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Metal Ion Catalyzed Hydrolysis of Acidopentaamminecobalt(III) Complexes. Kinetics and Mechanism of Spontaneous, Acid and Metal Ion Catalyzed Hydrolysis of Salicylatopentaamminecobalt(III) Ion

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The acid hydrolysis of salicylatopentaamminecobalt(III) complex has been studied by spectrophotometric and titrimetric methods. Fe(III), Al(III), and Ga(III) ions are found to catalyze the aquation of the complex. The rate of aquation of the complex is described by the rate laws

$$-\mathrm{d}(\ln [(\mathrm{NH_3})_5\mathrm{CoOCOC_6H_4OH}^{2+}])/\mathrm{d}t = k_0 + k_1[\mathrm{H}^+]$$

$$-\mathrm{d}(\ln [(\mathrm{NH_3})_5\mathrm{CoOCOC_6H_4OH}^{2+}])/\mathrm{d}t = \frac{k_0 + k_1[\mathrm{H}^+] + k_2K_1[\mathrm{M}^{3+}]/[\mathrm{H}^+]}{1 + K_1[\mathrm{M}^{3+}]/[\mathrm{H}^+]}$$

in the absence and presence of the catalyst metal ions, respectively. At 65° and $\mu = 0.6\ M$ (adjusted with $\mathrm{NaClO_4}$), the parameters of the rate equations calculated from the titrimetric rate data are $k_0 = 2.01\ (\pm 0.12) \times 10^{-6}$ sec^{-1}, $k_1 = 1.82\ (\pm 0.04) \times 10^{-5}$ sec^{-1} M^{-1}; for Fe(III), $k_2 = 2.0\ (\pm 0.2) \times 10^{-5}$ sec^{-1}, $K_1 = 2.2\ (\pm 0.5)$; for Al(III), $k_2 = 6.7\ (\pm 1.6) \times 10^{-6}$ sec^{-1}, $K_1 = 0.16\ (\pm 0.11)$; for Ga(III), $k_2 = 1.1\ (\pm 0.5) \times 10^{-5}$ sec^{-1}, $K_1 = 0.85\ (\pm 0.42)$. The formation of binuclear species $(\mathrm{NH_3})_5\mathrm{CoOCOC_6H_4OM}^{4+}$ is invoked to account for the observed kinetic patterns of salicylato complex in the presence of M^{3+} ions and is substantiated by equilibrium measurements at 28°. The catalytic activities of the metal ions and the thermodynamic stabilities of the binuclear complexes are found to follow the sequence Fe(III) > Ga(III) > Al(III). The activation parameters for k_0, k_1, and k_2 paths have been determined. Both the k_0 and k_2 paths are tentatively suggested to involve a Co–O bond fission process.

The acid hydrolysis reactions of cobalt(III)-amine complexes have been extensively studied.[1] Complexes containing basic ligands like carboxylate,[2] fluoride,[3] etc. are known to undergo acid catalyzed aquation. The observed acceleration in the rate of aquation of such complexes under the influence of hydrogen ion has been attributed to a fast protonation equilibrium involving the cobalt(III) substrate and the subsequent loss of the carboxylic acid or HF in the rate-determining step to give the aquo product. It is further known that Cr(II) reduction of the carboxylatopentaamminecobalt(III) ions yields inner-sphere carboxylatochromium(III) species[4-6] as the major product. This is in keeping with the fact that Cr(II) associates with the Co(III) complex through the bound carboxylato group prior to the electron-transfer process. These observations led us to investigate the effects of hydrogen ion and nonreducing substitution labile metal ions on the kinetics of acid hydrolysis of carboxylatopentaammine complexes of cobalt(III). The results obtained in the case of metal ion catalyzed aquation of oxalatopentaamminecobalt(III) complex[7] indicated that trivalent metal ions are more efficient catalysts and associate with the Co(III) substrate (through the oxalate moiety) to form stabler complexes than bivalent metal ions. In this paper we report the Al(III), Ga(III), and Fe(III) ion catalyzed aquation of the salicylatopentaamminecobalt(III) complex in order to (i) examine the external complexing ability of the half-bonded salicylate moiety in the Co(III) substrate and (ii) explore the mechanism of acid hydrolysis of the above complex in the presence of added metal ions. The acid hydrolysis of salicylatopentaamminecobalt(III) complex in the absence of added metal ions has also been studied.

Experimental Section

Salicylatopentaamminecobalt(III) perchlorate was prepared by the method of Gould and Taube[8] and was purified by repeated crystallization from aqueous perchloric acid solution. The sample was dried over fused calcium chloride at room temperature. The purity of the sample was checked by estimating Co. About 0.1 g of the complex was weighed into a silica crucible and was moistened with a few drops of $\mathrm{H_2SO_4}$. It was then heated carefully till evolution of $\mathrm{SO_3}$ fumes ceased and then strongly for about 30 min. The residue (black oxide) was extracted with fused potassium pyrosulfate and the amount of cobalt in the melt was estimated by the method of Laitinen and Burdett.[9] *Anal.* Calcd for $[(\mathrm{NH_3})_5\mathrm{CoOCOC_6H_4OH}](\mathrm{ClO_4})_2$: Co, 12.27. Found: Co, 12.15.

The absorption spectrum of salicylatopentaamminecobalt(III) ion in the visible and ultraviolet regions was found to be independent of pH in the range 0–1.7. The absorption maxima (in nm) and the corresponding molar absorbancy indices (in l. mol^{-1} cm^{-1}) at $[\mathrm{H}^+] = 0.05$–$0.6\ M$ and $\mu = 0.6\ M$ are found to be as follows: 235 (20,800 ± 200), 298 (4417 ± 16), 510 (82.4 ± 0.6). At $[\mathrm{H}^+] = 0.05$–$0.6\ M$ and $0.6\ M$ ionic strength the molar absorbancy indices (in l. mol^{-1} cm^{-1}) of the complex at 260, 270, and 500 nm are 3143 ± 20, 2100 ± 15, and 81.7 ± 0.6, respectively. The absorption maxima (nm) and the corresponding molar absorbancies (l. mol^{-1} cm^{-1}) of the $[(\mathrm{NH_3})_5\mathrm{CoOCOC_6H_4OH}]^{2+}$ ion have been reported by Gould and Taube[8] to be 235 (22,000), 298 (4400) and 503 (76.0).

Aquopentaamminecobalt(III) perchlorate was prepared and purified by the method of Splinter, Harris, and Tobias.[10] The molar absorbancies of aquopentaamminecobalt(III) perchlorate (ϵ_{aquo}) at various wavelengths (in nm) are 46.9 (500), 44.0 (510), 40.4 (520), and 27.0 (540). The values are in good agreement with those of Splinter, *et al.*[10] [$\epsilon_{\mathrm{aquo}} = 46.45$ (500 nm), 43.7 (510 nm), 39.3 (520 nm), 26.9 (540 nm)].

Ferric perchlorate solution was prepared by repeated evaporation of iron(III) chloride (AR) with 70% perchloric acid (AR) until the solution was free from chloride. Gallium metal 99.99% pure was dissolved in hydrochloric acid (AR) and then converted to perchlorate by boiling off hydrochloric acid in the presence of perchloric acid. Aluminum(III) perchlorate was prepared by dissolving freshly pre-

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(2) See ref 1, p 231.

(3) K.-W. Kuo and S. K. Madan, *Inorg. Chem.*, **10**, 229 (1971), and references cited therein.

(4) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1965, p 122.

(5) H. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(6) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

(7) A. C. Dash and R. K. Nanda, in preparation.

(8) See ref 6.

(9) H. A. Laitinen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

(10) R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 898 (1968).

cipitated aluminum(III) hydroxide in excess standard perchloric acid solution. Al(III) and Ga(III) contents of stock solutions were estimated gravimetrically as oxides.[11] Fe(III) was estimated volumetrically.[12]

Free acid in the stock metal perchlorate solutions was estimated as follows. The metal ions, in a known volume of the stock solution of their perchlorates, were exchanged with Dowex 50W-X8 resin in acid form and the liberated acid was titrated against standard alkali. The free acid content of the metal perchlorate solutions was calculated from the known concentration of the metal ions and the total amount of the acid liberated in the ion-exchange experiments.

