measured on a Leeds and Northrup pH meter to within $\pm 10^{-2}$ pH unit. The pH meter was calibrated just prior to use each time with standard buffer with an error of ±0.01 pH unit. The concentration of the indicator (Phenol Red) was maintained at 10^{-5} M. The ionic strength of the solution was taken equal to that of the solvent, namely 0.10 M KNO_3 in water.

Instrumentation. A temperature jump apparatus (Joule heating type) similar to the one described by Eigen[4] was used.

The magnitude of the temperature jump was determined to be 4.8 ± 0.4° by using a thermistor (Fenwal Model GB43P8) and microvoltammeter (Keathly Model 150A). The response of the detection system was $<10^{-2}$ sec. The jump was monitored for initial temperatures ranging from 5 to 30° and a discharge of 25 kV.

Blank experiments with solutions containing only the metal nitrate and indicator, or ligand and indicator, did not show any relaxation effect within the range of the instrument.

Results and Calculations

The formation constants K_{ML} for the first metal–ligand complexation are reported in Table I along with the dissociation constants of the ligand and the indicator. The data have been taken from the literature. In the cases where K_{ML} was not available, the method of calculation is reported below.

In Table II the relaxation times for the solutions and temperatures investigated are reported as τ^{-1} along with the initial experimental conditions (stoichiometric concentration of metal ion and ligand, pH of the solutions, and equilibrium concentrations of metal plus ligand).

The ionic strength was 0.1 M for all cases, the "solvent" being a 0.1 M solution of KNO_3. The relaxation times reported are the average of at least five oscillographic recordings calculated as the abscissa corresponding to $1/e$ of the maximum initial displacement. All the relaxation terms corresponded to a single relaxation function, plots of log displacements (in arbitrary units) *vs.* time being invariably linear.

For all the solutions investigated, since a large excess of metal ion over ligand was employed, the concentration of MeL_2 was always negligible. The data were interpreted according to the relation

$$M + L \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ML \tag{7}$$

where charge symbols have been omitted. The symbol L corresponds to the unprotonated form of the acid for anthranilic, salicylic, and sulfosalicylic acids. Indeed, from the reported pH in Table II and the acid dissociation constants of Table I, it may be calculated that the carboxylate group in anthranilic and in salicylic acids is mainly in the unprotonated form. The same holds true for both the sulfonate and carboxylate groups of sulfosalicylic acid. Data taken at lower pH show that in this time range no attack of the metal by HL (or H_2L) occurs. In fact, at low pH, the relaxation effect disappears.

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(10) A. Kolawak, K. Kustin, R. F. Pasternak, and S. Petrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

Table II. Stoichiometric Concentrations, pH, Σc_i, and Reciprocal Relaxation Times for the Solutions and Temperatures Investigated

