

in the Fe-Sb bond is quite similar to that in the Fe-Sn bond. What small differences there are in  $(\Delta E_Q)_{Fe}$  are consistent with the expected changes in  $\sigma$ -donor and  $\pi$ -acceptor properties between Sn and Sb. This result reinforces the conclusions drawn above from  $^{57}Fe$ ,  $^{119}Sn$ , and  $^{121}Sb$  isomer shift data, namely, that antimony and tin are nearly isoelectronic in these compounds. Thus in the ionic antimony derivatives most of the positive charge must reside on antimony rather than being delocalized onto the ligands. This agrees with a similar conclusion reached on the basis of crystal structure data.<sup>18</sup>

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**Registry No.** [Sb(Co(CO)<sub>2</sub>PPh<sub>3</sub>)<sub>4</sub>][PF<sub>6</sub>], 38415-54-2; [(CF<sub>3</sub>)<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][Cr(SCN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>], 49772-08-9; [Cl<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][Cr(SCN)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>], 37279-45-1; [Cl<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 50297-90-0; [Cl<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][SbCl<sub>4</sub>], 50437-44-0; [Br<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 50297-87-5; [(CF<sub>3</sub>)<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 49772-09-0; [ClSb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][FeCl<sub>4</sub>], 49772-10-3; [BrSb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 50297-88-6; [ISb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 50297-89-7; [ISb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][I<sub>3</sub>], 50297-93-3; [PhSb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 50297-94-4; [Ph<sub>2</sub>Sb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][PF<sub>6</sub>], 50297-92-2; [Ph<sub>2</sub>SbFe(CO)<sub>2</sub>Cp][PF<sub>6</sub>], 49772-11-4; [Bu<sub>3</sub>SbFe(CO)<sub>2</sub>Cp][PF<sub>6</sub>], 49772-12-5; NaFe(CO)<sub>2</sub>Cp, 12152-20-4; Ph<sub>2</sub>SbCl<sub>3</sub>, 21907-22-2; [C<sub>6</sub>H<sub>5</sub>NH]<sup>+</sup>[C<sub>6</sub>H<sub>5</sub>SbCl<sub>4</sub>]<sup>-</sup>, 5425-93-4; Bu<sub>3</sub>Sb, 2155-73-9; ClFe(CO)<sub>2</sub>Cp, 12107-04-9; [BrSb(Fe(CO)<sub>2</sub>Cp)<sub>2</sub>][FeBr<sub>4</sub>], 50322-06-0;  $^{121}Sb$ , 14265-72-6;  $^{57}Fe$ , 14762-69-7.

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## Metal Ion Catalyzed Acid Hydrolysis of Acidopentaamminecobalt(III) Complexes. Kinetics and Mechanism of Metal Ion Catalyzed Hydrolysis of Oxalatopentaamminecobalt(III) Complex

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The acid hydrolysis of oxalatopentaamminecobalt(III) complex has been studied in the presence and absence of Al(III), Ga(III), In(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal ions are found to catalyze the aquation of the complex. The rate of aquation of the oxalato complex is described by the rate laws

$$\frac{-d \ln C_t}{dt} = \frac{k_0 K_1 / [H^+] + k_1 + k_2 [H^+]}{1 + K_1 / [H^+]}$$

$$\frac{-d \ln C_t}{dt} = \frac{k_0 K_1 / [H^+] + k_1 + k_2 [H^+] + k_3 K_2 K_1 [M^{n+}] / [H^+]}{1 + K_1 / [H^+] + K_1 K_2 [M^{n+}] / [H^+]}$$

in the absence and presence of the catalyst metal ions, respectively. At 55° and  $\mu = 0.3 M$  (adjusted with NaClO<sub>4</sub>) the values of the parameters of the rate equations are  $k_0 = 0.78 \times 10^{-6} \text{ sec}^{-1}$ ,  $k_1 = 4.16 \times 10^{-6} \text{ sec}^{-1}$ ,  $k_2 = 7.5 \times 10^{-6} \text{ sec}^{-1} M^{-1}$ ,  $K_1 = 1.49 \times 10^{-2} M$ ; for Al(III),  $k_3 = 701 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 38.1 M^{-1}$ ; for Ga(III),  $k_3 = 568 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 516 M^{-1}$ ; for In(III),  $k_3 = 100 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 140 M^{-1}$ ; for Fe(III),  $k_3 = 1450 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 610 M^{-1}$ ; for Mn(II),  $k_3 = 4.6 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 10 M^{-1}$ ; for Co(II),  $k_3 = 14.6 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 25.2 M^{-1}$ ; for Ni(II),  $k_3 = 15.4 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 51.5 M^{-1}$ ; for Cu(II),  $k_3 = 83.8 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 148 M^{-1}$ ; for Zn(II),  $k_3 = 7.12 \times 10^{-6} \text{ sec}^{-1}$ ,  $K_2 = 38.9 M^{-1}$ . The formation of binuclear species  $(NH_3)_5CoCO_2RCO_2M^{(n+1)+}$  is invoked to account for the observed kinetic patterns of the oxalato complex in the presence of the metal ions. The catalytic activities of the metal ions follow the sequences Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) and In(III) < Al(III) < Ga(III) < Fe(III). Parallelism between the thermodynamic stabilities and the chemical reactivities of the binuclear complexes is noted. The activation parameters for  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  paths have been determined. Like the  $k_0$  and  $k_1$  paths, aquation *via*  $k_3$  path is believed to occur with Co-O bond fission.

Several carboxylatopentaamminecobalt(III) complexes of the type  $(NH_3)_5CoCO_2RCO_2H^{2+}$  have been reported in the literature.<sup>1,2</sup> The cation formed by deprotonation of the unbound carboxyl group of such complexes is capable of coordination, and if this cation ligates to a polyvalent metal ion through the free carboxyl group, the resulting coordination compound will have the novel feature of containing two positive charge centers, the pentaamminecobalt(III) moiety and the associated metal ion. The carboxylate ion bridged binuclear complexes of various metal ions will undergo ligand substitution at the cobalt(III) center at rates which are likely to be dictated by the charge, size, and various other properties

of the associated metal ions. It is also normally expected that the group R separating the positive charge centers will have some influence on the stabilities and the reactivities of the binuclear complexes.

The thermodynamic and kinetic aspects of the binuclear species  $(NH_3)_5CoCO_2RCO_2M^{(n+1)+}$  have not been investigated as yet. We have been interested in the study of the effects of nonreducing and substitution labile metal ions on the kinetics of aquation of some suitable cationic carboxylatopentaamminecobalt(III) complexes in order to (i) examine their complexing abilities toward metal ions, (ii) estimate the catalytic efficiencies of various metal ions in promoting aquation of such cobalt(III) substrates, (iii) find a correlation between the thermodynamic stabilities and the chemical reactivities of the binuclear complexes, and (iv) explore the mechanism of aquation of such carboxylatopentaamminecobalt-

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(III) complexes in the presence of the added metal ions.