Reagent grade sodium perchlorate was used to maintain ionic strength of the reaction medium. Salicylic acid (AR, BDH) was used as such wherever necessary. Dowex 50W-X8 cation-exchange resin in the acid form was used in all ion-exchange experiments. Spectrophotometric measurements were made with a Beckmann DU2 spectrophotometer using 1-cm matched quartz cells.

Kinetics. A 50-ml volumetric flask containing sodium perchlorate, perchloric acid, and metal perchlorate solutions in requisite amounts was allowed to equilibrate in the thermostat maintained at the desired temperature. After the thermal equilibrium was attained, a known weight of the complex was transferred into the reaction flask and the volume was made up with distilled water previously equilibrated at the same temperature. The solid dissolved rapidly on shaking. Aliquots (5 ml) of the reaction mixture were withdrawn at convenient time intervals into a beaker containing sufficient ice-cold $HClO_4$ solution such that the mixture was between 0.3 and 0.4 N with respect to $HClO_4$. A few grams of the cation-exchange resin in the acid form was then added to the acidified solution and the contents were stirred until the supernatant liquid was colorless indicating thereby that the unreacted complex and the aquo product were taken up by the resin. The colorless solution was carefully filtered through a well-packed bed of glass wool (since the resin particles were heavy and granular, most of them remained behind in the beaker and the smaller particles were retained in the bed of glass wool). The resin was washed repeatedly with 0.3 N $HClO_4$ and the colorless washings were collected along with the main filtrate. Data given in Table I indicate that under the above conditions of exchange salicylic acid is quantitatively separated from a mixture of salicylic acid and Fe(III) etc. ions.

To the above solution (main filtrate and washings), taken in a 250-ml glass-stoppered iodine flask a known volume (10 or 5 ml) of standard $KBrO_3$ (0.01 or 0.015 N) solution containing a large excess of KBr was added followed by about 20 ml of 6 N HCl. The flask was stoppered tightly and the contents were allowed to stand at room temperature for 1 hr, after which, 5 ml of 10% KI solution was added and the liberated iodine was titrated rapidly with vigorous shaking against 0.02 N thiosulfate (which had been standardized against 0.02 N bromate under similar conditions) using starch as indicator. The amount of salicylic acid liberated at any time t was computed from the following relationships: 10 ml of standard $BrO_3^- \equiv V_0$ ml of 0.02 N $Na_2S_2O_3$; 10 ml of standard BrO_3^- + 5 ml of reaction mixture at time t (after exchange) $\equiv V_t$ ml of 0.02 N $Na_2S_2O_3$; amount of salicylic acid liberated at time t per 5 ml of the mixture $\equiv (V_0 - V_t)$ ml of 0.02 N $Na_2S_2O_3$. The amount of salicylic acid that would be liberated per 5 ml of the reaction mixture at "infinite" time (complete reaction) was computed from the known weight of the complex taken and was converted to the volume equivalent of the titrant (0.02 N $Na_2S_2O_3$) by the relationship: 1000 ml of (M) salicylic acid $\equiv$ 6000 ml of (N) $Na_2S_2O_3$, which is based upon the stoichiometry of the salicylic acid–bromine reaction[13]

$$C_6H_4(OH)COOH + 3Br_2 = C_6H_2Br_3(OH) + 3HBr + CO_2 \qquad (1)$$

In the absence of added metal ions, the concentration of salicylic acid calculated from the volume of thiosulfate consumed on the basis of reaction 1 agrees within 1% with that calculated from the weight of salicylic acid taken. In the presence of aluminum(III) and gallium(III) perchlorate the concentration of salicylic acid found, as above, deviated from that calculated from the weight of salicylic acid taken by 2% and in the presence of iron(III) perchlorate this deviation was about 3%. The experimental data are given in Table I.

Table I. Stoichiometry of Salicylic Acid–Bromine Reaction and Ion-Exchange Separation of Salicylic Acid[a]

Metal	x, vol of 0.3 M $M(ClO_4)_3$, ml	y, vol of 0.9779×10^{-3} M[b] S acid, ml	Vol of 0.015 N[c] BrO_3^-, ml	Vol of 0.0193 N[d] $Na_2S_2O_3$ consumed, ml	$10^3 \times$ concn of S acid found,[e] M
None	0.00	0.00	10.0	7.77	
	0.00	10.0	10.0	4.76	0.968
Al(III)	1.0	10.0	10.0	4.78	0.962
	3.0	10.0	10.0	4.79	0.958
Ga(III)	0.5	10.0	10.0	4.78	0.962
	1.0	10.0	10.0	4.78	0.962
Fe(III)	0.5	10.0	10.0	4.80[f]	0.956
	1.0	10.0	10.0	4.82[f]	0.949
	1.5	10.0	10.0	4.82[f]	0.949

[a] Solution exchanged in 0.3 M $HClO_4$ acid medium contained x ml of 0.3 M $M(ClO_4)_3$ + y ml of 0.9779×10^{-3} M S (salicylic) acid. The details of exchange and analytical procedures are outlined in the Experimental Section. [b] Concentration calculated from the weight of S acid. [c] $KBrO_3$ solution contained sufficiently large excess of KBr. [d] Standardized against 0.015 N BrO_3^-. Each entry for the titer values is the average of triplicate readings and the experimental error in the average titer value is ±0.02 ml of 0.0193 N $Na_2S_2O_3$. [e] Based on reaction 1. [f] After correction for the titration blank. Fe(III) solution in absence of S acid was exchanged under identical conditions and the filtrate + washings + 5 ml of 10% KI + 20 ml of 6 N HCl consumed 0.1–0.25 ml of 0.0193 N $Na_2S_2O_3$ (titration blank).

The procedure for the study of the acid hydrolysis reaction of the complex in the absence of metal ions was similar except that the unreacted cobalt(III) complex and the aquo product were exchanged in ice-cold condition in the absence of added acid and that the resin was washed with distilled water instead of perchloric acid (salicylic acid in the absence of M(III) ions was found not to be taken up by the resin in the acid form; distilled water was, therefore, used as the wash liquid).

For following the kinetics of acid hydrolysis of the salicylato complex in the presence and absence of M(III) ions spectrophotometrically, appropriate reaction mixtures were prepared and equilibrated at desired temperatures as before. Aliquots (5 ml) of the reaction mixture were withdrawn at convenient time intervals and rapidly cooled down to room temperature in ice-cold water, and the optical density was measured at room temperature using 1-cm matched quartz cells. The acid hydrolysis of the complex in the presence and absence of Al(III) and Ga(III) ions was followed at either 260 or 270 nm. When Fe(III) was used as the catalyst, rate measurements were made at any suitable wavelength between 500 and 600 nm such that $(D_\infty - D_0)$ or $(D_0 - D_\infty)$ was sufficiently large (0.05–0.1 OD unit) under the experimental conditions.

Evaluation of Kinetic Data. For runs followed titrimetrically the relationship $\ln \beta = \ln \alpha - k_{obsd}t$ was used to calculate the pseudo-first-order rate constants where α and β stand for the volume of the titrant (0.02 N $Na_2S_2O_3$) equivalent to the amount of salicylato complex per 5.0 ml of the reaction mixture at zero time and time t, respectively. The observed rate constants for spectrophotometric runs were computed from $\ln (D_t - D_\infty) = \ln (D_0 - D_\infty) - k_{obsd}t$ or $\ln (D_\infty - D_t) = \ln (D_\infty - D_0) - k_{obsd}t$, where D_0, D_t, and D_∞ stand for the optical densities of the reaction mixture at zero time, time t, and infinite time, respectively. All observed rate constants calculated from spectrophotometric measurements are based on D_∞ values determined as follows. D_∞ for any run was taken to be the measured optical density of a solution whose composition corresponded exactly to that for complete reaction for that run. Computer programs were used to calculate the observed rate constants from the least-squares best slopes for the straight-line plots of $\ln \beta$ *vs.* t, $\ln (D_t - D_\infty)$ *vs.* t, or $\ln (D_\infty - D_t)$ *vs.* t. The errors quoted for the observed rate constants (Tables II,III) were calculated from the least-squares standard deviations of the slopes for such plots. The IBM 1130 computer of Utkal University was used to carry out these calculations. Data for some of the runs followed titrimetrically are given in Table II.