$[Ni^{2+}]^0 \times 10^3$	$[HL]^0 \times 10^3$	pH	$\Sigma c_i = ([Ni^{2+}] + [L]) \times 10^3$	τ^{-1}, sec^{-1}
Ni^{2+}–Anthranilic Acid, $t = 25°$				
8.25	0.73	8.09	8.24	28.91 ± 1.12
6.70	0.62	7.82	6.76	24.39 ± 1.53
5.45	0.48	7.93	5.53	22.08 ± 1.03
3.85	0.34	8.10	3.97	18.56 ± 0.75
2.55	0.27	8.35	2.68	15.68 ± 0.47
Ni^{2+}–Salicylic Acid, $t = 15°$				
9.35	0.85	7.81	8.50	18.56 ± 0.56
7.85	0.75	8.04	7.10	16.32 ± 0.59
6.75	0.63	7.81	6.12	13.18 ± 0.61
5.40	0.48	8.05	4.92	11.33 ± 0.43
4.25	0.35	7.95	3.90	8.34 ± 0.17
3.15	0.28	7.93	2.87	6.94 ± 0.36
$t = 20°$				
10.00	2.00	7.88	8.00	31.90 ± 1.58
8.20	0.70	7.73	7.50	31.87 ± 1.37
8.00	1.00	7.78	7.00	28.34 ± 1.45
6.15	0.55	7.71	5.60	22.82 ± 1.61
6.00	1.50	7.72	4.50	19.21 ± 0.43
5.00	1.00	7.98	4.00	16.87 ± 1.09
3.10	0.28	7.95	2.82	11.25 ± 0.52
2.05	0.18	7.97	1.87	7.23 ± 0.34
$t = 25°$				
9.35	0.85	7.81	8.50	44.92 ± 2.16
7.85	0.75	8.04	7.10	38.28 ± 2.03
6.75	0.63	7.81	6.12	32.74 ± 2.41
5.40	0.48	8.05	4.92	25.18 ± 1.08
4.25	0.35	8.16	3.90	20.34 ± 0.85
3.15	0.28	7.93	2.87	16.50 ± 0.04
2.05	0.18	8.19	1.87	10.05 ± 0.66
$t = 30°$				
7.85	0.75	8.02	7.10	53.97 ± 1.73
6.75	0.63	7.91	6.12	45.96 ± 5.06
5.40	0.48	8.08	4.92	35.92 ± 1.80
4.25	0.35	8.16	3.90	30.36 ± 1.82
3.15	0.28	8.13	2.87	21.84 ± 1.27
2.05	0.18	8.19	1.87	14.44 ± 0.92
Ni^{2+}–5-Sulfosalicylic Acid, $t = 20°$				
10.15	0.48	7.84	9.67	28.34 ± 0.60
9.25	0.85	7.76	8.40	23.88 ± 2.63
8.15	0.74	7.92	7.41	21.05 ± 2.64
6.45	0.58	7.80	5.87	17.09 ± 0.72
4.98	0.82	7.84	4.16	13.28 ± 1.12
3.20	0.64	7.92	2.56	7.50 ± 0.91
$t = 25°$				
9.35	0.85	7.99	8.50	39.76 ± 1.45
8.15	0.74	7.89	7.41	31.54 ± 0.97
6.45	0.58	7.91	5.87	27.42 ± 1.38
4.95	0.47	8.19	4.48	18.28 ± 0.90
2.90	0.28	7.91	2.62	11.04 ± 0.25
$t = 30°$				
9.35	0.85	7.81	8.50	52.14 ± 2.78
8.15	0.74	7.89	7.41	46.19 ± 1.36
6.45	0.58	7.84	5.87	37.50 ± 2.11
4.95	0.47	8.19	4.48	25.64 ± 1.63
2.90	0.28	7.91	2.62	15.63 ± 0.43
$t = 35°$				
9.35	0.85	7.81	8.50	78.68 ± 2.62
8.15	0.74	7.73	7.41	64.29 ± 2.84
6.45	0.58	7.81	5.87	52.85 ± 2.09
4.95	0.47	8.19	4.48	38.37 ± 1.02
2.90	0.28	7.91	2.62	25.44 ± 1.30

$[Co^{2+}]^0$	$[HL]^0 \times 10^3$	pH	$\Sigma c_i = ([Co^{2+}] + [L])$	$\tau^{-1} \times 10^{-3}$, sec^{-1}
Co^{2+}–Salicylic Acid, $t = 20°$				
9.50	0.80	7.63	8.70	1.198 ± 0.133
7.80	0.68	7.99	7.12	0.923 ± 0.084
6.20	0.57	8.01	5.63	0.746 ± 0.038
3.95	0.38	7.90	3.57	0.534 ± 0.029
2.75	0.25	7.98	2.50	0.347 ± 0.110
Co^{2+}–5-Sulfosalicylic Acid, $t = 20°$				
8.30	0.78	7.70	7.52	1.988 ± 0.018
6.90	0.62	7.77	6.28	1.580 ± 0.011
5.50	0.47	7.79	5.03	1.441 ± 0.016
4.08	0.36	7.91	3.72	0.991 ± 0.055
2.80	0.25	7.91	2.55	0.564 ± 0.078
1.75	0.15	7.71	1.60	0.439 ± 0.016

The reciprocal relaxation time for a system containing a coupled reaction of type 7 is[4,11]

$$\tau^{-1} = k_f\left(\frac{[M]}{1 + \alpha} + [L]\right) + k_r \qquad (8)$$

where[11]

$$\alpha = \frac{[H]}{K_{HL} + [L]\left(\dfrac{K_{Ind} + [H]}{K_{Ind} + [H] + [Ind]}\right)} \qquad (9)$$

The terms K_{HL} and K_{Ind} refer to the acid dissociation constants of ligand and indicator, respectively. For the systems investigated in this work $\alpha \ll 1$.

Plots of τ^{-1} *vs.* $\Sigma c_i = [M] + [L]$ are shown in Figure 1 for nickel(II) anthranilate, salicylate, and sulfosalicylate, respectively, at the temperatures investigated. In Figure 2, the same quantities are shown for cobalt(II) salicylate and sulfosalicylate at 20°.

The quantity Σc_i in the abscissa has been calculated as follows. For nickel(II) anthranilate, where the literature value of K_{ML} was available, combination of the mass law expression $K_{ML} = [ML]/[M][L]$ with the two mass balance relations $[M]^0 = [M] + [ML]$ and $[L]^0 = [L] + [ML]$ yields [ML] and consequently [M], [L], and Σc_i.

For the other ligands K_{ML}, when known, is so large (Table I) that one can write in all cases $[L] = 0$, $[L]^0 = [ML]$, $[M] = [M]^0 - [L]^0 = \Sigma c_i$.

