ranges: $[\mathrm{Co^{III}}] = (4.03\text{–}36.3) \times 10^{-4}$ M, $[\mathrm{I^-}] = (1.0 - 20.0) \times 10^{-2}$ M, and $[\mathrm{H^+}] = 0.1\text{–}1.8$ M at 25 °C and ionic strength 2.0 M.

Kinetics. Kinetic measurements were made under identical conditions used for stoichiometry measurements. The appearance of iodine (as I_3^-) was monitored at fixed wavelength in the range 388–460 nm with iodide in sufficient excess to ensure first-order conditions. Plots of ln $(A_\infty - A_t)$ vs. time were linear for at least 4 half-lives, indicating that the formation of iodine is first order in $[\mathrm{Co^{III}}]$. Derived first-order rate constants k_{obsd} at three different acidities at 25.0 °C and I = 2.0 M are collected in Table IV. At each acidity the data are well described by rate law 18, where $k_{\mathrm{obsd}} = k_e + k_f[\mathrm{I^-}]$.

$$d[\mathrm{I_2}]/dt = -\tfrac{1}{2}d[\mathrm{Co^{III}}]/dt = k_{\mathrm{obsd}}[\mathrm{Co^{III}}] \tag{18}$$

Values of k_e and k_f from a linear regression fit are given in Table IV. The first-order rate constant k_e increases with increasing acidity, while the rate constant k_f is acid independent. The mechanism of eq 19–22 predicts the observed stoichiometry and rate law.

$$\mathrm{Co(py)_2(CO_3)(H_2O)_2^+ \xrightarrow[H^+]{k_4} Co(py)_2(H_2O)_4^{3+} + CO_2} \tag{19}$$

$$\mathrm{Co(py)_2(CO_3)(H_2O)_2^+ + I^- \xrightarrow[H^+]{k_5} Co^{2+}(aq) + 2pyH^+ + I\cdot + CO_2} \tag{20}$$

$$\mathrm{Co(py)_2(H_2O)_4^{3+} + I^- \xrightarrow[H^+]{} Co^{2+} + 2pyH^+ + I\cdot} \tag{21}$$

$$\mathrm{2I\cdot \xrightarrow{fast} I_2} \tag{22}$$

The rate constant for reaction 21 (1.60 $\mathrm{M^{-1}\,s^{-1}}$) at 25 °C and I = 2.0 M)[25] is much higher than that for reaction 20, ensuring that reactions 19 and 20 are the rate-determining steps. For this mechanism, $2k_e = k_4$ and $2k_f = k_5$. The value of $2k_e = k_a + k_b[\mathrm{H_3O^+}]$ calculated from the data in Table I for decarboxylation of $\mathrm{Co(py)_2(CO_3)(H_2O)_2^+}$ at each experimental acidity used for the reaction with iodide is in agreement, within experimental error, with the observed value. This confirms (within the precision limits of the data) that the k_e terms corresponds to decarboxylation reaction 19 and that the k_f term arises from direct reduction of $\mathrm{Co(py)_2(CO_3)(H_2O)_2^+}$ by iodide (reaction 20).

The rate constant k_5 is about 40 times less than that for the corresponding reduction of $\mathrm{Co(py)_2(H_2O)_4^{3+}}$ by $\mathrm{I^-}$ (reaction 21) at 25 °C.[25] The rate constants for reduction of $\mathrm{Co(py)_2(CO_3)(H_2O)_2^+}$, $\mathrm{Co(py)_2(H_2O)_4^{3+}}$,[25] and $\mathrm{Co(NH_3)_2(H_2O)_4^{3+}}$[26] by iodide are all independent of reaction acidity, indicating that they all proceed through outer-sphere mechanisms.[25,26]

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Registry No. *cis*-K[$\mathrm{Co(py)_2(CO_3)_2}$], 54967-61-2; *cis*-$\mathrm{Co(py)_2(CO_3)(H_2O)_2}$, 73104-76-4; *cis*-$\mathrm{Co(py)_2(H_2O)_4^{3+}}$, 73136-37-5; $\mathrm{I^-}$, 20461-54-5.

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Kinetics and Mechanism of the Complex Formation between Iron(III) and Some (Salicylato)pentaaminecobalt(III) Ions

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Kinetic studies by the stopped-flow technique were made at 20–30 °C and I = 1.0 M ($\mathrm{ClO_4^-}$) of the formation and the dissociation of the binuclear complex of Fe(III) with (salicylato)pentaaminecobalt(III) ions, where the pentaamine residues are 5 $\mathrm{NH_3}$, $\mathrm{(en)_2(NH_3)}$, and tetraethylenepentamine. The formation of $\mathrm{N_5CoSalFe^{4+}}$ involves the reaction of the phenol form of the cobalt(III) substrates with $\mathrm{Fe(OH_2)_6^{3+}}$ and $\mathrm{Fe(OH_2)_5(OH)^{2+}}$. The rate constants and the activation parameters for both the paths are reported and compared with the available data for the corresponding reaction of the Fe(III) species with various other ligands. The carboxylate-bound (salicylato)pentaaminecobalt(III) substrates behave effectively as phenol with regard to their rate of complexation with the Fe(III) species. The rate data for the formation reactions are virtually independent of the nature of the amine function attached to the cobalt(III) center. It is concluded that the $\mathrm{I_d}$ mechanism applies in the reaction with $\mathrm{Fe(OH_2)_5(OH)^{2+}}$, while for the corresponding reaction with $\mathrm{Fe(OH_2)_6^{3+}}$, the mechanism is most likely of the $\mathrm{I_a}$ type. The binuclear species $\mathrm{N_5CoSalFe^{4+}}$ undergoes dissociation to yield the cobalt(III) substrates and the Fe(III) species via spontaneous and acid-catalyzed paths. The rate parameters for both the paths are sensitive to the nature of the amine function and decrease in the sequence tetren > $\mathrm{(en)_2(NH_3)}$ > 5 $\mathrm{NH_3}$. A comparison of the rate data for the spontaneous dissociation of the binuclear complexes with that for the mono(phenolato)iron(III) species ($\mathrm{C_6H_5OFe^{2+}}$) reveals that the former are $\sim 10^3$ times kinetically less labile than the latter. This suggests that Fe(III) is chelated by the salicylate moiety through the Co(III)-bound carboxylate group and the free phenol group after deprotonation. The chelate ring opening appears to be rate determining in both the spontaneous and the acid-catalyzed paths. To make possible the comparisons just mentioned, we have made a separate study of the formation and decomposition reactions of the mono(salicylato)iron(III) complex in perchlorate media. Previous work on this system involved only the formation reaction and was done in nitrate media, which we have found to exhibit moderate catalytic behavior.

Introduction

In earlier studies, kinetic data for the metal ion catalyzed aquation of the (carboxylato)pentaamminecobalt(III) complexes derived from oxalic,[2] malonic,[3] and salicylic acids[4] have been reported. It was postulated that the metal ions associated with the cobalt(III) substrates to form binuclear complexes in a rapid and reversible step. These species, however, undergo ligand substitution at the cobalt(III) center at rates charac-

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Table I. UV-Visible Absorption Spectra of $N_5CoSalH^{2+}$

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
$Co(NH_3)_5SalH^{2+}$	505, 298	78.0, 4410	this work
	503, 298	76.0, 4400	10
	510, 298	82.4, 4417	4a
cis-$Co(en)_2(NH_3)SalH^{2+}$	498, 298	110, 4420	this work
	500, 298	113, 4474	6
($\alpha\beta S$)-Co(tetren)$SalH^{2+}$	491, 298	170, 4318	9

teristic of the charge and size of the catalyst–metal ions and also the nature of the bridging carboxylate ligand. Independent equilibrium studies[4–6] have also established that the equilibria $N_5CoOCOR^+ + M^{n+} \rightleftarrows N_5CoOCORM^{(n+1)+}$ (where R = CO_2^-, M^{n+} = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ga^{3+}, Al^{3+}, In^{3+}; R = $(C_6H_4\text{-}o)O^-$, M^{n+} = Fe^{3+}, Al^{3+}, Ga^{3+}) are attained much more rapidly than the subsequent reaction, M^{n+}-catalyzed aquation at the cobalt(III) center of the binuclear species. Recently,[7] we have been able to study the kinetics of formation and decomposition of binuclear ferric (oxalato)pentaamminecobalt(III) complex utilizing the stopped-flow technique. In continuation of this we now report a similar study involving the formation and decomposition of binuclear complexes of the (salicylato)pentaamminecobalt(III) moieties ($N_5CoSalH^{2+}$, N_5 = 5 NH_3, $(en)_2(NH_3)$, and tetren) with Fe(III).