We have shown in our earlier work<sup>3</sup> that Fe(III), Al(III), and Ga(III) ions catalyze the aquation of salicylatopentaamminecobalt(III) ion. The catalytically active species were found to be the binuclear complexes in which the associating metal ion is presumed to be chelated by the unbound phenate ion and the carboxylate group coordinated to the cobalt(III) center. In this paper we report the results of our investigation on the kinetics of aquation of oxalatopentaamminecobalt(III) in the presence of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Ga(III), In(III), and Fe(III). This work is a sequel to our earlier work and forms a part of our current research program. As a part of the present work, the acid hydrolysis of oxalatopentaamminecobalt(III) has also been studied in the absence of the catalyst metal ions.

### Experimental Section

$[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}](\text{ClO}_4)_2$  was prepared by the method of Saffir and Taube.<sup>4</sup> The purity of the sample was checked by analysis of cobalt and oxalate. Anal. Calcd for  $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}](\text{ClO}_4)_2$ : Co, 13.63;  $\text{C}_2\text{O}_4^{2-}$ , 20.37. Found: Co, 13.6;  $\text{C}_2\text{O}_4^{2-}$ , 20.3. The molar extinction coefficient of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  at 507 nm was found to be 73.8 as compared to 74.0 reported by Taube, *et al.*<sup>5</sup>

Stock solutions of Fe(III), Al(III), Ga(III), and In(III) perchlorates were prepared and the metal ion contents estimated as described earlier.<sup>3</sup> Stock solutions of Mn(II), Co(II), Ni(II), and Zn(II) perchlorates were prepared by digesting a slight excess of the metal(II) carbonates (BDH, LR) with standard perchloric acid. Copper(II) perchlorate was prepared by digesting copper(II) carbonate (BDH, LR) in a slight excess of standard perchloric acid. Mn(II) and Co(II) contents were estimated by exchanging a known volume of their perchlorate solutions with Dowex 50W-X8 resin in the acid form and then titrating the liberated acid against a standard alkali. Ni(II) and Zn(II) were estimated gravimetrically as nickel dimethylglyoximate and  $\text{Zn}(\text{NH}_4)_2\text{PO}_4$ , respectively. Cu(II) was estimated iodometrically.

The free acid contents of Fe(III), Al(III), Ga(III), In(III), and Cu(II) solutions were estimated as follows. Known volumes of the metal perchlorate solutions (0.03 M) were exchanged with Dowex 50W-X8 resin in acid form and the total acid liberated was titrated against a standard alkali to the phenolphthalein end point. The concentration of the acid in the metal perchlorate solution was computed from the titer value after allowing for the amount of acid liberated due to the exchange of the metal ions.

BDH reagent grade sodium perchlorate and Baker Analyzed sample of perchloric acid were used to adjust ionic strength and acidity of the reaction medium, respectively. All ion-exchange experiments were performed with Dowex 50W-X8 resin in acid form.

Optical density measurements were made with a Beckman DU2 spectrophotometer using 1-cm matched silica cells.

**Determination of  $pK$  of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ .** Requisite amounts of sodium perchlorate and perchloric acid were mixed in 50-ml volumetric flasks and thermostated at the desired temperature. After thermal equilibrium was reached, a 1-ml aliquot of a freshly prepared solution of  $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}](\text{ClO}_4)_2$  was transferred into the flasks and the volume was made up with distilled water equilibrated at the same temperature. Two silica cells of 1.0-cm path length, one containing the reaction mixture and the other filled with distilled water (both at the reaction temperature), were quickly transferred into the spectrophotometer cell block maintained at the desired temperature. The optical densities of the reaction mixtures were measured at the preset wavelengths (290, 300, and 310 nm) against solvent as the reference blank. The absorbancies of the reaction mixtures remained steady during the time of measurement.

**Kinetics.** Sodium perchlorate, perchloric acid, and metal perchlorate, in requisite amounts, were mixed in a 100- or 50-ml volumetric flask and thermostated at the desired temperature. After thermal equilibrium was reached, a known weight of the complex was transferred into the reaction flask. The complex dissolved on rapid shaking and the volume was made up with distilled water

previously equilibrated at the same temperature. Measured volumes of the reaction mixture were withdrawn at definite time intervals, quickly transferred to a beaker containing ice-cold sulfuric or perchloric acid, and shaken with cation-exchange resin in acid form. The cobalt complex and the trivalent metal ions were exchanged in ice-cold 0.5 M  $\text{H}_2\text{SO}_4$  medium. The media of exchange were 0.2 M  $\text{HClO}_4$  (Co(II), Ni(II), Cu(II)) and 0.1 M  $\text{H}_2\text{SO}_4$  (Zn(II), Mn(II)) when bivalent metal ions were used as catalysts. The colorless supernatant liquid (after the cobalt complex and the metal ions were exchanged into the resin phase) was filtered through a well-packed bed of glass wool. The resin was washed with 10-ml portions of cold distilled water. The oxalic acid content of the filtrate and washings combined together was then titrated against 0.02 N  $\text{KMnO}_4$  to the conventional pale pink end point.

In the study of the acid aquation of the oxalato complex (in absence of the catalyst metal ions), the reaction mixture withdrawn at definite time intervals was diluted with equal volumes of ice-cold distilled water and subjected to cation exchange. The exchanged solutions were then worked up for estimation of the liberated oxalic acid in the manner mentioned earlier.

**Effect of Light.** In the Fe(III)-catalyzed hydrolysis experiments, the reaction mixtures before and after cation exchange did not consume 0.02 N dichromate. This indicated that Fe(II) was not produced during the course of the reaction. As a check, a few runs (where Fe(III) was used as catalyst) were performed in flasks painted black. The rate constants obtained under this condition agreed, within experimental error, with those measured in subdued light. Photocatalysis was, therefore, inferred to be insignificant.

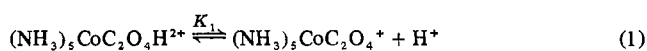
**Evaluation of Kinetic Data.** The aquation reaction of oxalatopentaamminecobalt(III) complex was studied under pseudo-first-order conditions with respect to the concentrations of hydrogen and metal ions. The observed pseudo-first-order rate constants ( $k_{\text{obsd}}$ ) were calculated from the relationship

$$\ln(V_\infty - V_t) = \ln V_\infty - k_{\text{obsd}}t$$

where  $V_t$  and  $V_\infty$  stand for the permanganate titer values at time  $t$  and for complete reaction, respectively. The theoretical permanganate titer value for complete reaction (calculated from the weight of the complex) after being corrected for the titration blank was taken to be  $V_\infty$ . A computer program was adopted to the IBM 1130 computer of Utkal University to calculate the pseudo-first-order rate constants from the least-squares slopes of  $\ln(V_\infty - V_t)$  vs. time plots.