The solid lines in Figures 1 and 2 are calculated least-squares functions of the final plots of τ^{-1} *vs.* Σc_i. The results for k_f and k_r are reported in Table III together with their standard errors calculated from statistical analysis of deviations of slope and intercept.[12]

Figure 3 reports the plots of log k_f/T *vs.* $1/T$ for nickel(II) anthranilate, nickel(II) salicylate, and nickel(II) sulfosalicylate according to the Eyring function

$$k_f = \frac{kT}{h}e^{-\Delta H_f^{\ddagger}/RT}e^{\Delta S_f^{\ddagger}/R} \qquad (10)$$

where the symbols have their usual meanings.[13] $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ have been calculated from the least-squares computed slope and intercept of the plots according

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Table III. Rate Constants, k_f and k_r, Activation Parameters, $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$, and Ratios, k_f/k_r, for the Metal Complexation Investigated

Metal	Ligand	t, °C	k_f, M^{-1} sec^{-1}	k_r, sec^{-1}	$\Delta H_f^{\ddagger}$, kcal/mol	$\Delta S_f^{\ddagger}$, esu	k_f/k_r, M^{-1}
Ni^{2+}	Anthranilate	25	$(2.32 \pm 0.10) \times 10^3$	(9.3 ± 0.6)			250
Ni^{2+}	Salicylate	15	$(2.15 \pm 0.11) \times 10^3$	(0.5 ± 1.5)	13.2 ± 0.6	2.9 ± 2.1	
		20	$(4.13 \pm 0.14) \times 10^3$	(-0.14 ± 0.78)			
		25	$(5.26 \pm 0.04) \times 10^3$	(0.35 ± 0.70)			
		30	$(7.47 \pm 0.22) \times 10^3$	(0.12 ± 1.1)			
Ni^{2+}	Sulfosalicylate	20	$(2.80 \pm 0.11) \times 10^3$	$(0.7_3 \pm 0.7_1)$	13.1 ± 1.3	2.1 ± 4.2	
		25	$(4.7_1 \pm 0.4_3) \times 10^3$	(-0.1 ± 2.6)			
		30	$(6.5 \pm 0.5_5) \times 10^3$	(-1.4 ± 3.4)			
		35	$(8.9 \pm 1.3) \times 10^3$	(0.3 ± 7.7)			
Co^{2+}	Salicylate	20	$(1.3_0 \pm 0.30) \times 10^5$	$(-0.0_3 \pm 0.04)10^3$			
Co^{2+}	Sulfosalicylate	20	$(2.6_7 \pm 0.06) \times 10^5$	$(-0.0_2 \pm 0.08)10^3$			

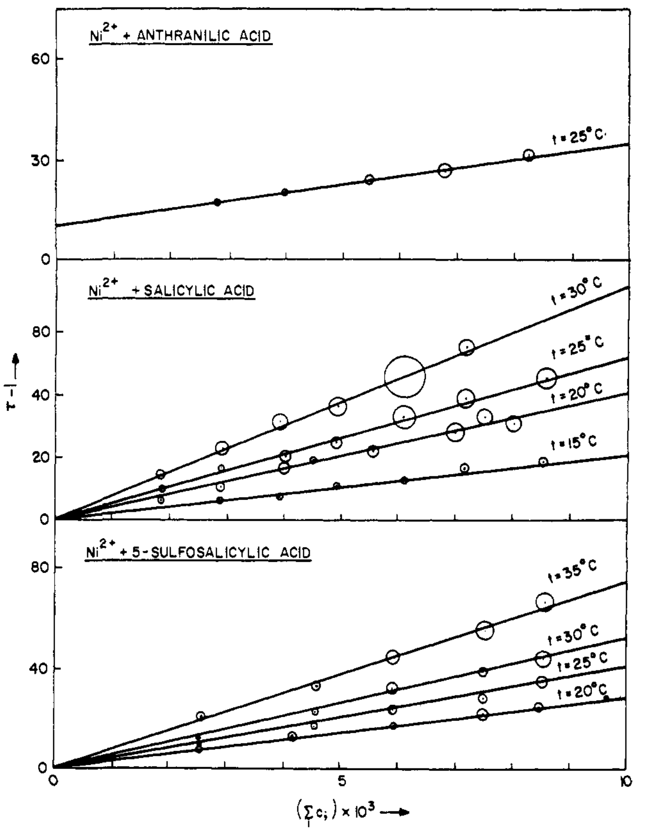

Figure 1. Plots of τ^{-1} (sec^{-1}) *vs.* $(\Sigma c_i) \times 10^3$ (M) for nickel(II) anthranilate, salicylate, and 5-sulfosalicylate at the temperatures investigated.