Equilibrium Studies. Complex formation between the salicylato complex and the added metal ions was studied spectrophotometrically. Requisite amounts of sodium perchlorate, perchloric acid, and the metal perchlorate solutions were taken in 25-ml calibrated flasks. A measured volume of a solution of the complex, freshly prepared in

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(11) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1962, p 472.

(12) See ref 11, p 310.

(13) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd revised ed, Interscience, New York, N. Y., 1947, p 216. $C_6H_2Br_3OBr$ liberates iodine quantitatively from aqueous acidic potassium iodide solution: F. J. Welcher, "Standard Methods of Chemical Analysis," Vol. 2, 6th ed, Van Nostrand, New York, N. Y., 1963, Part B, p 2465.

Table II. Titrimetric Data for Acid Hydrolysis of $[(NH_3)_5CoOCOC_6H_4OH]^{2+}$ at 65°[a]

	Run no.			
	1	2	3	4
10^3[complex], *M*	6.43	4.48	4.32	4.50
$[H^+]$, *M*	0.2	0.01	0.05	0.1
$[M^{3+}]$, *M*		0.06	0.048	0.033
$[BrO_3^-]$,[b] *N*	0.0118	0.010	0.010	0.010
$[Na_2S_2O_3]$,[c] *N*	0.0211	0.0206	0.0206	0.0206
V,[d] ml	9.14	6.52	6.29	6.55
$V(BrO_3^-)$,[e] ml	10.0	5.0	5.0	5.0
M	None	Al(III)	Ga(III)	Fe(III)
10^6k_{obsd},[f] sec^{-1}	5.56 (±0.12)	4.35 (±0.24)	6.68 (±0.28)	10.6 (±0.2)

Run 1		Run 2		Run 3		Run 4	
Time, min	V_t,[g] ml	Time, min	V_t,[g] ml	Time, min	V_t,[g] ml	Time, min	V_t,[g] ml
0	5.58	0	2.43	0	2.43	0	2.43
60	5.17	60	2.20	63	2.21	66	2.01
120	5.00	110	2.15	145	1.99	148	1.69
180	4.815	232	1.96	211	1.86	208	1.505
240	4.68	335	1.74	277	1.67	274	1.265
300	4.49	483	1.57	340	1.60	339	1.05
360	4.31			416	1.39	402	0.82
420	4.20						

[a] A 5-ml sample of the reaction mixture was analyzed. [b] Concentration of BrO_3^- in normality in the brominating solution. [c] Concentration of the titrant in normality. [d] $V = 6 \times 5 \times$ [complex]/[titrant]. [e] Volume of the brominating solution used for bromination. [f] $k_{obsd} = [(\Sigma t)(\Sigma \ln \beta) - N(\Sigma t \ln \beta)]/[N(\Sigma t^2) - (\Sigma t)^2]$, $\ln \alpha = [(\Sigma \ln \beta)(\Sigma t^2) - (\Sigma t)(\Sigma t \ln \beta)]/[N(\Sigma t^2) - (\Sigma t)^2]$, $\sigma(k_{obsd}) = \{[\Sigma(\ln \beta - \ln \alpha + k_{obsd}t)^2/[N(\Sigma t^2) - (\Sigma t)^2]][N/(N-2)]\}^{1/2}$, $\beta = V - V_0 + V_t$. *t* is time in seconds. [g] Titer values.

distilled water, was then added to the flask and the volume was made up. Optical density measurements were made at room temperature (28°) immediately after the reactants were mixed. Equilibrium between the salicylatopentaamminecobalt(III) complex and Fe(III) or Ga(III) ions was rapidly established. This is supported by the observation that the optical densities of the mixed solutions remained unchanged up to 30 min of mixing the reactants. Formation of the $(NH_3)_5CoOCOC_6H_4OAl^{4+}$ is probably slow as indicated by the gradual increase of optical density of mixed solutions containing Al(III) and the cobalt(III) complex. The optical density of such solutions became virtually constant after 10 min of mixing the reactants. The equilibrium optical densities of the solutions were used to calculate the equilibrium constants.

Results

Equilibrium Constant (K_1). The equilibrium in solutions containing metal(III) perchlorate, sodium perchlorate, perchloric acid, and the salicylatopentaamminecobalt(III) ion is represented as

$$(NH_3)_5CoOCOC_6H_4OH^{2+} + M^{3+} \overset{K_1}{\rightleftharpoons} (NH_3)_5CoOCOC_6H_4OM^{4+} + H^+ \qquad (2)$$

If d_1 and d_2 be the optical densities of solutions of the salicylato complex alone and the mixed solutions, respectively, and ϵ_1 and ϵ_2 be the extinction coefficients of $(NH_3)_5CoOCOC_6H_4OH^{2+}$ and $(NH_3)_5CoOCOC_6H_4OM^{4+}$, respectively, then

$$d_1 = \epsilon_1 C_1 l \qquad (3)$$

and

$$d_2 = \epsilon_2 x l + \epsilon_1(C_1 - x)l \qquad (4)$$

where $C_1 = [(NH_3)_5CoOCOC_6H_4OH]_{total}$, $x = [(NH_3)_5CoOCOC_6H_4OM^{4+}]_{total}$, and *l* is the cell path length. At constant ionic strength the equilibrium constant of reaction 2 is given by

$$K_1 = x[H^+]/(C_1 - x)(C_2 - x) \qquad (5)$$

where $C_2 = [M^{3+}]_{total}$. Combining eq 3-5 and assuming $C_2 - x = C_2$ (since $C_2 \gg C_1$, this appears to be a valid assumption) it is possible to derive the relationship

$$C_1/(d_2 - d_1) = \frac{1}{(\epsilon_2 - \epsilon_1)l} + \left(\frac{1}{(\epsilon_2 - \epsilon_1)lK_1}\right)\frac{[H^+]}{C_2} \qquad (6)$$

A least-squares computer program for eq 6 was adopted to calculate the best values of the slope and intercept of $C_1/(d_2 - d_1)$ *vs.* $[H^+]/C_2$ plots. The values of K_1 were computed from the least-squares best values of the slopes and intercepts of such plots. The error limits of K_1 (σK_1) were calculated from the relationship[14]

$$\sigma K_1 = m^{-2}(m^2\sigma c^2 + c^2\sigma m^2)^{1/2}$$

where $c = 1/(\epsilon_2 - \epsilon_1)l$, $m = (1/(\epsilon_2 - \epsilon_1)lK_1)$, and σc and σm are least-squares standard deviations of *c* and *m*, respectively. The data are presented in Table III.

Aquation of Salicylatopentaamminecobalt(III) Ion. The aquation of salicylatopentaamminecobalt(III) ion was studied in $HClO_4$ solutions over the acidity range 0.05-0.6 *M* at an ionic strength of 0.6 *M*, adjusted with $NaClO_4$ wherever necessary. The pseudo-first-order rate constants for the aquation reaction at 60, 65, and 70° are given in Table IV. The observed rate constants (k_{obsd}) obtained from spectrophotometric measurements agree satisfactorily with those obtained by the titrimetric method (Table IV). The nature of the hydrogen ion dependence of the pseudo-first-order rate constants, k_{obsd}, indicates the existence of two reaction pathways for the aquation of the complex ion $(NH_3)_5CoOCOC_6H_4OH^{2+}$. In the range of acidity at which the reaction was studied, k_{obsd} *vs.* $[H^+]$ plots are found to be linear with nonvanishing intercepts. The positive extrapolated value of k_{obsd} at zero hydrogen ion concentration indicates the presence of a reaction pathway whose rate law does not involve hydrogen ion concentration, and as such, its stoichiometry can be represented as

$$(NH_3)_5CoOCOC_6H_4OH^{2+} + H_2O \xrightarrow{k_0} (NH_3)_5CoOH_2^{3+} + C_6H_4(OH)COO^- \qquad (7)$$

The rate constant calculated from the slope of k_{obsd} *vs.* $[H^+]$ plots is presumed to be associated with the other reaction path whose stoichiometry may be represented by eq 8.