An earlier study by Saini and Mentasti[8] on the kinetics of formation of Fe(III)–monosalicylato complex was carried out in 1 M nitrate medium. Because of the possibility of appreciable medium effects, we deemed it worthwhile to reinvestigate the kinetics of the $FeSal^+$ formation in perchlorate medium. We have also included a study of the kinetics of its dissociation reaction, data concerning which have not been previously reported.

Experimental Section

Materials and Method. ($\alpha\beta S$)-(Salicylato)(tetraethylenepentamine)cobalt(III) perchlorate was prepared as described earlier.[9] *cis*-(Salicylato)(ammine)bis(ethylenediamine)cobalt(III) perchlorate and (salicylato)pentaamminecobalt(III) perchlorate were prepared by the published methods.[6,10] The UV–visible spectra of these complexes were in good agreement with those reported earlier (see Table I).

A stock solution of iron(III) perchlorate (G. F. Smith Chemical Co.) in perchloric acid was prepared and analyzed for iron(III) and acid contents by EDTA titration[11] and pH measurement, respectively. A Fisher Accumet pH meter, Model 420, equipped with a Markson combination electrode was used for pH measurements. The meter was standardized with perchloric acid solutions of known concentration. Sodium perchlorate was used for ionic strength adjustment. Solutions were prepared in laboratory distilled water, which was further purified by passing through a mixed-bed ion-exchange column. The spectral measurements were made on a Cary 118 spectrophotometer.

Kinetic Measurements. The kinetic studies were carried out at 20, 25 and 30 °C (±0.1 °C) and 1 M ionic strength with use of a Durrum 110 stopped-flow assembly. The concentraton of complex used was $(3.2\text{–}7.1) \times 10^{-4}$ M. The formation of the binuclear complex, $N_5CoSalFe^{4+}$, was observed through the increase of absorbance at 540 nm[12] with time when equal volumes of the thermally equilibrated solutions of iron(III) perchlorate and the complex (I = 1 M), both of known acid concentration, were mixed. The (salicylato)(tetraethylenepentamine)cobalt(III) complex was found to precipitate slowly in 1 M ClO_4^- medium during the time of thermal equilibration. It was, therefore, preferable for this system to use iron(III) perchlorate solution adjusted to I = 2 M; the complex solution was prepared in 0.001 M perchloric acid. The rate measurements were made under pseudo-first-order conditions, i.e., total [Fe(III)]/total [complex] = $[Fe^{3+}]_T/[\text{complex}]_T \geq 5$. For the study of the acid-catalyzed dissociation of the binuclear species, solutions of iron(III) perchlorate ($[Fe^{3+}]_T = 1.05 \times 10^{-3}$, $[HClO_4]_T = 1.2 \times 10^{-3}$ M) and the complex ($[\text{complex}]_T = (1.5\text{–}2.6) \times 10^{-4}$ M) were mixed and equilibrated. Equal volumes of this solution and thermally equilibrated perchloric acid solution of (I = 2 M) were mixed in the stopped-flow setup, and the disappearance of $N_5CoSalFe^{4+}$ was followed by observing the decrease of absorbance at 540 nm with time. The kinetics of formation and acid-catalyzed dissociation of $FeSal^+$ were studied by following exactly similar procedure; the wavelength of measurement was also 540 nm, at which $FeSal^+$ is the only absorbing species.[13] Each rate measurement was repeated at least five times. The observed rate constants were calculated from the digitalized stopped-flow data by a least-squares program adapted to a Wang 600 programmable calculator.

Results and Discussion

Formation of $FeSal^+$. Rate data under varying conditions of acidity and $[Fe^{3+}]_T$ are collected in Table II. The observed pseudo-first-order rate constants at a given acidity fit the equation

$$k_{obsd} = k_f[Fe^{3+}] + k_r \tag{1}$$

In this

$$[Fe^{3+}] = [Fe(OH_2)_6{}^{3+}] = [Fe^{3+}]_T[[H^+]/([H^+] + K_h)] \tag{2}$$

and K_h, the hydrolysis constant for $Fe(OH_2)_6{}^{3+}$, has values as found in the literature.[14] The parameter k_r increases with $[H^+]$, being virtually zero at the lowest acidity ($[H^+]$ = 0.01 M), and is assumed to relate to acid-catalyzed aquation of $FeSal^+$, the spontaneous aquation of which is negligible. The parameter k_f exhibits greater than first-order dependence on $1/[H^+]$, consistent with the assumption that both Fe^{3+} and $FeOH^{2+}$ ($\equiv Fe(H_2O)_5OH^{2+}$) react with both H_2Sal and $HSal^-$, as proposed by Saini and Mentasti.[8] A reaction mechanism based on these concepts is shown in Scheme I.

Scheme I

$$H_2Sal \overset{K_a}{\rightleftharpoons} HSal^- + H^+$$

$$Fe^{3+} + HSal^- \xrightarrow{k_1} FeSal^+ + H^+$$

$$FeOH^{2+} + HSal^- \xrightarrow{k_2} FeSal^+ + H_2O$$

$$FeOH^{2+} + H_2Sal \xrightarrow{k_3} FeSal^+ + H_3O^+$$

$$Fe^{3+} + H_2Sal \xrightarrow{k_4} FeSal^+ + 2H^+$$

$$FeSal^+ + H^+ \overset{K_H}{\rightleftharpoons} FeSalH^{2+}$$

$$FeSalH^{2+} \xrightarrow{k_5} Fe^{3+} + HSal^-$$

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(12) $N_5CoSalFe^{4+}$ species have a broad peak around 540 nm. ϵ values at 540 nm for $(NH_3)_5CoSalH^{2+}$ and $(NH_3)_5CoSalFe^{4+}$ are approximately 61 and 1590 M^{-1} cm^{-1}, respectively.[4a]

(13) Saini and Mentasti[8] report $\epsilon = 1470 \pm 30$ M^{-1} cm^{-1} for $FeSal^+$ at 540 nm and $K = 506 \pm 6$ at 20 °C (I = 1.0 M NO_3^-) for the forward equilibrium quotient of the reaction $Fe^{3+} + HSal^- \rightleftarrows FeSal^+ + H^+$. Our values for ϵ and K at 20 °C in 1.0 M perchlorate medium from an independent equilibrium study are 1390 ± 90 M^{-1} cm^{-1} and 540 ± 34, respectively.

(14) The hydrolysis constant (K_h) of $Fe(OH_2)_6{}^{3+}$ was taken to be 1.26×10^{-3}, 1.69×10^{-3}, and 2.29×10^{-3} M at 20, 25, and 30 °C (Milburn, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 537). The concentration of H^+ was calculated from the relationship $[H^+] = 0.5\{b + (b^2 + 4cK_h)^{1/2}\}$, where $b = [HClO_4] - K_h$ and $c = [HClO_4] + [Fe^{3+}]_T$.

Table II. Rate Data for the Formation of $FeSal^{+}$ [a,b]