### Results

**Acid Dissociation Constant of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ .** The ultraviolet spectrum of oxalatopentaamminecobalt(III) ion, in aqueous medium, is pH sensitive. Andrade and Taube<sup>5</sup> ascribed this behavior of the oxalato complex to its protonation equilibrium



For such a system, it can be easily shown that

$$\frac{a}{\Delta d} = \frac{1}{(E_1 - E_2)l} + \frac{K_1}{(E_1 - E_2)l} \frac{1}{[\text{H}^+]} \quad (2)$$

where  $a$  = [complex]<sub>total</sub>,  $E_1$  and  $E_2$  are the extinction coefficients of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$  and  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ , respectively,  $l$  is the cell path length, and  $\Delta d = E_1al$  - optical density due to the total complex concentration  $a$  at a definite hydrogen ion concentration.  $K_1$  was calculated from the least-squares slopes and intercepts of  $a/\Delta d$  vs.  $1/[\text{H}^+]$  plots. The acid dissociation constant of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  was measured at 25, 28, 35, and 45° in a medium of 0.3 M ionic strength. The effect of ionic strength on  $K_1$  was studied at 28°. The values of  $K_1$  determined in the present work and reported earlier have been collected in Table I.

**Acid Hydrolysis.** The acid hydrolysis of oxalatopentaamminecobalt(III) complex was studied in  $\text{HClO}_4$  solutions over the acidity range 0.002–0.3 M at an ionic strength of 0.3 M adjusted with  $\text{NaClO}_4$  wherever necessary. The pseudo-first-order rate constants for the aquation reaction

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

Table I. Effect of Temperature and Ionic Strength on the Acid Dissociation Constant of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ 

Ionic strength, $M$	$10^2 K_1, M$					
	25.0 ( $\pm 0.1$ ) <sup>o</sup>	28.0 ( $\pm 0.1$ ) <sup>o</sup>	35.0 ( $\pm 0.2$ ) <sup>o</sup>	45.0 ( $\pm 0.5$ ) <sup>o</sup>	66.1 ( $\pm 0.1$ ) <sup>o</sup>	70.0 <sup>o</sup>
0	0.63 ( $\pm 0.03$ ) <sup>a</sup>	2.1 <sup>b</sup>				
0.05		1.48 ( $\pm 0.12$ )				
0.10		1.36 ( $\pm 0.08$ )				
0.20		1.15 ( $\pm 0.04$ )				
0.30	0.94 ( $\pm 0.02$ )	1.03 ( $\pm 0.04$ )	1.11 ( $\pm 0.02$ )	1.27 ( $\pm 0.03$ )	1.86 ( $\pm 0.26$ ) <sup>c</sup>	
1.0	0.88 <sup>d</sup>			1.2 <sup>d</sup>		1.7 ( $\pm 0.3$ ) <sup>d</sup>

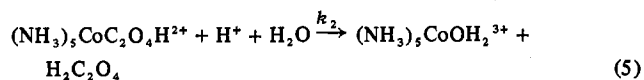
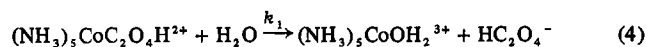
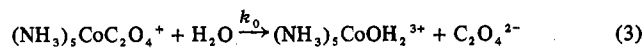
<sup>a</sup> S.-F. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, 5, 696 (1966). <sup>b</sup> Computed from the present work. <sup>c</sup> Kinetic data, this work. <sup>d</sup> See ref 5.

Table II. Rates of Aquation of the Oxalatopentaamminecobalt(III) Complex<sup>a</sup>

$10^2 [\text{H}^+], M$	$10^6 k, \text{sec}^{-1}$									
	50.0 $\pm$ 0.1 <sup>o</sup>		55.0 $\pm$ 0.1 <sup>o</sup>		60.0 $\pm$ 0.1 <sup>o</sup>		66.1 $\pm$ 0.1 <sup>o</sup>			
	Obsd <sup>b</sup>	Calcd <sup>c</sup>	Obsd <sup>b</sup>	Calcd <sup>c</sup>	Obsd <sup>b</sup>	Calcd <sup>c</sup>	Obsd <sup>b</sup>	Calcd <sup>c</sup>		
0.22							3.86 ( $\pm 0.07$ )	3.86		
1.2					3.85 ( $\pm 0.08$ )	3.85	7.20 ( $\pm 0.14$ )	7.17		
2.0			2.82 ( $\pm 0.05$ )	2.81	5.05 ( $\pm 0.10$ )	5.04	8.73 ( $\pm 0.23$ )	8.70		
5.0	1.79 ( $\pm 0.04$ )	1.79	3.62 ( $\pm 0.07$ )	3.68	6.60 ( $\pm 0.13$ )	6.63	11.4 ( $\pm 0.2$ )	11.6		
10.0	2.15 ( $\pm 0.04$ )	2.14	4.42 ( $\pm 0.09$ )	4.38	7.75 ( $\pm 0.15$ )	7.78	14.4 ( $\pm 0.3$ )	14.0		
15.0	2.36 ( $\pm 0.05$ )	2.39			8.71 ( $\pm 0.17$ )	8.53	15.7 ( $\pm 0.3$ )	15.7		
20.0	2.64 ( $\pm 0.05$ )	2.61	5.44 ( $\pm 0.11$ )	5.33	9.14 ( $\pm 0.18$ )	9.16	17.2 ( $\pm 0.3$ )	17.1		
25.0	2.85 ( $\pm 0.05$ )	2.82	5.72 ( $\pm 0.11$ )	5.75	9.65 ( $\pm 0.19$ )	9.73	18.3 ( $\pm 0.4$ )	18.5		
30.0	2.99 ( $\pm 0.06$ )	3.02	6.10 ( $\pm 0.12$ )	6.16	10.3 ( $\pm 0.2$ )	10.3	19.8 ( $\pm 0.4$ )	19.7		
	Rates		50.0 $\pm$ 0.1 <sup>o</sup>		55.0 $\pm$ 0.1 <sup>o</sup>		60.0 $\pm$ 0.1 <sup>o</sup>		66.1 $\pm$ 0.1 <sup>o</sup>	
	$10^9 k_0 K_1, \text{sec}^{-1} M$						4.98 ( $\pm 0.98$ )			
	$10^6 k_0, \text{sec}^{-1}$		0.23 ( $\pm 0.14$ )		0.78 ( $\pm 0.18$ )		1.26 ( $\pm 0.14$ )		2.67 ( $\pm 0.12$ )	
	$10^6 k_1, \text{sec}^{-1}$		2.04 ( $\pm 0.05$ )		4.16 ( $\pm 0.06$ )		7.86 ( $\pm 0.09$ )		13.8 ( $\pm 0.7$ )	
	$10^6 k_2, \text{sec}^{-1} M^{-1}$		3.7 ( $\pm 0.2$ )		7.5 ( $\pm 0.3$ )		9.7 ( $\pm 0.4$ )		23.2 ( $\pm 0.3$ )	
	$10^2 K_1, M$		1.40 <sup>d</sup>		1.49 <sup>d</sup>		1.59 <sup>d</sup>		1.86 ( $\pm 0.28$ )	