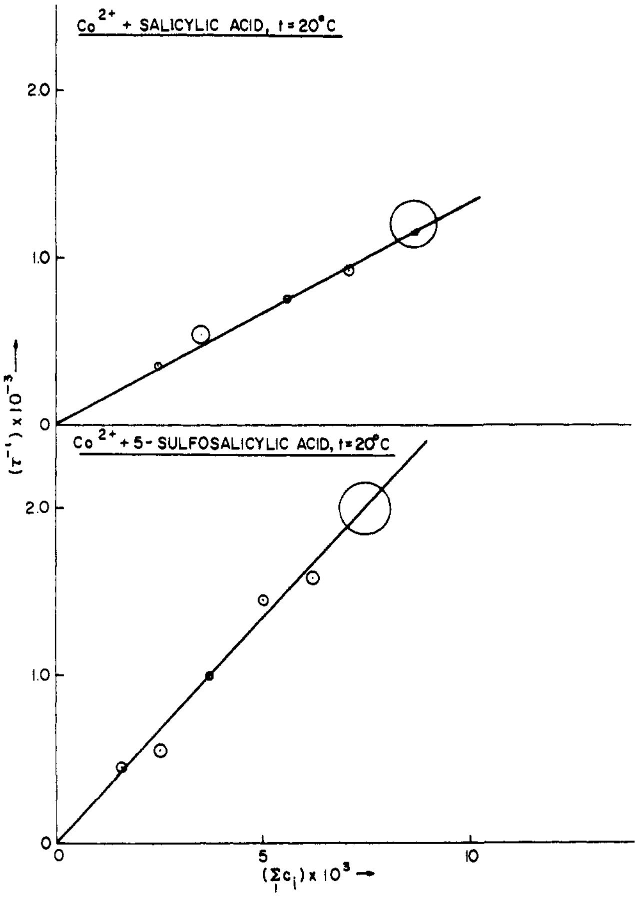

Figure 2. Plots of $\tau^{-1} \times 10^{-3}$ (sec^{-1}) *vs.* $(\Sigma_i c_i) \times 10^3$ (M) for cobalt(II) salicylate and cobalt(II) 5-sulfosalicylate at 20°.

to the relations

$$\text{slope} = -\Delta H_f^{\ddagger}/2.3R$$

$$\text{intercept} = \log \frac{k}{h} + \frac{\Delta S_f^{\ddagger}}{2.3R}$$

The values of $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ are reported in Table III.

Discussion

The equilibrium constant for ion-pair formation can be calculated by means of the Fuoss expression[7] 4.

Assuming $a = 5 \times 10^{-8}$ cm, the Fuoss constant at the ionic strength used (0.1) for a 2:1 electrolyte at 20° results in the value $K_0 = 2.05$ M^{-1}. At 25° $K_0 = 2.05$ M^{-1} also.

At 25° the rate constant for the exchange of water around Ni^{2+}, calculated from the latest activation parameters $\Delta H_{ex}^{\ddagger} = 13.9$ kcal/mol and $\Delta S_{ex}^{\ddagger} = 8.7$ eu, as reported by Connick,[14] is $k_{ex} = 3.4 \times 10^4$ sec^{-1}. This value is in good agreement with the figure reported earlier by Hunt, *et al.*,[15] $k_{ex} = (3.6 \pm 0.2) \times 10^4$ sec^{-1}, who also report $\Delta H_{ex}^{\ddagger} = 12.3 \pm 0.5$ kcal/mol and $\Delta S_{ex}^{\ddagger} = 3.6 \pm 1.5$ eu.

By retaining $k_{ex} = 3.4 \times 10^4$ sec^{-1}, the product K_0k_{ex} for Ni^{2+} is 7.0×10^4 M^{-1} sec^{-1}. The ratio $k_f/k_{ex}K_0$ for nickel(II) anthranilate and salicylate is 0.033 and 0.075, respectively. These values are lower than the ones calculated for nickel(II) malonate[16] (with the new

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[15] A. G. Desai, H. W. Dadgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 798 (1970).

[16] D. Saar, G. Macri, and S. Petrucci, *J. Inorg. Nucl. Chem.*, **33**, 4227 (1971).