	20.0 °C		25.0 °C		30.0 °C	
$10^2[HClO_4]$, M	$10^3[Fe^{3+}]_T$, M	k_{obsd}, s^{-1}	$10^3[Fe^{3+}]_T$, M	k_{obsd}, s^{-1}	$10^3[Fe^{3+}]_T$, M	k_{obsd}, s^{-1}
1.0	1.26	0.56 ± 0.04	1.05	0.84 ± 0.02	1.05	1.42 ± 0.02
1.0	1.86	0.82 ± 0.04	2.00	1.44 ± 0.04	2.00	2.53 ± 0.07
1.0	2.52	1.12 ± 0.08	2.96	2.26 ± 0.05	3.00	3.97 ± 0.11
1.0	3.36	1.53 ± 0.05	4.00	3.06 ± 0.03	4.00	5.30 ± 0.09
1.0	4.20	1.95 ± 0.02	5.05	3.80 ± 0.06	5.05	6.83 ± 0.10
k_f, M^{-1} s^{-1}	533 ± 9		856 ± 20		1636 ± 30	
k_r, s^{-1}	−0.05 ± 0.02		0.03 ± 0.06		0.07 ± 0.08	
2.5	5.25	0.87 ± 0.04	2.00	0.75 ± 0.03	2.00	1.28 ± 0.04
2.5	10.0	1.74 ± 0.04	4.00	1.25 ± 0.04	4.00	2.12 ± 0.08
2.5	10.5	1.65 ± 0.04	6.00	1.78 ± 0.09	6.00	3.01 ± 0.07
2.5	20.0	3.27 ± 0.13	10.0	2.98 ± 0.07	10.0	5.04 ± 0.06
2.5	21.0	3.42 ± 0.09				
k_f, M^{-1} s^{-1}	170 ± 5		297 ± 9		513 ± 16	
k_r, s^{-1}	0.03 ± 0.07		0.15 ± 0.05		0.27 ± 0.09	
5.0	2.00	0.45 ± 0.01	2.00	0.70 ± 0.02	2.00	1.13 ± 0.03
5.0	4.00	0.56 ± 0.01	4.00	0.92 ± 0.03	4.00	1.46 ± 0.02
5.0	6.00	0.71 ± 0.01	6.00	1.13 ± 0.01	6.00	1.83 ± 0.04
5.0	10.0	1.21 ± 0.02	10.0	1.60 ± 0.04	10.0	2.70 ± 0.07
5.0	20.0	1.80 ± 0.02	20.0	2.92 ± 0.08	20.0	4.86 ± 0.05
k_f, M^{-1} s^{-1}	78.4 ± 4.8		128 ± 3		219 ± 5	
k_r, s^{-1}	0.30 ± 0.06		0.41 ± 0.03		0.63 ± 0.05	
10.0	2.51	0.57 ± 0.01	2.00	0.91 ± 0.03	2.00	1.29 ± 0.05
10.0	5.25	0.63 ± 0.01	4.00	1.02 ± 0.04	4.00	1.53 ± 0.04
10.0	10.0	0.89 ± 0.07	6.00	1.14 ± 0.03	6.00	1.73 ± 0.04
10.0	10.5	0.80 ± 0.03	10.0	1.35 ± 0.04	10.0	2.08 ± 0.05
10.0	21.0	1.16 ± 0.02	20.0	1.89 ± 0.02	20.0	2.97 ± 0.18
10.0	40.0	1.94 ± 0.04				
k_f, M^{-1} s^{-1}	36.8 ± 1.8		55.3 ± 0.5		93.7 ± 2.4	
k_r, s^{-1}	0.46 ± 0.03		0.805 ± 0.005		1.15 ± 0.03	
20.0	5.25	0.88 ± 0.01	5.05	1.48 ± 0.05	5.05	2.26 ± 0.10
20.0	10.5	0.93 ± 0.03	10.0	1.65 ± 0.09	10.0	2.49 ± 0.03
20.0	21.0	1.01 ± 0.03	20.0	1.90 ± 0.01	20.0	3.00 ± 0.07
20.0	31.5	1.11 ± 0.04	29.6	2.12 ± 0.10	29.6	3.40 ± 0.06
20.0			40.0	2.51 ± 0.10	40.0	3.97 ± 0.06
20.0			80.0	3.75 ± 0.11	80.0	5.89 ± 0.17
20.0			100.0	4.40 0.08	100.0	6.67 ± 0.27
k_f, M^{-1} s^{-1}	8.74 ± 0.24		31.0 ± 0.6		47.6 ± 0.7	
k_r, s^{-1}	0.833 ± 0.005		1.29 ± 0.03		2.04 ± 0.04	
30.0	5.25	1.13 ± 0.02				
30.0	10.5	1.17 ± 0.02				
30.0	21.0	1.25 ± 0.05				
30.0	31.5	1.30 ± 0.02				
k_f, M^{-1} s^{-1}	6.57 ± 0.51					
k_r, s^{-1}	1.10 ± 0.01					

[a] $I = 1.0$ M (ClO_4^-); $[H_2Sal]_T = (2.86\text{–}5.73) \times 10^{-4}$ M. [b] Rate constants as defined in eq 1.

For such a scheme the observed pseudo-first-order rate constant is given by eq 1, with

$$k_f = \frac{(k_1K_d + k_3K_h) + k_2K_hK_d/[H^+] + k_4[H^+]}{[H^+] + K_d} \qquad (3)$$

and

$$k_r = \frac{k_5K_H[H^+]}{1 + K_H[H^+]} \qquad (4)$$

The concentration of hydrogen ion was computed after taking into account the hydrolysis of Fe^{3+} (i.e., $[H^+] = [HClO_4] + [FeOH^{2+}]$).[14] Values of k_f and k_r at specified acidities were obtained as the slope and intercept of the least-squares plots of k_{obsd} vs. $[Fe^{3+}]$ using the data of Table II and eq 2 and the known values of K_h.[14] Plots of $k_f([H^+] + K_d)$ vs. $[H^+]^{-1}$ also yielded straight lines, indicating that $k_4[H^+] << \{(k_1K_d + k_3K_h) + k_2K_hK_d/[H^+]\}$ under the experimental conditions. Our data, therefore, do not reveal the k_4 path (i.e., that involving reaction of Fe^{3+} with H_2Sal). At 25 °C and $I = 1.0$ M (NO_3^-) Saini and Mentasti,[8] however, report $k_4 = 3 \pm 1$ s^{-1} M^{-1}. The slopes and intercepts of these plots yield values of $(k_1K_d + k_3K_h)$ and $k_2K_hK_d$. At 25 °C ($I = 1$ M) the values of K_h and K_d are almost identical (1.6×10^{-3} M).[8,14] This enables us to deduce that $(k_1 + k_3) = 3 \times 10^3$ M^{-1} s^{-1} at 25 °C. A discussion of various substitution reactions of Fe^{3+} and $FeOH^{2+}$ has appeared recently,[15] which shows conclusively that reactions of ligands of charge 1− or 0 should react with second-order rate constants of the order of magnitude 10^3 M^{-1} s^{-1} with $FeOH^{2+}$ but in general very much more slowly with Fe^{3+}. We can, therefore, assume for our system that $k_3 >> k_1$, so that $k_3 \approx 3 \times 10^3$ M^{-1} s^{-1} at 25 °C, in good agreement with the value of $\sim 2 \times 10^3$ M^{-1} s^{-1} recorded for several other uncharged entering ligands.[15] The values deduced for k_2 and k_3 at various temperatures (neglecting k_1) are recorded in Table

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Table III. Rate Parameters for the Formation of $FeSal^+$ [a]

temp, °C	$k_1K_d + k_3K_h$, s^{-1}	$10^2k_2K_hK_dM$, s^{-1}	$10^{-4}k_2$, $M^{-1}\ s^{-1}$	$10^{-3}k_3$, $M^{-1}\ s^{-1}$
20.0	3.46 ± 0.01	2.97 ± 0.01	1.47 ± 0.01	2.75 ± 0.01
25.0	5.71 ± 0.28	4.85 ± 0.58	1.85 ± 0.22 (1.40 ± 0.10)[b]	3.48 ± 0.17 (5.5 ± 0.5)[b]
30.0	8.94 ± 0.28	11.6 ± 0.6	3.23 ± 0.17	3.99 ± 0.13
$\Delta H^\ddagger$, kcal mol^{-1}			13.3 ± 3.4	6.0 ± 0.9
$\Delta S^\ddagger$, cal K^{-1} mol^{-1}			+6 ± 11	−22 ± 3

[a] $I = 1.0$ M (ClO_4^-). [b] Data reported by Saini and Mentasti[8] at $I = 1.0$ M (NO_3^-).

Table IV. Rate Data for the Acid-Catalyzed Dissociation of $FeSal^+$

$[HClO_4]$, M	k_{obsd}, s^{-1} [a] 20.0 °C	25.0 °C	30.0 °C
0.051	0.375 ± 0.003	0.560 ± 0.008	0.813 ± 0.066
0.101	0.566 ± 0.003	0.846 ± 0.022	1.19 ± 0.02
0.151	0.745 ± 0.013	1.08 ± 0.03	1.57 ± 0.05
0.201	0.920 ± 0.023	1.33 ± 0.02	1.97 ± 0.05
0.251	1.07 ± 0.01	1.56 ± 0.02	2.28 ± 0.10
0.301	1.18 ± 0.02	1.78 ± 0.02	2.56 ± 0.06
0.351	1.31 ± 0.01	1.99 ± 0.05	2.90 ± 0.05
0.401	1.41 ± 0.03	2.20 ± 0.05	3.31 ± 0.06
0.451	1.44 ± 0.02	2.39 ± 0.08	3.67 ± 0.04
0.501	1.54 ± 0.03	2.55 ± 0.06	3.77 ± 0.12
0.601	1.80 ± 0.02	2.72 ± 0.10	3.92 ± 0.07
0.701	1.91 ± 0.06	2.93 ± 0.06	4.40 ± 0.13
0.801	2.12 ± 0.03	3.23 ± 0.06	4.68 ± 0.11
0.901	2.25 ± 0.04	3.45 ± 0.07	4.89 ± 0.12
1.001	2.39 ± 0.03	3.55 ± 0.10	5.37 ± 0.27
k_5, s^{-1}	3.31 ± 0.10	5.46 ± 0.20	9.20 ± 0.27
K_H, M^{-1}	1.88 ± 0.06	1.64 ± 0.06	1.32 ± 0.04

$\Delta H_5^\ddagger = 17.5 \pm 0.4$ kcal mol^{-1}
$\Delta S_5^\ddagger = +3.4 \pm 1.3$ cal K^{-1} mol^{-1}
$\Delta H_H^\circ = -6.2 \pm 0.9$ kcal mol^{-1}
$\Delta S_H^\circ = -20 \pm 2$ cal K^{-1} mol^{-1}

[a] $[Fe^{3+}]_T = 1.05 \times 10^{-3}$ M, $[H_2Sal]_T = 2.00 \times 10^{-4}$ M.