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[14] T. B. Crumpler and J. H. Yoe, "Chemical Computations and Errors," 1st ed, Wiley, New York, N. Y., 1949, p 178.

$$(NH_3)_5CoOCOC_6H_4OH^{2+} + H^+ + H_2O \xrightarrow{k_1} (NH_3)_5CoOH_2{}^{3+} + C_6H_4(OH)COOH \qquad (8)$$

The rate law for a reaction proceeding through the pathways represented by eq 7 and 8 will have the form

$$-\mathrm{d}C_t/\mathrm{d}t = (k_0 + k_1[H^+])C_t = k_{obsd}C_t \qquad (9)$$

where C_t represents the total concentration of the complex and the specific rate constants k_0 and k_1 are associated with the uncatalyzed (eq 7) and acid catalyzed (eq 8) paths, respectively. The rate constants for the aquation of the deprotonated species $(NH_3)_5CoOCOC_6H_4O^+$ is not amenable to measurement (at the high acidities at which the present work was carried out) because of the high pK value of the complex (pK_{OH}[15] = 9.77 at 25°, $\mu = 3\ M$; pK_{OH}[15] = 10.2 at 25°, $\mu = 1.0\ M$).

Table III. Equilibrium constant (K_1) of the Reaction $(NH_3)_5CoOCOC_6H_4OH^{2+} + M^{3+} \rightleftharpoons (NH_3)_5CoOCOC_6H_4OM^{4+} + H^+$ at 28° and $\mu = 0.6\ M$

$10^3[M^{3+}]$, M	$[H^+]$, M	10^4[complex], M	OD[a]
M = Fe(III)[b]			
0.00	0.05	4.90	0.03
2.20	0.05	4.90	0.209
4.41	0.05	4.90	0.325
6.61	0.05	4.90	0.399
8.82	0.05	4.90	0.455
11.0	0.05	4.90	0.500
8.82	0.1	4.90	0.3275
8.82	0.2	4.90	0.217
8.82	0.3	4.90	0.165
$1/(\epsilon_2 - \epsilon_1)l = 6.56\ (\pm 0.24) \times 10^{-4}$, $1/K_1(\epsilon_2 - \epsilon_1)l = 8.817\ (\pm 0.13) \times 10^{-5}$, $K_1 = 7.44\ (\pm 0.29)$			
M = Al(III)[c]			
0.00	0.002	4.89	0.166
0.00	0.004	4.89	0.166
0.00	0.006	4.89	0.166
14.4	0.002	4.89	0.289
28.8	0.002	4.89	0.345
14.4	0.004	4.89	0.255
28.8	0.004	4.89	0.297
14.4	0.006	4.89	0.2325
28.8	0.006	4.89	0.270
$1/(\epsilon_2 - \epsilon_1)l = 1.97\ (\pm 0.11) \times 10^{-3}$, $1/K_1(\epsilon_2 - \epsilon_1)l = 1.29\ (\pm 0.047) \times 10^{-2}$, $K_1 = 0.15\ (\pm 0.01)$			
M = Ga(III)[c]			
0.00	0.06	8.36	0.279
0.00	0.045	8.36	0.279
0.00	0.06	8.38	0.284
0.00	0.02	4.06	0.1375
10.0	0.06	8.36	0.338
20.0	0.06	8.36	0.379
10.0	0.045	8.36	0.3475
10.0	0.06	8.38	0.343
20.0	0.06	8.38	0.385
2.0	0.02	4.06	0.156
3.0	0.02	4.06	0.164
4.0	0.02	4.06	0.170
5.0	0.02	4.06	0.1775
$1/(\epsilon_2 - \epsilon_1)l = 2.73\ (\pm 0.33) \times 10^{-3}$, $1/K_1(\epsilon_2 - \epsilon_1)l = 1.922\ (\pm 0.058) \times 10^{-3}$, $K_1 = 1.42\ (\pm 0.18)$			

[a] l (cell path length) = 1 cm. [b] OD values at 540 nm. [c] OD values at 330 nm.

Effect of Metal Ions on the Aquation Rate. The aquation reaction of salicylatopentaamminecobalt(III) ion has been studied in the presence of Fe(III), Al(III), and Ga(III) ions. The data collected in Table V indicate that these metal ions catalyze the hydrolysis of the Co(III) complex. Of the three metal ions Fe(III) is found to be the most effective catalyst. Both the spectrophotometric and titrimetric data (Table V) indicate that k_{obsd} increases with increasing concentration of metal ions at a fixed acidity. Consistent with our observations the pathway for the metal ion catalyzed aquation of the Co(III) complex appears to involve a rapid and reversible equilibrium between the substrate and the metal ion followed by the rate-determining loss of the metal(III)-monosalicylato complex from the associated species as indicated below

$$(NH_3)_5CoOCOC_6H_4OH^{2+} + M^{3+} \overset{K_1}{\rightleftarrows} (NH_3)_5CoOCOC_6H_4OM^{4+} + H^+$$

$$(NH_3)_5CoOCOC_6H_4OM^{4+} + H_2O \xrightarrow{k_2} (NH_3)_5CoOH_2{}^{3+} + C_6H_4(O)COOM^+ \qquad (10)$$

Combination of eq 2, 7, 8, and 10 leads to the following relationship for the pseudo-first-order rate constant (k_{obsd}) of aquation of the complex in the presence of M^{3+} ions

$$k_{obsd} = \frac{k_0 + k_1[H^+] + k_2K_1[M^{3+}]/[H^+]}{1 + K_1[M^{3+}]/[H^+]} \qquad (11)$$

where K_1 and k_2 are the equilibrium and the rate constants as defined by eq 2 and 10, respectively.

Evaluation of the Rate Parameters. The pseudo-first-order rate constants (k_{obsd}) for the hydrolysis of the complex in the absence of M^{3+} ions and at varying acidities were fitted to eq 9 by the help of a least-squares computer program which varied both k_0 and k_1 and minimized the function

$$F = \sum_{i=1}^{i=n}(k_0 + k_1[H^+]_i - k_{obsd_i})^2/\sigma k_{obsd_i}{}^2 \qquad (12)$$

where σk_{obsd_i} is the error in the ith rate constant k_{obsd_i} corresponding to the hydrogen ion concentration $[H^+]_i$. The initial values of k_0 and k_1 used in this calculation were obtained from the k_{obsd} *vs.* $[H^+]$ plots (eq 9). k_0 and k_1 being known, eq 11 was treated as a two-parameter equation (the parameters being K_1 and k_2K_1). Utilizing the best values of k_0 and k_1 and assuming $[M^{3+}]_{total} = [M^{3+}]_{free}$ and $[H^+]_{total} = [H^+]_{free}$ ($[M^{3+}]_{total}$ and $[H^+]_{total}$ stand for the concentrations of metal and hydrogen ion neglecting hydrolysis and ion association equilibria) the observed rate constants for hydrolysis of the complex in the presence of M^{3+} ions were fitted to eq 11 with the help of a least-squares program (similar to that used for solving eq 9) which varied K_1 and k_2K_1 and minimized the parameter F (for eq 11) given by

$$F = \sum_{i=1}^{i=n}(k_{calcd_i} - k_{obsd_i})^2/\sigma k_{obsd_i}{}^2 \qquad (13)$$

where the terms have their usual significance. The approximate values of k_2K_1 and K_1 chosen for this calculation were computed from the relationship

$$1/(k_{obsd} - k_0 - k_1[H^+]) = 1/(k_2 - k_0 - k_1[H^+]) + (1/(k_2 - k_0 - k_1[H^+])x)[H^+]/[M^{3+}]K_1 \qquad (14)$$

to which eq 11 can be easily transformed. The data obtained from spectrophotometric and titrimetric methods were analyzed separately and the final values of k_0, k_1, k_2K_1, and K_1 are collected in Tables IV and VI, respectively.