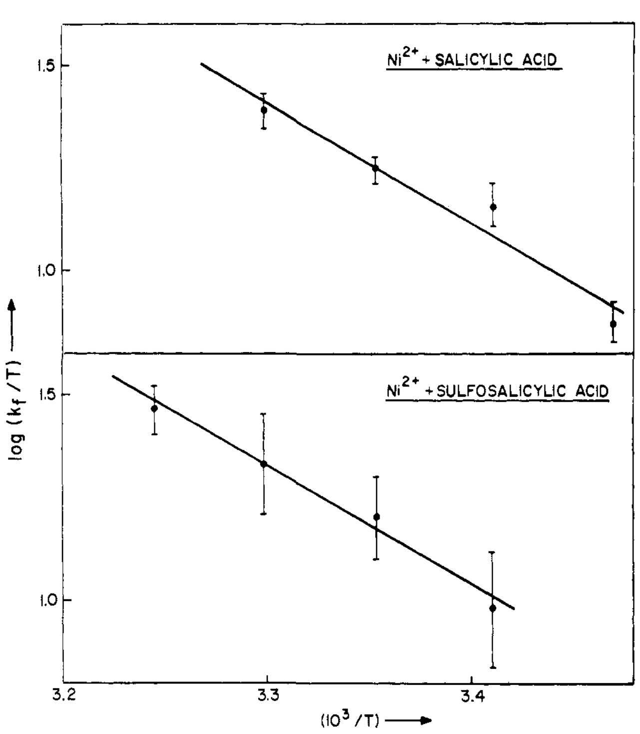

Figure 3. Plots of log k_f/T (M^{-1} sec^{-1} deg^{-1}) *vs.* $1/T$ (deg^{-1}) for nickel(II) salicylate and 5-sulfosalicylate.

value of k_{ex}),[14] namely, 0.14, nickel(II) glycinate[3] 0.18, and the monodentate nickel(II) thiocyanate[17] 0.16. Indeed, the statistical factor $1/S \simeq 0.2$ was proposed by Langford[5,6] to account for the differences between first-order rate constants of solvent substitution and exchange in the case of Co^{3+} complexation.

If one considers the ratios k_f/K_0k_{ex} to be too low to be satisfactorily accounted for by a statistical factor $1/S$, one alternative is to consider the possibility of the failure of the condition $k_3 \gg k_{-2}$ in eq 2, namely a steric or partially steric controlled mechanism.

In this respect notice that eq 2 for k_f may be written[18] as

$$k_f = K_0k_2\frac{1}{1 + (k_{-2}/k_3)}$$

For nickel(II) anthranilate and salicylate the factor $[1 + (k_{-2}/k_3)]^{-1}$ would then be 0.033 and 0.075, respectively. This leads to $k_{-2} = 32k_3$ and $k_{-2} = 12k_3$ for the two cases.

An immediate criticism to the above could be that in this calculation all the weight of the disagreement between the k_f and the $k_{ex}K_0$ values is assigned to the steric controlled mechanism whereas for other cases smaller differences were rationalized by the $1/S$ factor. It may be seen, however, that even by multiplying K_0k_{ex} by 0.2 one gets $[1 + (k_{-2}/k_3)]$ equal to 0.165 and 0.375 for nickel(II) anthranilate and salicylate, respectively. These values in turn give $k_{-2} = 5.1k_3$ and $k_{-2} = 1.7k_3$ for the two cases.

The above indicates that the condition $k_3 > k_{-2}$ as required by the "normal" chelation mechanism is not followed by the present systems, where the converse condition $k_{-2} > k_3$ seems to prevail.

From Table III, if one calculates for cobalt(II) salicylate the ratio $k_f/k_{ex}K_0$, one obtains 0.05. The value of $k_{ex} = (2.6 \pm 0.2)10^6$ sec^{-1} as reported by Matwiyoff, *et al.*,[19] has been used. This figure has been supported by Hoggard[20] who reports $(2.24 \pm 0.05) \times 10^6$ sec^{-1}. It may be seen that the ratio $k_f/k_{ex}K_0$ for cobalt(II) salicylate is of the same order of magnitude as the one for nickel(II) salicylate reported above.

Next we wish to examine the data for the sulfosalicylate ligand. From Table III, it may be seen that the values of k_f for the same temperature are within a factor of 2 of the values for salicylate ions. Although for sulfosalicylate k_f is larger, one would expect a much larger value on the basis of simple electrostatic theory, since both nickel(II) sulfosalicylate and cobalt(II) sulfosalicylate are 2:2 electrolytes. It is important to note that K_0 enters into the expression for k_f irrespective of the mechanism involved (*i.e.*, eq 5 and 6).

In fact, the Fuoss constant[7] K_0 for 2:2 electrolytes in water at 20° and ionic strength $I = 0.1$ is calculated to be $K_0 = 13.04$ M^{-1}. Then the product $k_{ex}K_0$ for Ni^{2+} and Co^{2+} (neglecting differences of k_{ex} between 25 and 20° for the present approximate calculation) is 35.1×10^4 and 33.8×10^6 M^{-1} sec^{-1}, respectively.

If one would compare the experimental k_f with the value predicted by the "normal" substitution mechanism, the ratio $k_f/k_{ex}K_0$ for the two metals would then be $(4.71/351) = 0.013$ and $(2.67/338) = 0.008$ for Ni^{2+} and Co^{2+}, respectively.

One would then be induced to assume, on the basis of the above considerations, that the mechanism for the sulfosalicylate ligand is more steric controlled than for the salicylate one.