III, and it is seen that k_2 also fits the general pattern for $FeOH^{2+}$ substitution,[15,16] since many singly charged anions ligate with second-order rate constants of $\sim 10^4\ M^{-1}\ s^{-1}$. It is noteworthy that, while we observed measurable NO_3^- catalysis in this reaction,[17] it is only moderately significant. It is not surprising, therefore, that our derived values for k_2 and k_3 do not differ greatly from those obtained previously[8] in nitrate media, as noted in Table III. It is possible, however, that the NO_3^- catalysis enlarges k_4 sufficiently to have permitted its estimation by Saini and Mentasti,[8] though not by us in perchlorate medium, as mentioned earlier.

Acid-Catalyzed Aquation of FeSal⁺. The rate constants (k_r) for the acid-catalyzed aquation of $FeSal^+$ at various acidities were obtained from the observed pseudo-first-order rate constants (see Table IV) after correcting for the contribution of the forward reaction ($k_r = k_{obsd} - k_f[Fe^{3+}]$). The plots of k_r vs. $[H^+]$ show asymptotic behavior at high $[H^+]$ and extrapolate to zero at $[H^+] = 0$. This establishes the absence of the spontaneous aquation path of $FeSal^+$ as pointed out earlier. The best-fit least-squares plots (Figure 1) of $1/k_r$ vs. $1/[H^+]$ (according to the reciprocal form of eq 4) yield the rate parameters that are given in Table IV. The protonation site is almost certainly the coordinated phenoxide group of $FeSal^+$ as this is by far the most basic site. It is of interest to point out the large enhancement of the acidity of ligands coordinated to Fe^{3+} ion. In the present instance, the value[18] of pK_{HSal^-} is ~ 13.6 at 25 °C, over 13 units higher than the pK for proton release from $FeSalH^{2+}$ under comparable conditions ($pK_H = -0.2$ at 25 °C). A similar change is noted in comparing the acidity of coordinated water in $Fe(OH_2)_6^{3+}$ ($pK_h = 2.8^{14}$ at 25 °C) with that of pure water. Such a large effect is observed in very few other triply charged aquo complex ions. The rate constant k_5 for the dissociation of $HSal^-$ from $FeSalH^{2+}$ most likely relates to the opening of the Fe–phenol chelate ring. The rate constant for the dissociation of a series of monodentate phenoxide species ($C_6H_4(X)OFe^{2+}$) is reported[19] to be $10^2\ M^{-1}\ s^{-1}$ at 25 °C and $I = 0.1$ M, about 50 times greater than k_5. This is consistent with the persistence of the relatively stable Fe(III)–salicylate chelate ring even after protonation of the bound phenoxide group. The high value of $\Delta H^\ddagger$ also supports the dissociative ring-opening concept of the reaction mechanism.

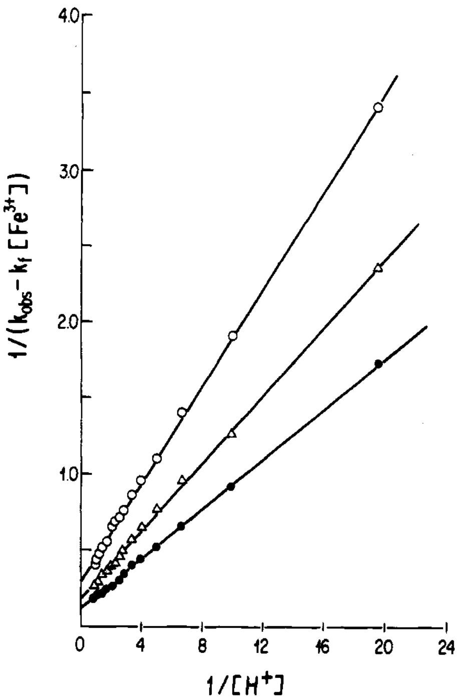

Figure 1. $1/(k_{obsd} - k_f[Fe^{3+}])$ vs. $1/[H^+]$ plot for the acid-catalyzed aquation of $FeSal^+$. Correlation coefficient is 0.999 at 20 °C (open circles), 25 °C (triangles), and 30 °C (closed circles).

Formation of N₅CoSalFe⁴⁺. Rate data for this formation reaction are collected in Table V. It is evident that the pseudo-first-order rate constants at a given acidity increase with $[Fe^{3+}]_T$. The slope and intercept of the plot of k_{obsd} vs. $[Fe^{3+}]_T$ at a fixed $[H^+]$ are identified with the pseudo-first-order rate constants for the formation and the dissociation of the binuclear species, respectively. The slopes of such plots at different acidities when plotted against $1/[H^+]$ yield straight lines with positive intercepts and slopes, indicating thereby that the formation of $N_5CoSalFe^{4+}$ occurs via two different paths, one independent of $[H^+]$ and another dependent on $1/[H^+]$. Over the whole experimental acidity range, the (salicylato)cobalt(III) substrate exists in the monoprotonated phenol form ($pK_{OH} > 10$).[6,20] It is, therefore, reasonable to assume that the acid dependence of the reaction results only from the $Fe(OH_2)_6^{3+}/Fe(OH_2)_5(OH)^{2+}$ equilibrium. The overall

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(16) Mentasti, E. *Inorg. Chem.* **1979**, *18*, 1512.

(17) At 20 °C and $I = 1.0$ M, the values of k_{obsd} (s^{-1}) in mixed NO_3^-/ClO_4^- media were found to be 1.94 ± 0.06, 2.15 ± 0.04, 2.46 ± 0.06, and 2.72 ± 0.08 at $[NO_3^-] = 0$, 0.1, 0.3, and 0.5 M, respectively, when $[Fe^{3+}]_T = 0.04$, $[HClO_4] = 0.1$, and $[H_2Sal]_T = 2.86 \times 10^{-4}$ M.

(18) Ernst, Z. L.; Menashi, J. *Trans. Faraday Soc.* **1963**, *59*, 2838.

(19) Cavasino, F. P.; Dio, E. D. *J. Chem. Soc. A* **1970**, 1151.

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(21) Gouger, S.; Stuehr, J. *Inorg. Chem.* **1974**, *13*, 379.

(22) Pandey, R. N.; Smith, M. W. *Can. J. Chem.* **1972**, *50*, 194.

Table V. Rate Data for the Formation of the Binuclear Species $N_5CoSalFe^{4+}$ [a]