<sup>a</sup>  $\mu = 0.3 M$ , [complex] =  $(2-3) \times 10^{-3} M$ . <sup>b</sup> Average of four determinations at 60 and 66.1<sup>o</sup> and average of duplicate runs at 50 and 55<sup>o</sup>. The errors are the average deviations from the mean values. <sup>c</sup> Calculated from eq 6 using the best values of the rate and equilibrium parameters. <sup>d</sup> Values used for calculating the rate parameters.

are given in Table II. The following facts are borne out by an examination of the observed rate constants ( $k_{\text{obsd}}$ ) of aquation of the complex (Table II): (i)  $k_{\text{obsd}}$  does not exhibit a simple first-order dependence on hydrogen ion concentration and (ii) a  $k_{\text{obsd}}$  vs.  $[\text{H}^+]$  plot extrapolated to zero hydrogen ion concentration leads to a nonvanishing intercept. Consistent with our observation and as suggested by Andrade and Taube,<sup>5</sup> various paths of aquation of the oxalato complex, in the range of acidities studied, may be delineated as



On the basis of such a scheme, the observed rate law for the aquation of the complex, under the pseudo-first-order condition of constant hydrogen ion concentration, will have the form

$$-d \ln C_t / dt = k_{\text{obsd}} = \frac{k_0 K_1 / [\text{H}^+] + k_1 + k_2 [\text{H}^+]}{1 + K_1 / [\text{H}^+]} \quad (6)$$

where  $C_t$  is the concentration of the total oxalato complex at time  $t$ ;  $k_0$ ,  $k_1$ , and  $k_2$  are the specific rate constants for the aquation reactions shown in eq 3-5, respectively, and  $K_1$  is the acid dissociation constant of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ . The intercept and slope of the straight-line plot of  $k_{\text{obsd}}$  vs.  $[\text{H}^+]$  at  $[\text{H}^+] = 0.15-0.3 M$  were taken to be  $k_1$  and  $k_2$ , respective-

ly. Utilizing the rate data at  $[\text{H}^+] < 0.15 M$ ,  $k_0 K_1$  and  $K_1$  were computed from the straight-line plot of  $(k_{\text{obsd}} - k_1 - k_2 [\text{H}^+]) / [\text{H}^+]$  vs.  $k_{\text{obsd}}$ . The observed rate constants were then fitted to eq 6 with the help of a least-squares computer program which varied  $k_0 K_1$ ,  $k_1$ ,  $k_2$ , and  $K_1$  and minimized  $\Sigma[(k_{\text{calcd}} - k_{\text{obsd}}) / \sigma(k_{\text{obsd}})]^2$ , where the sum is over all data points and  $\sigma(k_{\text{obsd}})$  is the error of  $k_{\text{obsd}}$ . The values of the parameters calculated from the rate data at 66.1<sup>o</sup> have been given in Table II. When the pseudo-first-order rate constants at 50, 55, and 60<sup>o</sup> were fitted to eq 6 by varying all the four parameters ( $k_0 K_1$ ,  $k_1$ ,  $k_2$ , and  $K_1$ ), reliable values of  $k_0 K_1$  and  $K_1$  were not obtained. As such  $K_1$  was fixed and the observed rate constants at these temperatures were fitted to eq 6 by varying  $k_0$ ,  $k_1$ , and  $k_2$ . The values of  $K_1$  chosen for calculating the rate parameters (at 50, 55, and 60<sup>o</sup>) were obtained from a  $\log K_1$  vs.  $1/T$  plot by combining the values of  $K_1$  at 25, 28, 35, 45, and 66.1<sup>o</sup>. The rate parameters  $k_0$ ,  $k_1$ , and  $k_2$  have been summarized in Table II.

**Metal Ion Catalysis.** The metal ion catalysis of the aquation reaction of oxalatopentaamminecobalt(III) complex has been examined with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Ga(III), In(III), and Fe(III). The observed pseudo-first-order rate constants for a few kinetic runs have been collected in Table III.<sup>6</sup> It is evident that  $k_{\text{obsd}}$  increases with increasing concentration of the metal ions at a constant hydrogen ion concentration and decreases with increasing acidity of the reaction medium at a fixed metal ion concentration. The observed rate constants in the presence of the metal ions at a given acidity are significantly higher (except in the case of Mn(II)) than the corresponding rate constants for the acid

(6) See paragraph at end of paper regarding supplementary material.

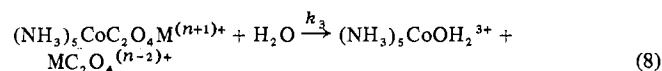
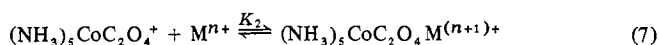
Table III. Rates of Metal Ion Catalyzed Aquation of Oxalatopentaamminecobalt(III) Complex

$10^2[M], M$	$10^2[\text{HClO}_4], M$	$10^3[\text{R-C}_2\text{O}_4\text{-H}], M$	$10^6 k, \text{sec}^{-1}$	
			Obsd <sup>b</sup>	Calcd <sup>c</sup>
$45.0 \pm 0.1^\circ$				
M = Fe(III)				
1.00	10.0	2.5	155 ( $\pm 6$ )	165
1.50	10.0	2.5	224 ( $\pm 17$ )	204
2.00	10.0	2.5	251 ( $\pm 16$ )	231
1.00	5.0	2.2	194 ( $\pm 12$ )	219
1.00	15.0	2.6	130 ( $\pm 3$ )	133
$55.0 \pm 0.1^\circ$				
M = Al(III)				
1.52	2.50	3.0	118 ( $\pm 3$ )	120
1.52	5.00	3.0	82.3 ( $\pm 0.3$ )	82.4
1.52	10.0	3.4	52.7 ( $\pm 1.8$ )	51.8
2.09	5.00	3.6	103 ( $\pm 7$ )	107
2.61	5.00	3.4	135 ( $\pm 4$ )	128
M = Ga(III)				
0.76	10.0	2.8	181 ( $\pm 5$ )	192
1.53	10.0	2.3	273 ( $\pm 17$ )	287
2.29	10.0	2.5	350 ( $\pm 7$ )	343
0.76	25.0	2.6	110 ( $\pm 5$ )	107
M = In(III)				
0.50	10.0	2.3	13.0 ( $\pm 1.0$ )	12.2
1.52	10.0	2.3	22.8 ( $\pm 0.5$ )	24.7
1.00	5.00	2.5	26.9 ( $\pm 0.6$ )	26.4
2.00	5.00	2.3	40.6 ( $\pm 0.8$ )	40.6
M = Mn(II)				
4.00	2.00	2.1	2.88 ( $\pm 0.06$ )	
6.00	2.00	2.1	3.12 ( $\pm 0.06$ )	
8.00	2.00	2.1	3.32 ( $\pm 0.07$ )	
M = Co(II)				
4.00	2.00	2.1	6.20 ( $\pm 0.12$ )	6.23
6.00	2.00	3.2	7.35 ( $\pm 0.16$ )	7.26
8.00	2.00	2.9	8.04 ( $\pm 0.15$ )	8.08
M = Ni(II)				
2.00	2.00	2.5	6.50 ( $\pm 0.18$ )	6.48
4.00	2.00	2.5	8.43 ( $\pm 0.20$ )	8.46
8.00	2.00	2.6	10.6 ( $\pm 0.2$ )	10.6
M = Cu(II)				
2.00	10.0	2.5	25.8 ( $\pm 0.6$ )	26.1
4.00	10.0	2.6	38.4 ( $\pm 0.7$ )	38.4
5.00	10.0	2.5	42.2 ( $\pm 1.3$ )	42.9
6.00	10.0	2.5	46.3 ( $\pm 0.7$ )	46.5
M = Zn(II)				
3.00	2.00	3.0	4.26 ( $\pm 0.10$ )	4.23
6.00	2.00	3.0	4.85 ( $\pm 0.12$ )	4.92
9.00	2.00	3.0	5.38 ( $\pm 0.11$ )	5.38