That this conclusion is incorrect can be seen by comparing the activation parameters in Table III for nickel(II) salicylate and sulfosalicylate. Both $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ for these two ligands are the same within experimental error, showing that the energetic profiles of the reaction of nickel ion with both ligands are indistinguishable.

The conclusion therefore is that the sulfosalicylate ion acts as a monovalent anion in terms of the outer-sphere ion-pair formation.

A rationalization of this statement may be found if one considers the delocalization of the sulfonate group with respect to the reaction site with the nickel, namely the carboxylic–hydroxylic position. Molecular models show that the charge–charge separation between COO^- and SO_3^- is about 6.3 Å. If one adds to it the radius of a solvated Ni^{2+} (namely the Pauling radius 0.8 Å and the diameter of a molecule of water 2.8 Å), 3.6 Å, one has an approximate distance of 10 Å between the Ni^{2+} charge and SO_3^- of the sulfosalicylate.

For a 2:1 electrolyte the Bjerrum[21] maximum distance of existence of ion pairs $q = |Z^+Z^-|e_0^2/2DkT = 3.57\,|Z^+Z^-| = 7.14$ Å. Clearly the Ni^{2+}–SO_3^- separation is larger than the above Bjerrum distance.

Further, the Debye distance x^{-1}, for the case in

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question, is 9.6 Å ($I = 0.1$); therefore, the Ni^{2+} should see the SO_3^- group mainly as part of the ionic atmosphere with an interaction parameter lumped in the $\gamma_\pm{}^2$ term of the Fuoss association expression. The principle of charge delocalization has been considered previously[22] in the literature. Qualitatively similar conclusions have been reached.[22]

Finally some attempt should be made to account for the source of the derivation from the "normal" chelation mechanism in terms of the activation profile of the reaction.

From the two limiting equations discussed above for k_f (eq 5 and 6) assuming $k_2 \simeq k_{ex}$ one has for the two cases the following. (1) Normal chelation

$$\begin{aligned} \Delta G_f{}^\ddagger &= \Delta G_0 + \Delta G_{ex}{}^\ddagger \\ \Delta H_f{}^\ddagger &= \Delta H_0 + \Delta H_{ex}{}^\ddagger \\ \Delta S_f{}^\ddagger &= \Delta S_0 + \Delta S_{ex}{}^\ddagger \end{aligned} \tag{11}$$

the ligand nature never influencing the activation profile of the reaction which is indistinguishable from the I_d mechanism where the rate determining steps is the removal of the first solvent molecule from the first coordination sphere of the cation. At the contrary for the second case, namely (2) steric controlled chelation

$$\begin{aligned} \Delta G_f{}^\ddagger &= \Delta G_0 + \Delta G_2 + \Delta G_3{}^\ddagger \\ \Delta H_f &= \Delta H_0 + \Delta H_2 + \Delta H_3{}^\ddagger \\ \Delta S_f{}^\ddagger &= \Delta S_0 + \Delta S_2 + \Delta S_3{}^\ddagger \end{aligned} \tag{12}$$

and the activation energy profile is influenced by the ligand through ΔG_2, $\Delta G_3{}^\ddagger$, or both.

In terms of rate constants this can be paraphrased by saying that if ring closure is difficult this will be reflected in k_f by the value of k_3 as Kustin, *et al.*, suggested.[9,10,23] Alternatively if k_{-2} is comparable to k_3 and $k_3 \simeq k_2$, as Wilkins[24] suggested, then the weakness of the first metal–ligand bond will influence k_f through k_{-2}. In both the latter cases the activation profile of the reaction will be influenced by the ligand.

From the present data it is only possible to account for the source of the deviations from the "normal" chelation mechanism in terms of the activation parameters.

The outer-sphere electrostatic contribution to the activation parameters is calculable through the Fuoss expression[7] (see Appendix). In water at 25° for a 2:1 electrolyte at ionic strength $I = 0.1$, $\Delta H_0 = 0.41$ kcal/mol and $\Delta S_0 = 2.8$ eu. For a normal substitution $\Delta H_f{}^\ddagger = \Delta H_0 + \Delta H_2{}^\ddagger$ and $\Delta S_f{}^\ddagger = \Delta S_0 + \Delta S_2{}^\ddagger$. This would give for nickel(II) salicylate $\Delta H_2{}^\ddagger = 12.8 \pm 0.6$ kcal/mol and $\Delta S_2{}^\ddagger = 0.1 \pm 2.1$ eu (by retention of the figures given in Table III for $\Delta H_f{}^\ddagger$). The activation parameters for solvent exchange around Ni^{2+} have widely oscillated[14,15] in their reported values during the last few years. This makes any final statement subject to revision. If one, however, retains the latest data reported by Connick[14] as the most reliable, namely $\Delta H_{ex}{}^\ddagger = 13.9$ kcal/mol and $\Delta S_{ex}{}^\ddagger = 8.7$ eu, one might tentatively conclude (comparing $\Delta H_2{}^\ddagger$ with $\Delta H_{ex}{}^\ddagger$ and $\Delta S_2{}^\ddagger$ with $\Delta S_{ex}{}^\ddagger$) that the source of the deviation from the normal chelation mechanism for nickel(II) salicylate appears to be entropic rather than enthalpic in nature.