N_5	$10^3[Fe^{3+}]_T$, M	$10^2[HClO_4]$, M	k_{obsd}, s^{-1}	$10^3[Fe^{3+}]_T$, M	$10^2[HClO_4]$, M	k_{obsd}, s^{-1}
			20 °C			
5 NH_3	2.62	2.60	0.228 ± 0.003	10.1	10.1	0.260 ± 0.013
	5.25	2.60	0.296 ± 0.008	15.7	10.1	0.330 ± 0.022
	10.5	2.60	0.469 ± 0.011	20.0	10.1	0.340 ± 0.010
	21.0	2.60	0.766 ± 0.007	29.6	10.1	0.443 ± 0.006
	2.62	5.10	0.190 ± 0.011	40.0	10.1	0.542 ± 0.006
	5.25	5.10	0.243 ± 0.008	5.25	20.1	0.136 ± 0.011
	10.5	5.10	0.342 ± 0.006	10.5	20.1	0.180 ± 0.010
	15.7	5.10	0.433 ± 0.014	21.0	20.1	0.247 ± 0.015
	20.0	5.10	0.495 ± 0.006	31.5	20.1	0.290 ± 0.009
	29.6	5.10	0.676 ± 0.020	5.25	30.1	0.147 ± 0.013
	40.0	5.10	0.91 ± 0.03	10.5	30.1	0.163 ± 0.013
	2.52	10.1	0.168 ± 0.003	21.0	30.1	0.190 ± 0.001
	5.25	10.1	0.197 ± 0.012	31.5	30.1	0.250 ± 0.010
			25 °C			
	2.52	2.60	0.332 ± 0.020	29.6	5.10	1.15 ± 0.01
	4.96	2.60	0.460 ± 0.010	40.0	5.10	1.48 ± 0.02
	10.0	2.60	0.717 ± 0.033	2.52	10.1	0.287 ± 0.010
	20.0	2.60	1.20 ± 0.02	4.96	10.1	0.332 ± 0.004
	2.52	5.10	0.309 ± 0.009	10.0	10.1	0.412 ± 0.011
	4.96	5.10	0.384 ± 0.007	20.1	10.1	0.565 ± 0.003
	10.0	5.10	0.547 ± 0.009	29.6	10.1	0.741 ± 0.030
	20.0	5.10	0.852 ± 0.014	40.0	10.1	0.908 ± 0.019
			30.0 °C			
	2.52	2.60	0.469 ± 0.014	29.6	5.10	1.91 ± 0.04
	4.96	2.60	0.787 ± 0.033	40.0	5.10	2.57 ± 0.15
	10.0	2.60	1.20 ± 0.14	2.52	10.1	0.483 ± 0.026
	20.0	2.60	2.04 ± 0.10	4.96	10.1	0.570 ± 0.013
	2.52	5.10	0.528 ± 0.020	10.0	10.1	0.687 ± 0.020
	4.96	5.10	0.642 ± 0.012	20.0	10.1	1.01 ± 0.05
	10.0	5.10	0.891 ± 0.011	29.6	10.1	1.30 ± 0.03
	20.0	5.10	1.43 ± 0.03	40.0	10.1	1.59 ± 0.03
			20.0 °C			
$(en)_2(NH_3)$	2.53	2.60	0.255 ± 0.005	29.6	5.10	0.683 ± 0.012
	4.96	2.60	0.318 ± 0.003	40.0	5.10	0.891 ± 0.022
	10.0	2.60	0.463 ± 0.012	2.53	10.1	0.219 ± 0.005
	20.0	2.60	0.760 ± 0.029	4.96	10.1	0.240 ± 0.006
	2.53	5.10	0.223 ± 0.009	10.0	10.1	0.296 ± 0.005
	4.96	5.10	0.264 ± 0.009	20.0	10.1	0.387 ± 0.013
	10.0	5.10	0.355 ± 0.014	29.6	10.1	0.472 ± 0.004
	20.0	5.10	0.510 ± 0.005	40.0	10.1	0.572 ± 0.005
			25 °C			
	2.52	2.60	0.443 ± 0.005	29.6	5.10	1.22 ± 0.03
	4.96	2.60	0.557 ± 0.003	40.0	5.10	1.51 ± 0.07
	10.0	2.60	0.903 ± 0.005	2.52	10.1	0.383 ± 0.022
	20.0	2.60	1.29 ± 0.04	4.96	10.1	0.423 ± 0.008
	2.52	5.10	0.400 ± 0.005	10.0	10.1	0.509 ± 0.008
	4.96	5.10	0.471 ± 0.009	20.0	10.1	0.675 ± 0.021
	10.0	5.10	0.601 ± 0.008	29.6	10.1	0.827 ± 0.017
	20.0	5.10	1.05 ± 0.05	40.0	10.1	0.982 ± 0.016
			30 °C			
	2.52	2.60	0.657 ± 0.006	29.6	5.10	1.78 ± 0.06
	4.96	2.60	0.810 ± 0.009	40.0	5.10	2.23 ± 0.04
	10.0	2.60	1.24 ± 0.02	2.52	10.1	0.561 ± 0.007
	20.0	2.60	1.94 ± 0.05	4.96	10.1	0.628 ± 0.009
	2.52	5.10	0.601 ± 0.011	10.0	10.1	0.784 ± 0.011
	4.96	5.10	0.723 ± 0.012	20.0	10.1	1.05 ± 0.05
	10.0	5.10	0.919 ± 0.010	29.6	10.1	1.29 ± 0.03
	20.0	5.10	1.39 ± 0.02	40.0	10.1	1.53 ± 0.02
			20.0 °C			
tetren	2.62	2.60	0.48 ± 0.01	21.0	10.0	0.63 ± 0.01
	5.25	2.60	0.52 ± 0.04	31.5	10.0	0.75 ± 0.01
	10.5	2.60	0.65 ± 0.02	5.25	20.0	0.49 ± 0.01
	21.0	2.60	0.867 ± 0.003	10.5	20.0	0.53 ± 0.01
	5.25	5.05	0.509 ± 0.004	21.0	20.0	0.60 ± 0.02
	7.85	5.05	0.561 ± 0.011	31.5	20.0	0.64 ± 0.01
	10.5	5.05	0.617 ± 0.011	5.25	30.0	0.48 ± 0.01
	13.1	5.05	0.662 ± 0.013	10.5	30.0	0.519 ± 0.008
	15.75	5.05	0.715 ± 0.004	21.0	30.0	0.54 ± 0.01
	21.0	5.05	0.764 ± 0.005	31.5	30.0	0.61 ± 0.02
	26.2	5.05	0.87 ± 0.07	5.25	40.0	0.485 ± 0.008
	31.5	5.05	0.96 ± 0.02	10.5	40.0	0.52 ± 0.01
	36.7	5.05	1.06 ± 0.01	21.0	40.0	0.540 ± 0.009

Table V (*Continued*)

N_5	$10^3[Fe^{3+}]_T$, M	$10^2[HClO_4]$, M	k_{obsd}, s^{-1}	$10^3[Fe^{3+}]_T$, M	$10^2[HClO_4]$, M	k_{obsd}, s^{-1}
tetren	42.0	5.05	1.10 ± 0.04			
	5.25	10.0	0.495 ± 0.009			
	10.5	10.0	0.560 ± 0.007			
			25 °C			
	2.52	2.60	0.83 ± 0.01	10.0	10.1	0.95 ± 0.01
	4.96	2.60	0.93 ± 0.01	20.0	10.1	1.12 ± 0.02
	10.0	2.60	1.15 ± 0.06	29.6	10.1	1.27 ± 0.02
	20.0	2.60	1.59 ± 0.04	40.0	10.1	1.45 ± 0.05
	2.52	5.10	0.835 ± 0.005	10.0	20.0	0.95 ± 0.03
	4.96	5.10	0.896 ± 0.005	20.0	20.0	1.05 ± 0.02
	10.0	5.10	1.03 ± 0.02	29.6	20.0	1.15 ± 0.02
	20.0	5.10	1.31 ± 0.08	40.0	20.0	1.27 ± 0.02
	29.6	5.10	1.58 ± 0.04	10.0	30.0	0.90 ± 0.02
	40.0	5.10	1.81 ± 0.05	20.0	30.0	0.99 ± 0.01
	2.52	10.1	0.83 ± 0.01	29.6	30.0	1.07 ± 0.02
	4.96	10.1	0.87 ± 0.02	40.0	30.0	1.17 ± 0.02
			30.0 °C			
	2.62	2.60	1.19 ± 0.02	5.25	10.1	1.34 ± 0.05
	5.25	2.60	1.48 ± 0.01	10.5	10.1	1.45 ± 0.02
	10.5	2.60	1.73 ± 0.03	15.7	10.1	1.56 ± 0.07
	21.0	2.60	2.43 ± 0.04	20.0	10.1	1.77 ± 0.03
	2.62	5.10	1.26 ± 0.04	29.6	10.1	1.82 ± 0.07
	5.25	5.10	1.34 ± 0.02	40.0	10.1	2.17 ± 0.07
	10.5	5.10	1.51 ± 0.05	10.0	30.0	1.38 ± 0.03
	15.7	5.10	1.72 ± 0.09	20.0	30.0	1.56 ± 0.06
	20.0	5.10	1.83 ± 0.08	29.6	30.0	1.71 ± 0.10
	29.6	5.10	2.31 ± 0.06	40.0	30.0	1.80 ± 0.10
	40.0	5.10	2.71 ± 0.02			

[a] I = 1.0 M (ClO_4^-), [complex] = (3.2-7.1) × 10^{-4} M.

scheme for the formation/dissociation of the binuclear complexes may thus be written as

$$Fe^{3+} + N_5CoSalH^{2+} \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} N_5CoSalFe^{4+} + H^+$$

$$\uparrow\downarrow K_h$$

$$FeOH^{2+} + N_5CoSalH^{2+} \underset{k_{-22}}{\overset{k_{22}}{\rightleftharpoons}} N_5CoSalFe^{4+} + H_2O$$

The components of k_{obsd} as defined by a relation analogous to eq 1 are therefore (since $K_h << [H^+]$) given by

$$k_f = k_{11} + k_{22}K_h/[H^+] \qquad (5)$$

and

$$k_r = k_{-11}[H^+] + k_{-22} \qquad (6)$$

The values of k_f and k_r obtained as the least-squares slopes and intercepts of the plots of k_{obsd} vs. $[Fe^{3+}]$ at specified hydrogen ion concentrations are given in Table VI. The rate parameters k_{11} and k_{22} calculated from the intercept and slope of the plot of k_f vs. $1/[H^+]$ utilizing the known values of K_h[14] are also collected in Table VI.