<sup>a</sup> Total concentration of the complex; R =  $(\text{NH}_3)_5\text{Co}^{3+}$ . <sup>b</sup> Observed pseudo-first-order rate constants ( $\mu = 0.3 M$ ). The errors are the least-squares standard deviations of the slopes of  $\ln(V_\infty - V_t)$  vs. time plots. <sup>c</sup> Calculated from eq 9 using the best values of the rate and the equilibrium parameters collected in Tables II and V.

hydrolysis of the oxalato complex alone. These observations are in keeping with the following facts: (i) the cobalt complex associates with the metal ions prior to its hydrolysis and (ii) the binuclear complexes so formed undergo water substitution at the cobalt(III) center at rates characteristic of the catalyst metal ions.

Incorporating the association equilibrium and the path of aquation of the binuclear complexes



in the general scheme of aquation of the oxalato complex, it can easily be shown that the observed rate constant ( $k_{\text{obsd}}$ ), under pseudo-first-order conditions of constant metal ion and hydrogen ion concentrations, will have the form

$$k_{\text{obsd}} = \frac{k_0 K_1 / [\text{H}^+] + k_1 + k_2 [\text{H}^+] + k_3 K_2 K_1 [\text{M}^{n+}] / [\text{H}^+]}{1 + K_1 / [\text{H}^+] + K_1 K_2 [\text{M}^{n+}] / [\text{H}^+]} \quad (9)$$

$k_3$  and  $K_2$  in eq 9 stand for the rate constant of aquation and equilibrium constant of formation of the binuclear species, respectively. The values of  $k_0$ ,  $k_1$ ,  $k_2$ , and  $K_1$  at any temperature in the interval  $35-66.1^\circ$  were obtained by the method of extrapolation ( $\log k_i$  vs.  $1/T$  plot). Equation 9 was treated as a two-parameter equation (the parameters are  $k_3 K_2$  and  $K_2$ ). The approximate values of  $k_3 K_2$  and  $K_2$  were computed from the straight-line plots of  $1/(k_{\text{obsd}} - k_{\text{obsd}}')$  vs.  $1/[\text{M}^{n+}]$  at constant hydrogen ion concentration where  $k_{\text{obsd}}' = k_{\text{obsd}}$  at  $[\text{M}^{n+}] = 0$ . The values of the parameters were then refined by the weighted least-squares procedure mentioned earlier. The calculations of  $k_3 K_2$  and  $K_2$  are based on  $[\text{M}^{n+}] = [\text{M}^{n+}]_{\text{total}}$  and  $[\text{H}^+] = [\text{HClO}_4] + [\text{complex}]_{\text{total}}$  (since the complex was added in the form of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ ). It may be mentioned that at 55 and  $60^\circ$ , the observed rate constant ( $k_{\text{obsd}}$ ) at the highest concentration of  $\text{Mn}^{2+}$  (0.08 M) was only 15% higher than the acid hydrolysis rate constant for the oxalato complex in the absence of  $\text{Mn}^{2+}$  (Tables II and III). The values of  $K_2$  for this system were estimated to be  $15.3 (\pm 1.4)$  at  $28^\circ$  and  $18.6 (\pm 11.9)$  at  $66.1^\circ$  (Tables V and VI). Utilizing an assumed value of  $K_2 = 10$  at 55 and  $60^\circ$ ,  $k_3$  for  $\text{Mn}^{2+}$  was calculated from eq 9. The values of the rate and equilibrium parameters for the binuclear complexes have been collected in Table V.

**Error Limits of the Parameters of Eq 6 and 9.** The error limit of  $x_i$ , i.e., the  $i$ th parameter of eq 6 or 9, is defined as  $\sigma(x_i) = \pm A_{ii}^{-1/2}$  where  $A_{ii}$  is the  $i$ th diagonal element of matrix  $A$  which is the inverse of the matrix  $H$ . The  $i$ th diagonal element of the matrix  $H$  is  $(1/2)d^2F/dx_i^2$ , where  $F$  stands for the sum of the weighted residuals minimized in the least-squares refinement and  $d^2F/dx_i^2$  is its second derivative with respect to  $x_i$ . The error quoted for  $k_3$  (Table V) is based on the error of  $k_3 K_2$  ( $\sigma(k_3) = \sigma(k_3 K_2) / K_2$ ). The errors quoted for  $k_0$  at 50 and  $66.1^\circ$  (Table II) have been calculated after fixing  $k_1$ ,  $k_2$ , and  $K_1$  at their best values.

**Activation Parameters.** The activation parameters for  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  paths were calculated from the transition-state equation

$$k = (RT/Nh) \exp(-\Delta H^\ddagger / RT + \Delta S^\ddagger / R) \quad (10)$$

The rate constants  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  were fitted to eq 10 by means of a nonlinear least-squares program which varied  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  and minimized the sum of the weighted residuals as mentioned earlier. Approximate values of the activation parameters used in this calculation were obtained from  $\log(k/T)$  vs.  $1/T$  plots. The error limits of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated by the method adopted for calculating the errors of the rate parameters ( $k_0$ ,  $k_1$ , etc.). The activation parameters for  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  paths are presented in Tables IV and V.