Calculation of the Error Limits of k_0, k_1, k_2, and K_1. On expanding the function F for eq 12 and 13 at $F = F_{min}$, it is possible to get the relationship

$$F = F_{min} + H_{11}\sigma x_1{}^2 + H_{12}\sigma x_1\sigma x_2 + H_{21}\sigma x_1\sigma x_2 + H_{22}(\sigma x_2)^2 \qquad (15)$$

(neglecting the higher order terms in σx_1 and σx_2) where

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(15) (a) See ref 6; (b) A. Liang and E. S. Gould, *J. Amer. Chem. Soc.*, **92**, 6791 (1970).

Table IV. Rate Data for the Acid Hydrolysis of $[(NH_3)_5CoOCOC_6H_4OH]^{2+}$ at $\mu = 0.6\ M$[a]

	10^6k_{obsd}, sec^{-1}					
	At 60 ± 0.1°		At 65.0 ± 0.1°		At 70.0 ± 0.1°	
$[H^+]$, M	TT	SP	TT	SP	TT	SP
0.05					6.05 (±0.25)	
0.1	1.6 (±0.25)		3.84 (±0.10)		8.22 (±0.25)	9.4 (±0.3)
0.2	2.92 (±0.24)	3.35 (±0.15)	5.56 (±0.12)	6.85 (±0.19)	10.9 (±0.5)	13.9 (±0.5)
0.3	3.47 (±0.29)	4.40 (±0.18)	7.77 (±0.24)	8.95 (±0.15)	14.4 (±0.5)	
0.4	4.60 (±0.25)	5.65 (±0.20)	9.52 (±0.20)			21.7 (±0.8)
0.5	5.83 (±0.16)	6.86 (±0.21)	11.0 (±0.14)	13.4 (±0.3)	20.6 (±1.7)	25.4 (±0.6)
0.6		8.22 (±0.20)		15.3 (±0.3)		29.6 (±0.4)
10^6k_0, sec^{-1}	0.63 (±0.25)	0.86 (±0.22)	2.01 (±0.12)	2.56 (±0.28)	4.64 (±0.26)	5.49 (±0.34)
10^5k_1, $sec^{-1}\ M^{-1}$	1.03 (±0.06)	1.21 (±0.06)	1.82 (±0.04)	2.14 (±0.08)	3.26 (±0.19)	4.02 (±0.09)

[a] TT = titrimetry; SP = spectrophotometry; [complex] = (6–12) × $10^{-3}\ M$ in TT runs and 2 × $10^{-4}\ M$ in SP runs. The errors quoted for k_{obsd} are least-squares standard deviations calculated from the pseudo-first-order kinetic plots. Each entry for k_{obsd} is based on a single experiment.

$H_{11} = {}^1\!/_2 d^2F/dx_1{}^2$, $H_{12} = H_{21} = {}^1\!/_2 d^2F/dx_1dx_2$, $H_{22} = {}^1\!/_2 d^2F/dx_2{}^2$, and x_1 and x_2 are the parameters with respect to which F is minimized ($x_1 = k_0, k_2K_1$ and $x_2 = k_1, K_1$ for eq 12 and 13, respectively). At $F - F_{min} = 1.0$, the errors of the parameters x_1 and x_2 are defined as $\sigma x_1 = \pm A_{11}{}^{1/2}$ and $\sigma x_2 = \pm A_{22}{}^{1/2}$ where A_{11} and A_{22} are the diagonal elements of the matrix A such that $A = H^{-1}$. The matrix H is defined as

$$H = \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} \tag{16}$$

The error limits of k_2 were derived from the estimated errors of k_2K_1 and K_1 by the relationship

$$\sigma(k_2K_1) = K_1\sigma k_2 + k_2\sigma K_1 \tag{17}$$

where $\sigma(k_2K_1)$, σk_2 and σK_1 stand for the errors of k_2K_1, k_2, and K_1, respectively.

The activation parameters for k_0, k_1, and k_2 paths were calculated from the transition state equation

$$k = (RT/Nh) \exp(-\Delta H^*/RT + \Delta S^*/R) \tag{18}$$

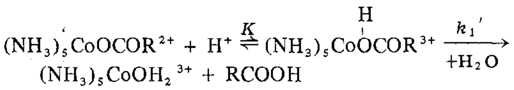
The rate constants k_0, k_1, and k_2 were fitted to eq 18 by means of a nonlinear least-squares program which varied the parameters ΔH^* and ΔS^* and minimized $\Sigma(Z - k)^2/\sigma k^2$, where Z is the right side of eq 18 (*i.e.*, calculated rate constant) and σk is the error of the rate constant k. Approximate values of ΔH^* and ΔS^* used in this calculation were obtained from log (k/T) *vs.* $1/T$ plots. The error limits of ΔH^* and ΔS^* were estimated by the method described earlier for the calculations of the errors of the rate parameters (k_0, k_1, etc.).

Discussion

In the acidity range studied, the aquation of salicylatopentaamminecobalt(III) ion proceeds *via* two pathways: an acid catalyzed and an acid independent pathway. The rate constants for the acid independent path (k_0) of the complex calculated from the spectrophotometric measurements agree reasonably with those obtained from the titrimetric data (Tables IV, VII). Comparing the values of k_0 (at 70°) for a series of carboxylatopentaamminecobalt(III) complexes collected in Table VII, it is evident that the rate data for the salicylato complex do not fit in with the usual correlation between the rate and the base strength of the carboxylate ions. The order of variation of pK of the acids[16] being $(CH_3)_3CCOOH > CH_3COOH > C_6H_4(OH)COOH > CF_3COOH$, the anticipated sequence for the rate constants would be $k_0(CF_3COO^-) > k_0(C_6H_4(OH)COO^-) > k_0(CH_3COO^-) > k_0((CH_3)_3COO^-)$. It is further worth noting that the values of k_0 for trimethylacetato and salicylato complexes are practically same at 70° (Table VII) although pK of trimethylacetic acid is about 2 units higher[16] than that of salicylic acid at 25°. It is, therefore, reasonable to believe that intramolecular hydrogen bonding in the salicylate moiety of salicylatopentaamminecobalt(III) ion[17] has little rate-accelerating influence on the aquation of this complex in the k_0 path.

The activation parameters for the k_0 path of salicylato complex do not compare well with those for the corresponding path of aquation of several other carboxylatopentaamminecobalt(III) complexes listed in Table VII. On the other hand ΔH^* (in kcal/mol) and ΔS^* (in eu) for the k_0 path of all such complexes (excluding the trimethylacetato complex for which relevant data are lacking) fit the equation $\Delta H^* = \alpha + \beta\Delta S^*$ with $\alpha = 27.5$ and $\beta = 0.385$. This linear relationship between ΔH^* and ΔS^* indicates that a single mechanism operates in the uncatalyzed path of aquation of all carboxylatopentaamminecobalt(III) complexes under consideration. Since the uncatalyzed path of aquation of trimethylacetato-, acetato-, bis(oxalato)-, and trifluoroacetatopentaamminecobalt(III) complexes[18–20] is reported to involve a rate-determining Co–O bond fission process, such a mechanism seems to be operative in the k_0 path of the salicylato complex. However, the proposed mechanism for the uncatalyzed path of aquation of the salicylato complex is but tentative and awaits further experimentations to be established.

The rate and activation parameters for the proton catalyzed paths of hydrolysis of carboxylatopentaamminecobalt(III) complexes have been collected[18,21] in Table VII. The acid catalyzed paths of aquation of such complexes have been suggested[18] to involve rapid and reversible equilibrium protonation of the Co(III) complex followed by the rate-limiting aquation of the protonated species as detailed in



$$(NH_3)_5CoOCOR^{2+} + H^+ \overset{K}{\rightleftharpoons} (NH_3)_5Co\overset{H}{O}COR^{3+} \xrightarrow[+H_2O]{k_1'} (NH_3)_5CoOH_2{}^{3+} + RCOOH$$

The equilibrium constant (K) for the protonation equilibrium

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(16) C. D. Hodgman, R. C. Weast, and R. S. Shankland, "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 1753.

(17) See ref 15b.

(18) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.* 24, 1241 (1962).

(19) C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

(20) C. Andrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, 9, 711 (1970).

(21) C. Andrade and H. Taube, *Inorg. Chem.*, 5, 1087 (1966).