The rate constant data (Table VI) show that the rates of formation of the $N_5CoSalFe^{4+}$ species are virtually independent of the N_5 ligand environment. Furthermore, as is seen in Table VII, k_{11} and k_{22} for $N_5CoSalH^{2+}$ are similar in magnitude (within a factor of about 6) to the corresponding values for several neutral ligands (H_2Sal, C_6H_5OH and a number of substituted phenols, CH_3CO_2H) and for the similarly monoprotonated complex ion $(NH_3)_5CoC_2O_4H^{2+}$. The only substantial divergences occur for the partially deprotonated salicylato ligand, $HSal^-$, and the fully deprotonated oxalato–pentaammine complex ion, $(NH_3)_5CoC_2O_4^+$. Both of these are much more reactive than any of the species already mentioned, showing increases of a factor of 5 or more. This acceleration is probably to be expected, since in each of these cases deprotonation of the ligand uncovers an additional coordination site and also reduces its charge by 1 unit, thus favoring its interaction with either of the positively charged Fe(III) species. The controversy with respect to the mechanism of ligand interchange with $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ has been recently discussed. The general conclusions, on evidence from both water-exchange rates[15] and volume of activation determinations,[23] is that for the hexaaquo species the mechanism is I_a, but it is I_d for the monohydroxo congener, and our study of the reactions with the (oxalato)pentamminecobalt(III) complex[7] supported these concepts. The data of Table VII clearly support the I_d mechanism for $Fe(H_2O)_5OH^{2+}$ since the water-exchange rate greatly exceeds the probable first-order rate constant k^*_{22} for water elimination in any of the ligand substitutions.[24] However, for the $Fe(H_2O)_6^{3+}$ reactions, k^*_{11} cannot be concluded to exceed k_{ex} for any reasonable value[21] of K_{os} other than for the $(NH_3)_5CoC_2O_4^+$ case,[7] so only for the latter is the I_a mechanism assignment supportable on the water-exchange rate basis. But the exchange rate criterion also fails for $Fe(H_2O)_6^{3+}$ reactions with the simple negative ligands Cl^- and Br^-, where rather small k_{11} values (4.8 and 1.6 M^{-1} s^{-1}, respectively[25]) are coupled with unequivocally negative ΔV^* values (−5 and −19 cm^3 mol^{-1}, respectively[25]), as expected for the I_a mechanism.

Dissociation of $N_5CoSalFe^{4+}$ Species. Rate data for the acid-catalyzed dissociation of $N_5CoSalFe^{4+}$ are collected in Table VIII. The observed rate constants were corrected with

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(23) Swaddle, T. W., paper presented at Conference on Inorganic Reaction Mechanisms, Wayne State University, Detroit, MI, June 10–12, 1981.

(24) It is generally accepted[15,21] that the derived second-order rate constants, k in substitutions of this type are a combination of rapid outer-sphere precursor complex formation with equilibrium constant K_{os} and a rate constant for dissociative water elimination such that $k = k^*K_{os}$ for small values of K_{os}.

(25) Hasinoff, B. B. *Can. J. Chem.* **1976**, *54*, 1820; **1979**, *57*, 77.

Table VI. Rate Parameters for the Formation of $N_5CoSalFe^{4+}$ Species

N_5	$10^2 \times$ $[H^+]$,[a] M	k_f, $M^{-1}\ s^{-1}$	k_{11}, $M^{-1}\ s^{-1}$	k_{22}, $M^{-1}\ s^{-1}$	k_r, s^{-1}
			20.0 °C		
5 NH_3	2.64	31.0 ± 0.8	2.1 ± 0.9	624 ± 36	0.148 ± 0.009
	5.14	19.3 ± 0.5			0.137 ± 0.010
	10.12	10.0 ± 0.4			0.151 ± 0.008
	20.11	5.9 ± 0.6			0.114 ± 0.009
	30.10	3.8 ± 0.6			0.122 ± 0.009
			25.0 °C		
	2.66	52.5 ± 0.6	5.6 ± 3.1	771 ± 75	0.214 ± 0.007
	5.16	32.1 ± 0.1			0.231 ± 0.002
	10.1	16.8 ± 0.2			0.245 ± 0.005
			30.0 °C		
	2.68	94.7 ± 4.5	9.0 ± 3.8	1036 ± 66	0.30 ± 0.05
	5.18	56.2 ± 1.2			0.37 ± 0.03
	10.1	30.3 ± 0.4			0.41 ± 0.01
			20.0 °C		
$(en)_2$-(NH_3)	2.64	30.4 ± 0.4	2.8 ± 1.4	585 ± 43	0.177 ± 0.004
	5.14	18.0 ± 0.4			0.174 ± 0.008
	10.12	9.49 ± 0.11			0.197 ± 0.002
			25.0 °C		
	2.65	51.8 ± 4.8	5.1 ± 2.8	766 ± 67	0.340 ± 0.050
	5.16	31.2 ± 1.9			0.340 ± 0.040
	10.12	16.3 ± 0.2			0.346 ± 0.004
			30.0 °C		
	2.67	80.2 ± 2.4	7.4 ± 0.3	869 ± 6	0.47 ± 0.03
	5.17	45.3 ± 0.5			0.50 ± 0.01
	10.14	26.5 ± 0.6			0.51 ± 0.01
			20.0 °C		
tetren	2.62	22.4 ± 0.8	3.3 ± 1.0	428 ± 47	0.418 ± 0.009
	5.10	16.7 ± 0.4			0.439 ± 0.010
	10.1	9.5 ± 0.6			0.450 ± 0.012
	20.1	5.8 ± 0.6			0.467 ± 0.012
	30.0	4.5 ± 0.7			0.460 ± 0.013
	40.0	3.3 ± 1.2			0.475 ± 0.016
			25.0 °C		
	2.65	46.2 ± 0.2	5.6 ± 0.4	663 ± 11	0.718 ± 0.003
	5.16	27.3 ± 0.5			0.770 ± 0.012
	10.1	16.7 ± 0.1			0.789 ± 0.002
	20.0	10.7 ± 0.3			0.840 ± 0.007
	30.0	8.9 ± 0.2			0.812 ± 0.005
			30.0 °C		
	2.67	70.1 ± 4.8	8.2 ± 0.8	741 ± 18	1.07 ± 0.05
	5.17	41.0 ± 1.3			1.12 ± 0.03
	10.1	23.5 ± 2.2			1.22 ± 0.05
	30.0	14.2 ± 1.6			1.26 ± 0.04

[a] Average concentration of hydrogen ion[14] for a given set of runs with constant $[HClO_4]$ and varying $[Fe^{3+}]_T$.

the rate constant for the formation reaction by utilizing the values of k_{11}, k_{22}, and K_h. The corrected pseudo-first-order rate constants for the dissociation reaction (i.e., $k_r = k_{obsd} - k_f\,[Fe^{3+}]$) compare satisfactorily with the values of k_r under comparable acidity obtained from the formation study (see Table VI). Values of k_r given in Table VIII exhibit a small acid dependence. Hence the major path of dissociation of Fe^{3+} from $N_5CoSalFe^{4+}$ is the spontaneous dissociation path, i.e., k_{-22} path. The intercepts and the slopes of the linear plots of k_r vs. $[H^+]$ yield the rate constants for the spontaneous dissociation (k_{-22}) and the acid-catalyzed dissociation (k_{-11}) of the binuclear species, respectively. In contrast to that of the formation reaction, the rate constant for the spontaneous dissociation (k_{-22}) of the binuclear species depends upon the nature of the N_5 grouping around the cobalt(III) center and decreases in the sequence tetren > $(en)_2(NH_3)$ > 5 NH_3 (see Table IX). Furthermore, a rate comparison shows that the $N_5CoSalFe^{4+}$ species are 200–2000 times kinetically more stable than mono(phenolato)iron(III) species, $C_6H_4(X)OFe^{2+}$ ($10^{-2}\ k_{-22}\ (s^{-1})$ = 5.0, 4.3, 4.8, 3.2, 2.9, 1.5, 2.5, and 1.7 for X = *p*-MeO, *m*-Me, H, *p*-Cl, *m*-Cl, *o*-Cl, *m*-NO_2, and *p*-NO_2, respectively; 25 °C, I = 0.1 M).[19] This is contrary to expectation if Fe^{3+} is bound to the salicylate moiety through the phenoxide oxygen in the unidentate fashion. On the other hand, the observed rate-influencing effect of the amine ligand and the rate sequence for $C_6H_4(X)OFe^{4+}$ and $N_5CoSalFe^{4+}$ species strongly suggest that Fe^{3+} is chelated by the salicylate moiety of the cobalt(III) substrates. The activation enthalpy and entropy for the chelate ring opening for all three $N_5CoSalFe^{4+}$ species (i.e., for the k_{-22} path) is close to 14.9 kcal mol^{-1} and −11 cal K^{-1} mol^{-1} (see Table IX). The large negative value of $\Delta S^{\ddagger}$ is indicative of higher degree of solvation of the transition state as compared to the ground state and is in keeping with the dissociative mechanism.