Appendix

In a previous work[24,25] we derived the quantities ΔH_0 and ΔS_0 from the Fuoss function at zero ionic strength. In general, for work of ionic association in the presence of a background electrolyte, it is useful to have expressions for ΔH_0 and ΔS_0 taking into account the medium. From the Fuoss expression[7]

$$K_0 = K_0{}^0 e^b \gamma_\pm{}^2$$

it results

$$\Delta G_0 = -RT \ln K_0{}^0 - RTb - RT \ln \gamma_\pm{}^2 \tag{1A}$$

$$\Delta S_0 = -\left(\frac{\partial \Delta G_0}{\partial T}\right)_p = R \ln K_0{}^0 + Rb + RT\frac{db}{dT} + R \ln \gamma_\pm{}^2 + RT\frac{d \ln \gamma_\pm{}^2}{dT} \tag{2A}$$

but[22]

$$\frac{db}{dT} = -b\left(\frac{d \ln D}{dT} + \frac{1}{T}\right) \tag{3A}$$

also

$$\ln \gamma_\pm{}^2 = -b\kappa a/(1 + \kappa a)$$

$$\frac{d \ln \gamma_\pm{}^2}{dT} = -\frac{(1 + \kappa a)\kappa a\, db/dT + ba\, d\kappa/dT}{(1 + \kappa a)^2} \tag{4A}$$

$$\kappa = \left(\frac{8\pi N e^2}{1000k} I\right)^{1/2}(DT)^{-1/2} = A(DT)^{-1/2}$$

$$\frac{d\kappa}{dT} = AT^{-1/2}\frac{dD^{-1/2}}{dD}\frac{dD}{dT} + AD^{-1/2}\frac{dT^{-1/2}}{dT}$$

which leads to

$$\frac{d\kappa}{dT} = -\frac{1}{2}\kappa\left(\frac{d \ln D}{dT} + \frac{1}{T}\right) \tag{5A}$$

but then introducing (3A) and (5A) into (4A) and rearranging

$$\frac{d \ln \gamma_\pm{}^2}{dT} = \frac{\kappa ab((3/2) + \kappa a)}{(1 + \kappa a)^2}\left(\frac{d \ln D}{dT} + \frac{1}{T}\right)$$

which can be simplified by approximating

$$\frac{(^3/_2 + \kappa a)}{(1 + \kappa a)^2} \approx \frac{1}{1 + \kappa a}$$

to[26]

$$\frac{d \ln \gamma_\pm{}^2}{dT} \simeq \frac{\kappa ab}{1 + \kappa a}\left(\frac{d \ln D}{dT} + \frac{1}{T}\right) = -\ln \gamma_\pm{}^2\left(\frac{d \ln D}{dT} + \frac{1}{T}\right) \tag{6A}$$

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(26) In our case with $a = 5 \times 10^{-8}$ cm, $\kappa a = 0.513$. This approximation introduces into the last term of eq 7A an error of 33% by dropping $(1.5 + \kappa a)/(1 + \kappa a) = 1.33$. The same error affects the $\ln \gamma_\pm{}^2$ in eq 8A.

Then introducing (3A) and (6A) into (2A)

$$\Delta S_0 = R \ln K_0{}^0 - RTb \frac{\mathrm{d} \ln D}{\mathrm{d}T} + R \ln \gamma_\pm{}^2 - RT \ln \gamma_\pm{}^2 \left(\frac{\mathrm{d} \ln D}{\mathrm{d}T} + \frac{1}{T}\right) \quad (7A)$$

also

$$\Delta H_0 = \Delta G_0 + T\Delta S_0 = -RT\left(1 + \frac{\mathrm{d} \ln D}{\mathrm{d} \ln T}\right)(b + \ln \gamma_\pm{}^2) \quad (8A)$$

In water at $T = 298.15$°K and $I = 0.1$ with $a = 5 \times 10^{-8}$ cm for a 2:1 electrolyte the following quantities are calculated: $K_0{}^0 = 0.3157$, $b = 2.855$, $\ln \gamma_\pm{}^2 = -0.9759$. This together with $\mathrm{d} \ln D/\mathrm{d}T = -4.6 \times 10^{-3}$ deg^{-1} gives $\Delta S_0 = -2.2910 + 7.7804 - 1.939 - 0.7204 = 2.83$ cal/(mol deg) and $\Delta H_0 = -592.42 - (0.3715)(2.855) - 0.9759) = 414$ cal/mol. One may compare these two figures with the corresponding values at zero ionic strength $\Delta S_0 = 5.49$ cal/(mol deg) and $\Delta H_0 = 628$ cal/mol to convince one's self that the differences are small but significant.