Table V. Metal Ion Catalyzed Hydrolysis of $(NH_3)_5CoOCOC_6H_4OH^{2+}$

$10^2 \times [M^{3+}]$, M	$[H^+]$, M	$10^6 k_{obsd}$ (TT),[a,c] sec^{-1}	$10^2 \times [M^{3+}]$, M	$[H^+]$, M	$10^6 k_{obsd}$ (SP),[b,c] sec^{-1}	Wavelength, nm
60.0 ± 0.1°						
M = Fe(III)						
1.0	0.1	3.25 (±0.20)	3.0	0.1	9.32 (±0.25)	500
2.0	0.1	4.55 (±0.25)	3.0	0.2	8.10 (±0.40)	560
3.0	0.1	5.42 (±0.28)	4.0	0.2	8.74 (±0.4)	580
4.0	0.1	6.12 (±0.25)	5.0	0.2	9.36 (±0.35)	540
			4.0	0.3	8.09 (±0.39)	520
M = Ga(III)						
1.2	0.05	1.95 (±0.20)	0.62	0.05	1.90 (±0.1)	260
2.4	0.05	2.45 (±0.25)	1.2	0.05	2.25 (±0.1)	260
4.8	0.05	3.32 (±0.28)	1.80	0.05	2.55 (±0.12)	260
4.8	0.045	3.30 (±0.27)	2.4	0.05	2.75 (±0.11)	260
2.4	0.044	2.75 (±0.3)				
2.4	0.023	2.97 (±0.21)				
M = Al(III)						
2.0	0.01	1.50 (±0.22)	2.0	0.01	1.7 (±0.15)	270
2.0	0.01	1.35 (±0.25)	4.0	0.01	2.1 (±0.18)	270
4.0	0.01	1.96 (±0.15)	6.0	0.01	2.37 (±0.18)	270
4.0	0.01	1.75 (±0.25)	6.0	0.05	1.86 (±0.19)	270
6.0	0.01	2.25 (±0.19)	9.0	0.05	2.00 (±0.22)	270
6.0	0.01	1.90 (±0.20)				
65.0 ± 0.1°						
M = Fe(III)						
1.1	0.1	6.98 (±0.13)	1.1	0.1	10.8 (±0.5)	520
2.2	0.1	9.0 (±0.12)	2.2	0.1	15.1 (±0.8)	500
3.3	0.1	10.6 (±0.2)	2.2	0.2	11.5 (±0.9)	600
			3.3	0.2	13.3 (±0.8)	560
			4.4	0.2	14.9 (±0.7)	560
			2.2	0.3	11.9 (±0.6)	560
			3.3	0.3	13.3 (±0.6)	540
			4.4	0.3	15.2 (±0.6)	540
M = Ga(III)						
1.2	0.05	4.41 (±0.17)	0.62	0.046	4.4 (±0.2)	260
2.4	0.05	5.17 (±0.19)	1.21	0.13	5.75 (±0.2)	260
4.8	0.05	6.68 (±0.28)	0.32	0.032	3.88 (±0.15)	260
			1.20	0.05	5.02 (±0.2)	260
			2.40	0.05	5.95 (±0.22)	260
M = Al(III)						
2.0	0.01	3.27 (±0.15)	2.0	0.01	3.46 (±0.15)	260
4.0	0.01	3.89 (±0.20)	4.0	0.01	3.85 (±0.21)	260
6.0	0.01	4.35 (±0.24)	6.0	0.01	4.1 (±0.20)	260
			8.0	0.01	4.26 (±0.18)	260
70.0 ± 0.1°						
M = Fe(III)						
1.1	0.2	15.9 (±0.5)	1.1	0.2	21.5 (±0.9)	540
2.2	0.2	19.6 (±0.7)	2.2	0.2	27.6 (±1.2)	540
4.4	0.2	25.4 (±0.7)	3.3	0.2	31.0 (±1.1)	560
4.4	0.3	24.5 (±0.8)	4.4	0.2	36.5 (±2.1)	560
			2.2	0.3	25.1 (±1.0)	540
			2.2	0.1	32.5 (±1.3)	500
M = Ga(III)						
4.8	0.088	9.95 (±0.25)	1.2	0.05	9.7 (±0.2)	260
2.4	0.044	9.12 (±0.25)	2.4	0.05	11.2 (±0.3)	260
2.4	0.1	9.15 (±0.20)	3.6	0.05	12.5 (±0.3)	260
			4.8	0.05	13.5 (±0.4)	260
M = Al(III)						
1.5	0.01	6.53 (±0.22)	2.0	0.01	8.4 (±0.25)	260
2.0	0.01	6.89 (±0.22)	3.0	0.01	9.15 (±0.22)	260
3.0	0.01	7.45 (±0.25)	4.0	0.01	9.75 (±0.25)	260
4.55	0.01	8.25 (±0.2)	5.0	0.01	10.0 (±0.3)	260
6.0	0.01	8.80 (±0.20)				

[a] $\mu = 0.6\ M$, titrimetric method, [complex] = (4–5) × $10^{-3}\ M$. [b] $\mu = 0.6\ M$, spectrophotometric method, [complex] = (1.91–2.2) × $10^{-4}\ M$ (Al(III), Ga(III)), (4.9–5.8) × $10^{-4}\ M$ (Fe(III)). [c] Each entry for the rate constants is based on a single experiment, and the errors quoted for k_{obsd} are the least-squares standard deviations calculated from the pseudo-first-order kinetic plots.

has been reported[22] in the case of $(NH_3)_5CoOCOCH_3{}^{2+}$ to be 0.25 and 2.2 M^{-1} at ionic strengths 1.0 and 4.0 M (25°), respectively. The first dissociation constant of salicylic acid being about 100 times larger than that of acetic acid, the protonation equilibrium constant (K) for the salicylato complex is expected to be much less than that for the acetato complex at comparable temperature and ionic strength. This is in fact supported by our observation that the hydrogen ion concentration (at $[H^+] = 0.05–1.0\ M$) had no measurable effect on the absorption spectrum of the salicylato complex in the range of wavelengths 230–310 nm. A low value for the equilibrium constant (K) for the salicylato complex is also in keeping with the observed dependence of rate with hydrogen ion concentration (eq 9). The rate constant k_1 for the salicylato complex is comparable with that of the bis(oxalato) complex and is about 10–30 times less than those for the trimethylacetato and acetato complexes at 70° (Table VII). The activation enthalpy and entropy for the acid catalyzed path of hydrolysis of the salicylato complex compare well with those for acetato, trimethylacetato-, and bis(oxalato)pentaamminecobalt(III) complexes (Table VII). Since oxygen-exchange experiments have demonstrated that Co–O bond breaking in the acetato complex[19,20] and C–O bond breaking in the bis(oxalato) and trifluoroacetato complexes[20] are involved in the k_1 path, it is difficult to assign a definite mechanism for the corresponding reaction of the salicylato complex by comparing its rate and activation parameters with those for the analogous Co(III) complexes cited in Table VII.

The results of Fe(III), Al(III), and Ga(III) ion catalyzed acid hydrolysis of the salicylato complex have been collected in Tables V and VI. The data presented in Table VI reveal the following facts: (i) the Co(III) substrate and the metal ions associate to form the binuclear complexes and (ii) the binuclear complexes act as the catalytically active labile intermediates in the course of aquation of the salicylato complex in the presence of the above metal ions. The binuclear complexes of Fe(III), Al(III), and Ga(III) ions have also been detected and characterized (by the equilibrium constants, K_1, Table III) by independent equilibrium studies at 28°, thus supporting their kinetic evidence. The results of the equilibrium studies are presented in Table III. In order to know about the nature of the binuclear complexes it is useful to compare their thermodynamic stabilities with the thermodynamic stabilities of monophenolato and monosalicylato complexes of the metal ions under investigation. The values of the equilibrium constants of the reaction

$$M^{3+} + L^{n-} \xrightleftharpoons{K_{ML}} ML^{(3-n)+}$$

where $L^{n-} = C_6H_4O^-$, $C_6H_4(O)COO^-$, $(NH_3)_5CoOCOC_6H_4O^+$), collected in Table VIII, indicate that the coordinating abilities of the ligands toward M^{3+} ions vary in the order $C_6H_4(O^-) \ll (NH_3)_5CoOCOC_6H_4O^+ \ll C_6H_4(O^-)COO^-$. The stabilities of the binuclear complexes as well as the monosalicylato complexes of the metal ions follow the sequence Fe(III) > Ga(III) > Al(III). $C_6H_4O^-$ and $(NH_3)_5CoOCOC_6H_4O^+$ being oppositely charged, $C_6H_4OFe^{2+}$ is expected to be thermodynamically more stable compared to $(NH_3)_5CoOCOC_6H_4OFe^{4+}$ if both the ligands coordinate to Fe(III) through the phenolic oxygen only. It is, however, worth noting that the stability constant (K_{ML}, Table VIII) of $(NH_3)_5CoOCOC_6H_4OFe^{4+}$ is 10^3 times larger than that of $C_6H_4OFe^{2+}$. This result can be accounted for if it is assumed

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[22] M. B. Barrett, *Diss. Abstr. B*, **29**, 2333 (1969), quoted by J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, **92**, 475 (1970).