The acid-catalyzed dissociation of Fe^{3+} from $N_5CoSalFe^{4+}$ is observed to be first order in hydrogen ion concentration in the range $[H^+]$ = 0.025–0.9 M. The values of the second-order rate constants are, however, too small to consider slow proton transfer to the bridged salicylate moiety as the rate-determining step. It is more reasonable to assume that the acid-catalyzed path involves two steps: (i) fast protonation preequilibrium of $N_5CoSalFe^{4+}$, presumably at the coordinated phenoxide group, and (ii) the rate-limiting dissociation of the protonated species to $Fe(OH_2)_6^{3+}$ and $N_5CoSalH^{2+}$. Our kinetic evidence above (Table IV) shows that the mono(salicylato)iron(III) complex has an equilibrium constant of 1.64 ± 0.06 M^{-1} at 25 °C (I = 1.0 M). For the binuclear complexes, the protonation equilibrium constant must be at least 100 times less than that for $FeSal^+$ (as k_{-11} was evaluated from eq 6 at $[H^+]$ = 0.025–0.9 M). It is also reasonable to expect that the values of the protonation equilibrium constant of the binuclear species will be independent of the nature of the amine envelope around cobalt(III). The observed second-order rate constants (k_{-11}) vary in the order tetren > $(en)_2(NH_3)$ > 5

Table VII. Rate and Activation Parameters for the Formation of FeL^{n+} Species[a]

LH	k_{11}, $M^{-1}\ s^{-1}$	$\Delta H_{11}^{\ddagger}$, kcal mol^{-1}	$\Delta S_{11}^{\ddagger}$, cal deg^{-1} mol^{-1}	$10^{-2}k_{22}$, $M^{-1}\ s^{-1}$	$\Delta H_{22}^{\ddagger}$, kcal mol^{-1}	$\Delta S_{22}^{\ddagger}$, cal deg^{-1} mol^{-1}	ref
$(NH_3)_5CoSalH^{2+}$	5.6	25 ± 5	+28 ± 16	7.7	8.4 ± 0.9	−17 ± 3	this work
cis-$(en)_2(NH_3)CoSalH^{2+}$	5.1	16.6 ± 2.1	0 ± 7	7.7	6.4 ± 1.4	−24 ± 5	this work
($\alpha\beta S$)-(tetren)$CoSalH^{2+}$	5.6	15.5 ± 1.3	−3 ± 5	6.6	9.1 ± 3.2	−15 ± 11	this work
H_2Sal	small[b]			35	6.0 ± 0.9	−22 ± 3	this work
$HSal^-$	small[b]			185	13.3 ± 3.4	+6 ± 11	this work
$(NH_3)_5CoC_2O_4^+$	870			370	14.5 ± 0.7	+11.0 ± 2.4	7
$(NH_3)_5CoC_2O_4H^{2+}$	small[b]			46			7
C_6H_5OH[c,d]	25			7.2			21
CH_3CO_2H[e]	27	26 ± 12	35 ± 36	28	11.1 ± 2.2	−5.4 ± 7.0	22
H_2O[f]	160	15.3 ± 0.6	2.9 ± 1.6	1400	10.1 ± 0.4	+1.3 ± 1.0	15

[a] At T = 25 °C; I = 1.0 M unless otherwise specified. [b] Not possible to measure by our procedure but probably not greater than 10 $M^{-1}\ s^{-1}$. [c] At I = 0.1 M. [d] Values of k_{22} for various substituted phenols differ very little from those for phenol itself.[19] [e] At I = 0.5 M. [f] Water-exchange rate constants (units s^{-1}).

Table VIII. Rate Data for the Dissociation of $N_5CoSalFe^{4+}$ Species[a]

N_5	$[HClO_4]$, M	k_{obsd}, s^{-1}	k_r,[b] s^{-1}	$[HClO_4]$, M	k_{obsd}, s^{-1}	k_r,[b] s^{-1}
			20.0 °C			
5 NH_3	0.025	0.163 ± 0.006	0.128	0.35	0.159 ± 0.004	0.155
	0.15	0.155 ± 0.008	0.147	0.60	0.156 ± 0.002	0.152
				0.80	0.162 ± 0.006	0.159
	$k_{-11} = 0.031 \pm 0.013\ M^{-1}\ s^{-1}$			$k_{-22} = 0.136 \pm 0.006\ s^{-1}$		
			25.0 °C			
	0.025	0.275 ± 0.002	0.216	0.40	0.265 ± 0.007	0.256
	0.10	0.254 ± 0.007	0.236	0.70	0.262 ± 0.007	0.254
	0.20	0.251 ± 0.004	0.239	0.90	0.272 ± 0.005	0.265
	$k_{-11} = 0.045 \pm 0.011\ M^{-1}\ s^{-1}$			$k_{-22} = 0.227 \pm 0.006\ s^{-1}$		
			30.0 °C			
	0.025	0.404 ± 0.008	0.297	0.50	0.402 ± 0.013	0.388
	0.05	0.389 ± 0.010	0.331	0.90	0.402 ± 0.012	0.390
	0.10	0.392 ± 0.009	0.358			
	$k_{-11} = 0.085 \pm 0.034\ M^{-1}\ s^{-1}$			$k_{-22} = 0.326 \pm 0.016\ s^{-1}$		
			20.0 °C			
$(en)_2(NH_3)$	0.025	0.214 ± 0.002	0.180	0.60	0.228 ± 0.004	0.223
	0.05	0.207 ± 0.005	0.196	0.80	0.237 ± 0.006	0.233
	0.15	0.214 ± 0.005	0.206	0.90	0.256 ± 0.004	0.252
	0.40	0.219 ± 0.003	0.214			
	$k_{-11} = 0.064 \pm 0.008\ M^{-1}\ s^{-1}$			$k_{-22} = 0.188 \pm 0.004\ s^{-1}$		
			25.0 °C			
	0.025	0.363 ± 0.005	0.305	0.40	0.354 ± 0.010	0.345
	0.050	0.342 ± 0.007	0.310	0.80	0.387 ± 0.006	0.380
	0.10	0.311 ± 0.011	0.312	0.90	0.397 ± 0.005	0.390
	0.20	0.340 ± 0.010	0.328			
	$k_{-11} = 0.09 \pm 0.02$			$k_{-22} = 0.301 \pm 0.011\ s^{-1}$		
			30.0 °C			
	0.025	0.545 ± 0.007	0.455	0.40	0.533 ± 0.013	0.520
	0.050	0.503 ± 0.011	0.454	0.60	0.551 ± 0.006	0.540
	0.10	0.498 ± 0.009	0.470	0.80	0.588 ± 0.003	0.578
	0.20	0.503 ± 0.009	0.485			
	$k_{-11} = 0.157 \pm 0.006\ M^{-1}\ s^{-1}$			$k_{-22} = 0.452 \pm 0.003\ s^{-1}$		
			20.0 °C			
tetren	0.025	0.450 ± 0.009	0.424	0.35	0.533 ± 0.017	0.528
	0.050	0.453 ± 0.008	0.438	0.45	0.537 ± 0.015	0.532
	0.150	0.503 ± 0.009	0.496	0.60	0.547 ± 0.021	0.543
	0.250	0.517 ± 0.010	0.511	0.80	0.570 ± 0.008	0.566
	$k_{-11} = 0.168 \pm 0.030\ M^{-1}\ s^{-1}$			$k_{-22} = 0.448 \pm 0.012\ s^{-1}$		
			25.0 °C			
	0.025	0.724 ± 0.010	0.672	0.40	0.869 ± 0.010	0.860
	0.150	0.794 ± 0.010	0.780	0.70	0.910 ± 0.025	0.902
	0.300	0.841 ± 0.012	0.831	0.90	0.969 ± 0.032	0.962
	$k_{-11} = 0.288 \pm 0.048\ M^{-1}\ s^{-1}$			$k_{-22} = 0.716 \pm 0.025\ s^{-1}$		
			30.0 °C			
	0.025	1.07 ± 0.01	0.99	0.40	1.28 ± 0.03	1.27
	0.150	1.22 ± 0.04	1.20	0.60	1.31 ± 0.03	1.30
	0.300	1.27 ± 0.07	1.25	0.90	1.47 ± 0.07	1.46
	$k_{-11} = 0.44 \pm 0.09\ M^{-1}\ s^{-1}$			$k_{-22} = 1.07 \pm 0.04\ s^{-1}$		

[a] $[Fe^{3+}]_T = 1.05 \times 10^{-3}$; [complex] = 2.6×10^{-4} M (N_5 = 5 NH_3, $(en)_2(NH_3)$), 1.56×10^{-4} M (N_5 = tetren). [b] $k_r = k_{obsd} - (k_{11} + k_{22}K_h/[H^+])[Fe^{3+}]$.