In order to have a check on the reliability of this calculation, the Fuoss function $K_0{}^0 e^b \gamma_\pm{}^2$ has been calculated at 0, 25, and 50° giving $K_0 = 1.976$, 2.057, and 2.175 M^{-1}, respectively. A plot of $\ln K_0$ *vs.* $1/T$ was slightly concave. Least-squares fitting to a straight line gave average values from slope and intercept $\Delta H_0 = 333$ cal/mol and $\Delta S_0 = 2.57$ cal/(mol deg) in fair accord with the corresponding quantities calculated above.

Kinetics and Mechanism for the Production of a Dinitrogen Complex

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Abstract: The kinetics for the attack of NO(aq) upon $Ru(NH_3)_6{}^{3+}$ have been investigated from pH 3 to 12.8. The reaction proceeds through a two step rate law. Below a pH ~7, the product corresponds to substitution of NO onto $Ru(NH_3)_6{}^{3+}$ yielding $Ru(NH_3)_5NO^{3+}$. Above pH 8.3, the product results exclusively in the production of $Ru(NH_3)_5N_2{}^{2+}$. While there is no significant acid dependent path below pH 7, the reaction is first order in hydroxide ion above pH 8.3. Both paths exhibit first-order behavior in $Ru(NH_3)_6{}^{3+}$ and $[NO]_{aq}$. While the values of $\Delta H^{\ddagger}$ are similar for the two paths, the values of $\Delta S^{\ddagger}$ are quite different. Labeling studies in alkaline solution indicate that the NO attacks the ammine ligand (possibly after the NO coordinates to the metal center). The results are discussed with respect to the importance of ion-pair formation, and criteria for parallel reactions in other metal complexes are offered.

Since the original discovery of the dinitrogen complex $Ru(NH_3)_5N_2{}^{2+}$, several alternative methods of preparation have arisen. These preparative methods have found application to other metal systems and can be loosely grouped into at least five mechanistic classifications: (I) metal complex + N_2 (+ ligands), *e.g.*[1]

$$Ru(NH_3)_5OH_2{}^{2+} + N_2 \longrightarrow Ru(NH_3)_5N_2{}^{2+} + H_2O \quad (1)$$

(II) reaction of a dinitrogen complex to produce another dinitrogen complex, *e.g.*[2]

$$Ru(NH_3)_5N_2{}^{2+} + Ru(NH_3)_5OH_2{}^{2+} \rightleftarrows [(Ru(NH_3)_5)_2N_2]^{4+} + H_2O \quad (2)$$

(III) metal complex + nitrogen-containing reagent (*e.g.*, N_2H_4, $N_3{}^-$), *e.g.*[3]

$$RuCl_3 + N_2H_4 \cdot H_2O \xrightarrow[\text{reflux}]{} Ru(NH_3)_5N_2{}^{2+} \quad (3)$$

(IV) external reduction (or oxidation) of a nitrogen-containing ligand, *e.g.*[4]

$$2H^+ + Ru(NH_3)_5N_2O^{2+} + 2Cr^{2+} \longrightarrow Ru(NH_3)_5N_2{}^{2+} + 2Cr(III) + H_2O \quad (4)$$

(V) redox-coupling reaction, *e.g.*[5]

$$Ru(en)_2N_3N_2{}^+ + HONO \longrightarrow \textit{cis}\text{-}Ru(en)_2(N_2)_2{}^{2+} + N_2O \quad (5)$$

The last category offers the greatest possibility of new and interesting mechanisms of dinitrogen formation. In the course of our work on nitrosyl complexes, we discovered another example of method V. The reaction results in the quantitative[6] production of $Ru(NH_3)_5N_2{}^{2+}$

$$Ru(NH_3)_6{}^{3+} + NO + OH^- \longrightarrow Ru(NH_3)_5N_2{}^{2+} + 2H_2O \quad (6)$$

In addition, the reaction is simple to run, rapid, and requires no external reducing agents.[6] Because of the advantages cited above, we are now able to report a detailed study of the mechanism of this reaction. The results lend some insight into why this particular reaction proceeds and allow one to draw upon these results to predict other systems where similar reactions may occur.

Experimental Section

Materials. All reagents used were of primary standard grade. $[Ru(NH_3)_6]Cl_3$, purchased from Matthey-Bishop, was recrystallized according to previously described procedures.[7] Nitric oxide was

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