## Discussion

The data for the acid dissociation constant of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  at various temperatures and ionic strengths have been summarized in Table I. From the values of  $K_1$  at  $28^\circ$  and  $\mu = 0.05-0.3 M$ , it is evident that  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  ion

Table IV. Rates and Activation Parameters for the Acid Hydrolysis of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$ <sup>a</sup>

Rate data		Value	$\Delta F^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , eu
Constant					
$10^6 k_0$ , sec <sup>-1</sup>		0.78 ( $\pm 0.18$ ) [0.91]	28.4 ( $\pm 0.3$ ) [28.3]	27.3 ( $\pm 3.0$ ) [26.2 $\pm 1$ ]	-3.8 ( $\pm 8.9$ ) [-5]
$10^6 k_1$ , sec <sup>-1</sup>		4.16 ( $\pm 0.06$ ) [2.2]	27.3 ( $\pm 0.0$ ) [27.7]	27.0 ( $\pm 0.7$ ) [28.4 $\pm 1$ ]	-1.0 ( $\pm 2.2$ ) [+1]
$10^6 k_2$ , sec <sup>-1</sup> M <sup>-1</sup>		7.5 ( $\pm 0.3$ ) [6.3]	27.0 ( $\pm 0.1$ ) [27.1]	18.9 ( $\pm 1.5$ ) [22.7 $\pm 1$ ]	-24.6 ( $\pm 4.6$ ) [-14]

<sup>a</sup>  $\mu = 0.3$  M, 55°. Values given in brackets refer to  $\mu = 1.0$  M (see ref 5).

Table V. Rate and Equilibrium Constants and the Activation Parameters for the Metal Ion Catalyzed Path

$r_c$ , Å	Metal	Temp., °C	$10^4 k_3 K_2$ , <sup>a</sup> sec <sup>-1</sup> M <sup>-1</sup>	$K_2$ , <sup>a</sup> M <sup>-1</sup>	$10^6 k_3$ , sec <sup>-1</sup>	$\Delta F^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , eu
0.91	Mn(II)	55.0	0.46 ( $\pm 0.03$ )	10 <sup>b</sup>	4.6 ( $\pm 0.3$ )	27.3		
		60.0	0.70 ( $\pm 0.08$ )	10 <sup>b</sup>	7.0 ( $\pm 0.8$ )			
		66.1	2.7 ( $\pm 1.3$ )	18.6 ( $\pm 11.9$ )	14.6 ( $\pm 7.2$ )			
0.82	Co(II)	55.0	3.67 ( $\pm 0.54$ )	25.2 ( $\pm 7.3$ )	14.6 ( $\pm 2.1$ )	26.7	30.4 ( $\pm 4.3$ )	11.8 ( $\pm 12.8$ )
		60.0	5.73 ( $\pm 0.99$ )	24.7 ( $\pm 8.3$ )	23.2 ( $\pm 4.6$ )			
		66.1	6.06 ( $\pm 0.85$ )	8.9 ( $\pm 4.0$ )	68.1 ( $\pm 9.5$ )			
0.78	Ni(II)	55.0	7.85 ( $\pm 0.77$ )	51.5 ( $\pm 8.1$ )	15.4 ( $\pm 1.5$ )	26.5	29.6 ( $\pm 2.6$ )	9.3 ( $\pm 7.9$ )
		60.0	8.45 ( $\pm 1.05$ )	35.6 ( $\pm 7.6$ )	23.7 ( $\pm 2.9$ )			
		66.1	11.0 ( $\pm 0.9$ )	16.4 ( $\pm 3.4$ )	67.1 ( $\pm 5.5$ )			
0.72	Cu(II)	55.0	124 ( $\pm 4$ )	148 ( $\pm 11$ )	83.8 ( $\pm 2.7$ )	25.4	22.3 ( $\pm 1.1$ )	-9.3 ( $\pm 3.3$ )
		60.0	234 ( $\pm 14$ )	163 ( $\pm 21$ )	144 ( $\pm 8$ )			
		66.1	366 ( $\pm 16$ )	139 ( $\pm 16$ )	263 ( $\pm 11$ )			
0.83	Zn(II)	55.0	2.77 ( $\pm 0.65$ )	38.9 ( $\pm 13.0$ )	7.12 ( $\pm 1.71$ )	27.0	27.9 ( $\pm 5.1$ )	2.9 ( $\pm 15.0$ )
		60.0	4.32 ( $\pm 0.97$ )	31.4 ( $\pm 10.6$ )	13.8 ( $\pm 3.1$ )			
		66.1	7.16 ( $\pm 1.08$ )	23.9 ( $\pm 6.3$ )	30.0 ( $\pm 4.5$ )			
0.57	Al(III)	35.0	18.3 ( $\pm 0.4$ )	39.8 ( $\pm 4.4$ )	46.0 ( $\pm 1.0$ )	24.0	26.7 ( $\pm 3.7$ )	8.3 ( $\pm 11.7$ )
		45.0	81.9 ( $\pm 1.6$ )	43.8 ( $\pm 4.2$ )	187 ( $\pm 4$ )			
		55.0	267 ( $\pm 8$ )	38.1 ( $\pm 10.0$ )	701 ( $\pm 22$ )			
0.62	Ga(III)	35.0	246 ( $\pm 28$ )	584 ( $\pm 91$ )	42.1 ( $\pm 4.7$ )	24.1	24.4 ( $\pm 0.9$ )	0.9 ( $\pm 2.9$ )
		45.0	879 ( $\pm 74$ )	401 ( $\pm 55$ )	219 ( $\pm 18$ )			
		55.0	2930 ( $\pm 100$ )	516 ( $\pm 32$ )	568 ( $\pm 19$ )			
0.81	In(III)	35.0	23.7 ( $\pm 1.9$ )	340 ( $\pm 38$ )	6.97 ( $\pm 0.56$ )	25.3	24.9 ( $\pm 0.6$ )	-0.9 ( $\pm 1.9$ )
		45.0	50.0 ( $\pm 1.1$ )	151 ( $\pm 10$ )	33.1 ( $\pm 0.7$ )			
		55.0	140 ( $\pm 5$ )	140 ( $\pm 19$ )	100 ( $\pm 4$ )			
0.67	Fe(III)	35.0	591 ( $\pm 13$ )	694 ( $\pm 30$ )	85.2 ( $\pm 1.9$ )	23.5	28.5 ( $\pm 0.7$ )	15.1 ( $\pm 2.4$ )
		40.0	1080 ( $\pm 30$ )	625 ( $\pm 32$ )	173 ( $\pm 5$ )			
		45.0	2550 ( $\pm 80$ )	664 ( $\pm 48$ )	384 ( $\pm 12$ )			
		55.0		610 <sup>c</sup>	1450 ( $\pm 50$ ) <sup>c</sup>			