Table IX. Rate and Activation Parameters for the Spontaneous and Acid-Catalyzed Dissociation of Iron(III)-Mono(salicylato) Species[a]

complex	k_{-11}(25 °C), $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal $K^{-1}\ mol^{-1}$	k_{-22}(25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal $K^{-1}\ mol^{-1}$
$(NH_3)_5CoSalFe^{4+}$	0.05	17.1 ± 2.9	−7 ± 9	0.23	14.9 ± 1.3	−12 ± 4
cis-$(en)_2(NH_3)CoSalFe^{4+}$	0.09	15.3 ± 2.3	−12 ± 8	0.30	14.9 ± 0.5	−11 ± 2
(αβ*S*)-(tetren)$CoSalFe^{4+}$	0.29	16.6 ± 0.9	−5 ± 3	0.72	14.8 ± 0.5	−10 ± 2
$FeSal^+$	8.8[b]	11.3 ± 1.0	−17 ± 3.0			
$FeSalH^{2+}$				5.5 ± 0.2	17.5 ± 0.4	+3.4 ± 1.3

[a] $I = 1.0$ M (ClO_4^-). [b] $k_{-11} = k_5K_H$; spontaneous dissociation of $FeSal^+$ was not observable.

NH_3, suggesting that, as for the spontaneous dissociation path, the rate of dissociation of Fe^{3+} from the protonated binuclear species $N_5CoSalFe^{4+}$ increases with steric crowding at the cobalt(III) center. Alternatively, the effect may be the result of mediation of the electrostatic repulsion between the Fe(III) and Co(III) centers by the solvation shells of the bridged binuclear species, repulsion being least for the most highly solvated $(NH_3)_5$ species and greatest to the least solvated tetren analogue.

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Registry No. $Co(NH_3)_5SalH^{2+}$, 30931-74-9; *cis*-$Co(en)_2(NH_3)SalH^{2+}$, 59296-02-5; ($\alpha\beta S$)-Co(tetren)$SalH^{2+}$, 78715-92-1; Fe, 7439-89-6; $Fe(OH_2)_6^{3+}$, 15365-81-8; $Fe(OH_2)_5(OH)^{2+}$, 15696-19-2; H_2Sal, 69-72-7.

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Demethylation of Methylcobalamin by Tetrahaloaurates. Kinetics and Mechanism

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The stoichiometries and kinetics of reactions of methylcobalamin (CH_3-B_{12}) with AuX_4^- (X = Cl or Br) in acidic solution have been examined. Under anaerobic conditions, the reactions occur with a 2:1 stoichiometry (AuX_4^-:CH_3-B_{12}), producing aquocobalamin with an oxidized corrin ring, CH_3X, and metallic gold. The stoichiometry and reaction products are interpreted in terms of one-electron oxidative demethylation of CH_3-B_{12}. Kinetic data support a mechanism which involves an equilibrium prior to the electron transfer between CH_3-B_{12} and AuX_4^-. Effects of pH and ionic strength on the kinetics are also examined. The detailed mechanism for the Co–C bond cleavage is discussed.

Introduction

Oxidation–reduction reactions and their related cleavage of the cobalt–carbon bond are important in our understanding of the biological roles of methylcobalamin (CH_3-B_{12}).[1] They are also of considerable mechanistic interest.[2] Several modes of cleavage of the Co–C bond of CH_3-B_{12} induced by metal ions have been described in detail. These include electrophilic demethylation by Hg^{2+} [3] and $PdCl_4^{2-}$,[4], reductive demethylation by Cr^{2+} [5] and Sn(II),[6] and redox switch by $PtCl_6^{2-}$/$PtCl_4^{2-}$.[7]

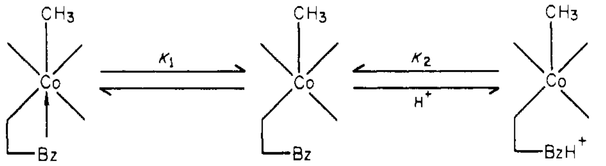
It has been briefly reported that CH_3-B_{12} can be demethylated by $AuCl_4^-$.[8] The mechanism for this reaction was suggested to be similar to that proposed for the methylation of platinum complexes by CH_3-B_{12}.[7] We undertook the study on the demethylation of CH_3-B_{12} by gold complexes to determine whether this mechanism occurs. In contrast to the previous report, our work provides results which support the single-electron oxidative demethylation of CH_3-B_{12} by gold complexes.

Experimental Section

Materials. Fine gold powder and $NaAuCl_4{\cdot}2H_2O$ were purchased from either Goldsmith or Ventron, Inc., and were used as received. $KAuBr_4{\cdot}2H_2O$ was synthesized by the method of Block.[9] AuX_2^- solutions were generated by reducing AuX_4^- with zinc amalgam in acidic solution under an atmosphere of argon. CH_3-B_{12} was synthesized by the method described by Dolphin[10] or purchased from Sigma, Inc. Cob(II)alamin (B_{12r}) solutions were generated by reducing aquocob(III)alamin (H_2O-B_{12}^+) with equimolar amounts of Eu^{2+} under argon. Concentrations of CH_3-B_{12}, H_2O-B_{12}^+, and B_{12r} in solution were determined from their published molar absorptivities.[11,12] All other chemicals were reagent grade and were used as received.

Stoichiometric Studies and Reaction Products. Consumption ratios for the reactions between CH_3-B_{12} and $AuCl_4^-$ or $AuBr_4^-$ were determined spectrophotometrically at 351 or 537 nm with a GCA/McPherson spectrophotometer in subdued light under an atmosphere of argon. B_{12} products were identified spectrophotometrically. Demethylation products under various conditions were identified with a Becker gas chromatograph Model 417 with a column (8 ft by 2 mm) of 5% FFAP on chromasorb W-AW-DMCS, 80–100 mesh at 45 °C, and with a Brüker 270 MHz proton NMR spectrometer.

Equilibrium Constant Measurements. The equilibrium constants for 5,6-dimethylbenzimidazole "base-on" and "base-off" conversion of CH_3-B_{12} (reaction 1) were estimated spectrophotometrically according to eq 2.[13] Measurements were made at 1.0 M ionic strength which was maintained with NaCl, NaBr, or $NaClO_4$ (23 °C).



(1)

$$\frac{A_{305\text{nm}}}{[CH_3\text{-}B_{12}]_T} = \frac{K_2\epsilon_{\text{base-on}} + K_1[H^+]\epsilon_{\text{base-off}}}{K_2 + K_1[H^+]} \qquad (2)$$

pK_2 can be considered as 4.7, which is the pK_a for free 5,6-dimethylbenzimidazole in aqueous solution.[14] According to eq 2, pK_1 in 1.0 M perchlorate, 1.0 M chloride, and 1.0 M bromide solutions were estimated to be 0.92, 1.7, and 2.1, respectively (at 23 °C).

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(13) Equation 2 was derived from equilibria presented in eq 1. The molar absorptivities at 305 nm for the base-on and base-off CH_3-B_{12} are given respectively by $\epsilon_{\text{base-on}} = 1.3 \times 10^4$ M^{-1} cm^{-1} and $\epsilon_{\text{base-off}} = 2.2 \times 10^4$ M^{-1} cm^{-1}. It is assumed that protonated base-off CH_3-B_{12} has the same molar absorptivity as unprotonated base-off CH_3-B_{12}.
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