Table VI. Equilibrium Constants (K_1), Rate Constants (k_2), and the Activation Parameters for the k_2 Path[a]

		60.0°		65.0°		70.0°	
M	Parameter	TT	SP	TT	SP	TT	SP
Fe(III)	$10^5 k_2 K_1$, sec^{-1}	2.22 (±0.43)	7.0 (±2.7)	4.37 (±0.46)	8.7 (±2.1)	11.9 (±2.4)	19.2 (±4.2)
	K_1	1.8 (±0.8)	4.9 (±3.0)	2.2 (±0.5)	3.2 (±1.5)	2.1 (±1.0)	2.66 (±1.39)
	$10^5 k_2$, sec^{-1}	1.2 (±0.3)	1.4 (±0.3)	2.0 (±0.2)	2.7 (±0.6)	5.7 (±1.6)	7.1 (±2.2)
		$\Delta H^* = 32.6\ (\pm 12.3)$ (TT), $34.7\ (\pm 9.3)$ (SP) kcal/mol $\Delta S^* = +16.0\ (\pm 36)$ (TT), $+23\ (\pm 28)$ (SP) eu					
Al(III)	$10^6 k_2 K_1$, sec^{-1}	0.70 (±0.37)	0.68 (±0.37)	1.08 (±0.47)	1.03 (±0.57)	2.09 (±0.50)	3.48 (±1.23)
	K_1	0.22 (±0.18)	0.19 (±0.17)	0.16 (±0.11)	0.20 (±0.14)	0.16 (±0.06)	0.26 (±0.13)
	$10^6 k_2$, sec^{-1}	3.2 (±0.9)	3.6 (±1.3)	6.7 (±1.6)	5.15 (±0.76)	13.1 (±1.7)	13.0 (±2.0)
		$\Delta H^* = 30.9\ (\pm 6.5)$ (TT), $36.2\ (\pm 9.1)$ (SP) kcal/mol $\Delta S^* = +9\ (\pm 19)$ (TT), $+24\ (\pm 27)$ (SP) eu					
Ga(III)	$10^5 k_2 K_1$, sec^{-1}	0.56 (±0.21)	0.57 (±0.23)	0.95 (±0.24)	1.0 (±0.37)	1.68 (±1.13)	1.62 (±0.37)
	K_1	1.1 (±0.7)	1.1 (±0.9)	0.85 (±0.42)	0.87 (±0.68)	1.2 (±1.1)	0.74 (±0.3)
	$10^5 k_2$, sec^{-1}	0.51 (±0.14)	0.52 (±0.21)	1.1 (±0.5)	1.15 (±0.47)	1.4 (±0.37)	2.19 (±0.39)
		$\Delta H^* = 22.2\ (\pm 8.3)$ (TT), $31.5\ (\pm 9.3)$ (SP) kcal/mol $\Delta S^* = -16\ (\pm 24)$ (TT), $+11.7\ (\pm 27)$ (SP) eu					

[a] TT = titrimetric data; SP = spectrophotometric data; $\mu = 0.6\ M$.

Table VII. Rate and Activation Parameters for the Aquation of Some Carboxylatopentaamminecobalt(III) Complexes at 70°

		k_0 path			k_1 path			
Complex	Ionic strength, M	k_0, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	k_1, sec^{-1} M^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	Ref
$(NH_3)_5CoOCOCH_3{}^{2+}$	0.1	8.0×10^{-6}	25	−8	9.3×10^{-4}	25	+2	18
$(NH_3)_5CoOCOC(CH_3)_3{}^{2+}$	0.1	5.2×10^{-6}			2.5×10^{-4}	26	+6	18
$(NH_3)_5CoOCOCF_3{}^{2+}$	0.1	5.7×10^{-5}	26	−2	3.0×10^{-5}			18
$(NH_3)_5CoOCOCOOH^{2+}$	1.0	1.5×10^{-5}	28.4 (±1)	+1	2.8×10^{-5}	22.7 (±1)	−14	21
$(NH_3)_5CoOCOC_6H_4OH^{2+}$	0.6	4.6×10^{-6} [a]	39.0 (±3.4)[a]	+30 (±10)[a]	3.3×10^{-5} [a]	25.4 (±1.9)[a]	−5 (±5.6)[a]	This work
		5.5×10^{-6} [b]	38.3 (±4.0)[b]	+29 (±12)[b]	4.0×10^{-5} [b]	26.9 (±1.0)[b]	−0.6 (±3)[b]	This work

[a] Titrimetric data. [b] Spectrophotometric data.

Table VIII. Stabilities of $C_6H_4OM^+$, $(NH_3)_5CoOCOC_6H_4OM^{4+}$, and $C_6H_4(O)COOM^+$ Complexes for the Reaction $L^{n-} + M^{3+} \rightleftharpoons ML^{(3-n)+}$ ($K_{ML} = [ML^{(3-n)+}]/[M^{3+}][L^{n-}]$)

	K_{ML}, M^{-1}		
L^{n-}	M = Fe(III)	M = Al(III)	M = Ga(III)
$C_6H_5O^-$	5.9×10^7 [a]		
$(NH_3)_5CoOCOC_6H_4O^+$	7.4×10^{10} [b]	1.5×10^9 [b]	1.4×10^{10} [b]
$C_6H_4(O^-)COO^-$	6.6×10^{15} [c]	9.6×10^{13} [d]	5.0×10^{14} [d]

[a] $\mu = 0.1\ M$, 25°. Calculated from A. G. Desai and R. M. Milburn, *J. Amer. Chem. Soc.*, **91**, 1958 (1969). [b] $\mu = 0.6\ M$, 28°. Calculated from the values of K_1 given in Table III assuming $pK_{OH} = 10.0$[15b] for $(NH_3)_5CoOCOC_6H_4OH^{2+}$. [c] $\mu = 3.0\ M$, 25°. J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, *Chem. Soc., Spec. Publ.*, **No. 6** (1957). [d] $\mu = 0.05\ M$, 28°. Calculated from B. Das and S. Aditya, *J. Indian Chem. Soc.*, **36**, 581 (1959); R. C. Das, R. K. Nanda, and S. Aditya, *ibid.*, **40**, 163 (1963); assuming $pK_{OH} = 14.0$ for $C_6H_4(OH)COO^-$.

that Fe(III) is chelated by the salicylate moiety in $(NH_3)_5CoOCOC_6H_4OFe^{4+}$ species. Since the stability constants (K_{ML}) of the binuclear complexes of Al(III) and Ga(III) are comparable with that of Fe(III) and differ by a factor of 10^2 from that of $C_6H_5OFe^{2+}$ (which is expected to be stabler than $C_6H_5OAl^{2+}$ and $C_6H_5OGa^{2+}$), it is believed that Ga(III) and Al(III) ions are also chelated in their binuclear complexes, $(NH_3)_5CoOCOC_6H_4OM^{4+}$.