<sup>a</sup> The values of  $k_0$ ,  $k_1$ ,  $k_2$ , and  $K_1$  used for calculation of  $k_3 K_2$  and  $K_2$ :  $10^7 k_0$ , sec<sup>-1</sup> = 0.40 (35°), 1.20 (40°), 1.71 (45°), 7.8 (55°), 12.6 (60°), 26.8 (66.1°);  $10^7 k_1$ , sec<sup>-1</sup> = 2.6 (35°), 7.0 (40°), 10.8 (45°), 41.0 (55°), 78.0 (60°), 140 (66.1°);  $10^7 k_2$ , sec<sup>-1</sup> M<sup>-1</sup> = 9.5 (35°), 16.7 (40°), 26.5 (45°), 75.0 (55°), 97.0 (60°), 232 (66.1°);  $10^2 K_1$ , M = 1.14 (35°), 1.21 (40°), 1.30 (45°), 1.49 (55°), 1.59 (60°), 1.72 (66.1°). <sup>b</sup> Assumed. <sup>c</sup> Extrapolated value.

behaves as a stronger acid as the ionic strength of the reaction medium decreases. The value of  $K_1$  at zero ionic strength obtained from our results is, however, at variance with the same reported by Harris, *et al.* (Table I), from conductance measurements. The temperature coefficient of  $K_1$  is small and positive. Considering the effects of temperature and ionic strength, the values of  $K_1$  obtained in the present work agree reasonably well with those reported by Andrade and Taube.<sup>5</sup>

The rate and activation parameters for  $k_0$ ,  $k_1$ , and  $k_2$  paths obtained in the present work compare well with those reported by Taube, *et al.*<sup>5</sup> (Table IV). The activation parameters for the  $k_0$  path compare well with the same for the  $k_1$  path. A common rate limiting step appears to be involved in both the paths. Oxygen-exchange experiments<sup>7</sup> have indicated that Co-O bond fission occurs in the  $k_0$  and  $k_1$  paths and C-O bond breaking occurs in the  $k_2$  path. Linear free energy correlations<sup>8</sup> have substantiated the proposed dissociative mechanism for the spontaneous aquation of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$  and  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$ .

**Metal Ion Catalysis.** The rate and equilibrium constants characterizing the chemical reactivities and the thermodynamic stabilities of the binuclear complexes have been collected in Table V. The binuclear complexes  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{M}^{(n+1)+}$  of the concerned metal ions have also been detected by ultraviolet spectrophotometry and characterized by independent equilibrium studies at 28° (Table VI).

The stability constants of  $\text{C}_2\text{O}_4\text{M}^{(n-2)+}$ ,  $\text{C}_2\text{H}_5\text{C}_2\text{O}_4\text{M}^{(n-1)+}$ , and  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{M}^{(n+1)+}$  species of the concerned metal ions have been collected in Table VI. It is evident that the stability constants of the monooxalato complexes of M(II) ions are at least  $10^3$  times larger than the same for their binuclear complexes. The monooxalato complexes of Al(III) and Fe(III) are  $10^6$  times thermodynamically more stable relative to their binuclear complexes. Mono(ethyl oxalato) complexes of Co(II), Ni(II), Cu(II), and Zn(II) are, however, less stable compared to their binuclear complexes. These results indicate that the coordinating ability of the ligands varies in the sequence  $\text{C}_2\text{O}_4^{2-} \gg (\text{NH}_3)_5\text{CoC}_2\text{O}_4^+ > \text{C}_2\text{H}_5\text{C}_2\text{O}_4^-$ . Presumably  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$  ion does not act as a monodentate ligand toward the metal ions under investigation.

The metal ions used in the present study are found to be efficient catalysts in promoting aquation of the oxalato complex. It is, however, worth noting that the rate constants

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

(8) A. Haim, *Inorg. Chem.*, **9**, 426 (1970).

Table VI. Stability Constants of Oxalato Complexes

$M^{n+} + A^{m-} \xrightleftharpoons{K_{MA}} MA^{(n-m)+}$	
log $K_{MA}$	
$A^{m-}$	Mn <sup>2+</sup> Co <sup>2+</sup> Ni <sup>2+</sup> Cu <sup>2+</sup> Zn <sup>2+</sup> Al <sup>3+</sup> Fe <sup>3+</sup> Ga <sup>3+</sup> In <sup>3+</sup>
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	3.97 <sup>a</sup> 4.79 <sup>a</sup> 5.16 <sup>a</sup> 6.2 <sup>a</sup> 4.89 <sup>b</sup> 7 <sup>c</sup> 9.4, <sup>c</sup> 7.6 <sup>d</sup>
C <sub>2</sub> H <sub>5</sub> C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	1.0 <sup>e</sup> 1.1 <sup>e</sup> 1.9 <sup>e</sup> 1.1 <sup>e</sup>
(NH <sub>3</sub> ) <sub>5</sub> CoC <sub>2</sub> O <sub>4</sub> <sup>+</sup>	1.2 <sup>f</sup> 1.7 <sup>f</sup> 2.1 <sup>f</sup> 2.7 <sup>f</sup> 1.8 <sup>f</sup> 1.7 <sup>f</sup> 3.2 <sup>f</sup> 2.7 <sup>f</sup> 2.4 <sup>f</sup>

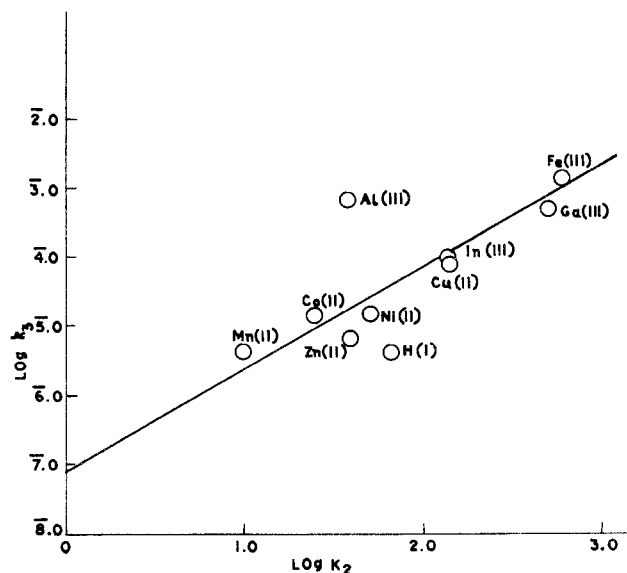
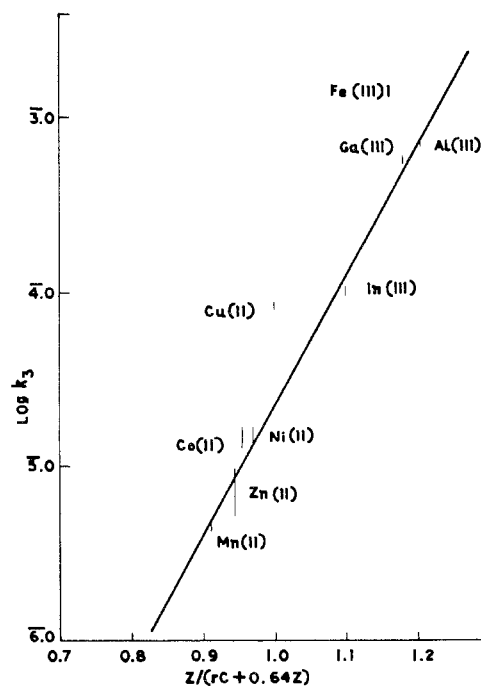
<sup>a</sup>  $\mu = 0$ , 25°. A. McAuley, G. H. Nancollas, and K. Torrance, *J. Inorg. Nucl. Chem.*, 28, 917 (1966). <sup>b</sup>  $\mu = 0$ , 25°. C. E. Evans and C. B. Monk, *Trans. Faraday Soc.*, 66, 1491 (1970). <sup>c</sup>  $\mu = 0$ . J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, *Chem. Soc., Spec. Publ.*, No. 6 (1957). Estimated value for Al<sup>3+</sup> (log  $\beta_3 = 13$ ). <sup>d</sup>  $\mu = 1 M$ , 25°. E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 5, 1866 (1966). <sup>e</sup>  $\mu_{\text{Co}^{2+}} = 0.3 M$ . G. L. Johnson and R. J. Angelici, *J. Amer. Chem. Soc.*, 93, 1106 (1971). <sup>f</sup>  $\mu = 0.3 M$ , 28°. A. C. Dash and R. K. Nanda, *J. Inorg. Nucl. Chem.*, in press.