The rate constants (k_2) for the metal in catalyzed path of aquation of the salicylato complex are collected in Table VI. The values of k_2 calculated from the spectrophotometric data agree reasonably well with those computed from the titrimetric data. Based on the values of k_2, the catalytic activity of the metal ions is found to follow the sequence Fe(III) > Ga(III) > Al(III). Thus it is evident that the chemical reactivities of the binuclear complexes (*i.e.*, substitution of salicylate by water at the Co(III) center) parallel their thermodynamic stabilities as well as the thermodynamic stabilities of the corresponding monosalicylato complexes of the catalyst metal ions. Such a stability reactivity sequence for the k_2 path is analogous to the rate *vs.* pK (of carboxylic acids) correlation for the k_0 path of carboxylatopentaamminecobalt(III) complexes for which a Co–O bond fission mechanism has been invoked.[18-20] The order of variation of the stabilities of the monosalicylato complexes of Fe(III), Ga(III), and Al(III) indicates that their basicity toward a proton as well as the $(NH_3)_5Co^{3+}$ moiety decreases in the sequence $C_6H_4(O)COOFe^+ < C_6H_4(O)COOGa^+ < C_6H_4(O)COOAl^+$. The observed dependence of k_2 on the nature of the leaving group (*i.e.*, monosalicylato complexes of M^{3+} ions) is, therefore, consistent with an SN1 mechanism involving the rate-determining Co–O bond fission process for the k_2 path of aquation of the salicylato complex.

The metal ion promoted C–O bond cleavage mechanism for the k_2 path also appears to be less likely by considering the inverse stability–reactivity sequence observed by Hix and Jones[23] in the acid hydrolysis of mono(ethylglycinato) complexes of Co(II), Ni(II), Cu(II), and Zn(II).

Assuming a dissociative mechanism for the k_2 and k_0 paths and following Haim's[24] approach, the aquation for the uncatalyzed and the metal ion catalyzed paths can be delineated as Scheme I (where the activated states are designated by asterisks).

In Scheme I k_0 and k_2 are the rate constants as defined earlier and k_{ex} is the water-exchange rate constant of the

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(23) J. E. Hix, Jr., and M. M. Jones, *Inorg. Chem.*, **5**, 1863 (1966).
(24) A. Haim, *Inorg. Chem.*, **9**, 426 (1970).

Scheme I

k_0 path

$$\begin{tikzcd}
((NH_3)_5CoOCOC_6H_4OH^{2+})^* + H_2O \rightleftharpoons ((NH_3)_5CoOH_2{}^{3+})^* + C_6H_4(OH)COO^- \\
(NH_3)_5CoOCOC_6H_4OH^{2+} + H_2O \rightleftharpoons (NH_3)_5CoOH_2{}^{3+} + C_6H_4(OH)COO^- \arrow[u, "k_0\quad\quad\quad\quad k_{ex}"]
\end{tikzcd}$$

k_2 path

$$\begin{tikzcd}
((NH_3)_5CoOCOC_6H_4OM^{4+})^* + H_2O \rightleftharpoons ((NH_3)_5CoOH_2{}^{3+})^* + C_6H_4(O)COOM^+ \\
(NH_3)_5CoOCOC_6H_4OM^{4+} + H_2O \rightleftharpoons (NH_3)_5CoOH_2{}^{3+} + C_6H_4(O)COOM^+ \arrow[u, "k_2\quad\quad\quad\quad k_{ex}"]
\end{tikzcd}$$

$(NH_3)_5CoOH_2{}^{3+}$ ion. In terms of k_{ex} and the formal equilibrium quotients Q_1 and $Q_1{}^*$ as given in

$$Q_1 = \frac{[(NH_3)_5CoOH_2{}^{3+}][C_6H_4(O)COOM^+]}{[(NH_3)_5CoOCOC_6H_4OM^{4+}][H_2O]} \tag{19}$$

$$Q_1{}^* = \frac{[((NH_3)_5CoOH_2{}^{3+})^*][C_6H_4(O)COOM^+]}{[((NH_3)_5CoOCOC_6H_4OM^{4+})^*][H_2O]} \tag{20}$$

k_2 can be expressed as

$$k_2 = k_{ex}Q_1/Q_1{}^* \tag{21}$$

Equation 21 can easily be transformed to

$$k_2 = k_0K_1{}^*/K_1 \tag{22}$$

Since $Q_1/Q_1{}^*$ can be expressed as

$$Q_1/Q_1{}^* = (K_1{}^*/K_1)(k_0/k_{ex}) \tag{23}$$

the equilibrium quotients K_1 and $K_1{}^*$ in eq 22 and 23 are defined by the relationships

$$K_1 = \frac{[(NH_3)_5CoOCOC_6H_4OM^{4+}][H^+]}{[(NH_3)_5CoOCOC_6H_4OH^{2+}][M^{3+}]} \tag{24}$$

$$K_1{}^* = \frac{[((NH_3)_5CoOCOC_6H_4OM^{4+})^*][H^+]}{[((NH_3)_5CoOCOC_6H_4OH^{2+})^*][M^{3+}]} \tag{25}$$

It has been shown by earlier workers[25] that the logarithms of the stability constants of complexes of two similar ligands with a series of metal ions in their common valency state are linearly related. As such it is justifiable to express $K_1{}^*$ as

$$K_1{}^* = AK_1{}^\alpha \tag{26}$$

where A and α are constants. Substituting eq 26 into eq 22, the dependence of k_2 on K_1 can be expressed by

$$\log k_2 = \log k_0 + \log A + (\alpha - 1)\log K_1 \tag{27}$$

The plots of $\log k_2$ *vs.* $\log K_1$ yielded good, fair, and reasonable straight lines at 60, 65, and 70° in accordance with eq 27. The slopes and intercepts of such plots were found to be +0.5, −5.16; +0.5, −4.86; and +0.6, −4.54 at 60, 65, and 70°, respectively. The plot of $\log k_2$ *vs.* $\log K_1$ at 65° is shown in Figure 1. The validity of eq 27 stands in support of the dissociative mechanism for the metal ion catalyzed path of aquation of the salicylato complex. Since a Co-O bond rupture process appears to be involved in the k_0 and k_2 paths, catalysis of aquation of the salicylato complex by the metal ions (*i.e.*, $k_2 > k_0$) and the dependence of the extent of catalysis (*i.e.*, k_2(Fe(III)) > k_2(Ga(III)) > k_2(Al(III))) on the nature of the catalyzing metal ions are ascribed to $K_1{}^*/K_1$ ratios (eq 22).

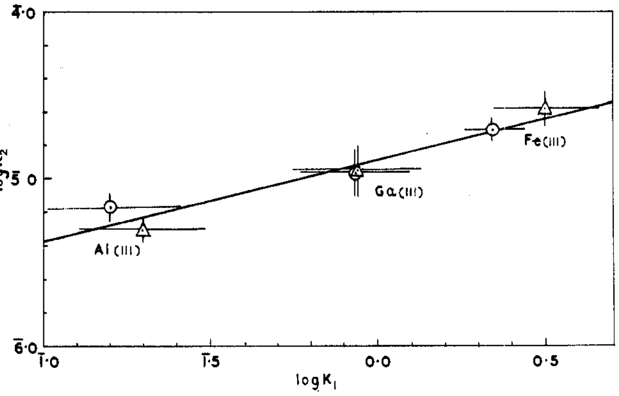

Figure 1. Log k_2 *vs.* log K_1 plot at 65°: ⊙, TT data; △, SP data.

The average values of k_2/k_0 turn out to be 10.3, 2.6, and 5.0 for Fe(III), Al(III), and Ga(III) ions at 65°, respectively, and are found to decrease with increasing temperature for all the three metal ions. This means that the activation enthalpy for the k_2 path is less than that for the k_0 path. This is in fact evident for the average values of ΔH^* for the k_2 and k_0 paths given in Tables VI and VII. However, the large uncertainties for the activation parameters (for k_0 and k_2 paths) do not permit a reliable estimate of the energetic roles of the metal ions concerned in the k_2 path of aquation of the salicylato complex.

Registry No. $[(NH_3)_5CoOCOC_6H_4OH](ClO_4)_2$, 40354-69-6; Fe, 7439-89-6; Ga, 7440-55-3; Al, 7429-90-5.

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[25] J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 52.