of aquation of the species (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub><sup>+</sup> ( $k_0$ ), (NH<sub>3</sub>)<sub>5</sub>-CoC<sub>2</sub>O<sub>4</sub>H<sup>2+</sup> ( $k_1$ ), (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub>M<sup>3+</sup> ( $k_{3(M^{3+})}$ ), and (NH<sub>3</sub>)<sub>5</sub>-CoC<sub>2</sub>O<sub>4</sub>M<sup>4+</sup> ( $k_{3(M^{4+})}$ ) for which the leaving groups are C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub>H<sup>-</sup>, C<sub>2</sub>O<sub>4</sub>M, and C<sub>2</sub>O<sub>4</sub>M<sup>+</sup>, respectively, vary in the order  $k_0 < k_1 < k_{3(M^{2+})} < k_{3(M^{3+})}$ . From the electrostatic consideration, the leaving groups may be arranged in the order of decreasing basicity as C<sub>2</sub>O<sub>4</sub>M<sup>+</sup> < C<sub>2</sub>O<sub>4</sub>M < C<sub>2</sub>O<sub>4</sub>H<sup>-</sup> < C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. Thus it is apparent that the rate of aquation of (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub><sup>+</sup>, (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub>H<sup>2+</sup>, (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub>M<sup>3+</sup>, and (NH<sub>3</sub>)<sub>5</sub>-CoC<sub>2</sub>O<sub>4</sub>M<sup>4+</sup> increases in the order in which the basicity of the leaving group decreases.

Furthermore the reactivities of the binuclear complexes of M(II) ions follow the familiar Irving-Williams order (Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)) which holds good for the thermodynamic stabilities of several complexes of these metal ions including their mono-oxalato and binuclear complexes (Table VI). The reactivities of the binuclear complexes of M(III) ions follow the sequence In(III) < Al(III) < Ga(III) < Fe(III). The above sequence (*i.e.*, In(III) < Al(III) < Ga(III) < Fe(III)) also holds good for the thermodynamic stabilities of the inner-sphere chelates of M(III) ions.

$k_3$  and  $K_2$  for various metal ions and the corresponding data for H<sup>+</sup> ion (*i.e.*,  $k_1$  and  $1/K_1$ ) were fitted to the relationship  $\log k_3 = B + \beta \log K_2$ . We obtained  $B = -7.08 (\pm 0.12)$  and  $\beta = 1.46 (\pm 0.05)$  at 55° and  $\mu = 0.3 M$ . The least-squares best-line plot of  $\log k_3$  vs.  $\log K_2$  is shown in Figure 1. Thus it is evident that the thermodynamic stabilities of the binuclear complexes parallel their chemical reactivities.

The observed dependence of  $\log k_3$  on  $\log K_2$  is indicative of the fact that common factors determine the stabilities and reactivities of the binuclear complexes. From the electrostatic considerations,<sup>9</sup> it is reasonable to expect that  $\log K_2$  will be a linear function of  $Z/(r_c + d)$ , where  $Z$  and  $r_c$  stand for the charge and ionic radius of M<sup>n+</sup> ions, respectively, and  $(r_c + d)$  is the distance of closest approach of the charge centers of (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub>M<sup>(n+1)+</sup> species. The value of  $d$  is likely to be dependent upon the electrostatic repulsion between the like-charge centers of the binuclear complexes as well as the solvation effect. Treating  $d$  as an adjustable parameter, it is possible to express the observed dependence of  $\log k_3$  on  $\log K_2$  as  $\log k_3 = A + CZ/(r_c + \alpha Z)$ , where  $\alpha$ ,  $C$ , and  $A$  are constants and all other terms have their usual meaning as mentioned earlier. The rate data ( $k_3$ ) at 55° yielded  $\alpha = 0.64$ ,  $C = 7.5$ , and  $A = -12.1$ . Thus the adjusted ionic potential ( $Z/(r_c + \alpha Z)$ ) of the metal ions appears to be

Figure 1.  $\log k_3$  vs.  $\log K_2$  plot, 55°.Figure 2.  $\log k_3$  vs.  $Z/(r_c + 0.64Z)$  plot, 55°.

a suitable parameter which governs the stabilities and the reactivities of the binuclear complexes.

**Mechanism.** Duality of mechanism (*i.e.*, rate-determining Co-O or C-O bond fission) is anticipated in the  $k_3$  path of aquation of the oxalato complex. Metal ions in their binuclear complexes will polarize the acyl carbon of the carboxyl group bound to (NH<sub>3</sub>)<sub>5</sub>Co<sup>3+</sup> and make it susceptible to nucleophilic attack by water. This might result in the formation of the tetrahedral intermediate I postulated in the proton-catalyzed path of aquation of (NH<sub>3</sub>)<sub>5</sub>CoC<sub>2</sub>O<sub>4</sub>H<sup>2+</sup>. The tetrahedral intermediate, in turn, would undergo acyl cleavage with proton reorganization to yield (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> and C<sub>2</sub>O<sub>4</sub>M<sup>(n-2)+</sup>. These steps are shown in Scheme I. On making a steady-state approximation for the intermediate I and assuming  $k_r \gg k_3'$ , it can be shown that  $k_3 = (k_f/k_r)k_3'$  where  $k_f$ ,  $k_r$ , and  $k_3'$  are the specific rate constants for the hydration of the binuclear complex, dehydration of the tetrahedral intermediate, and decomposition of the latter to the

(9) E. A. Moelwyn-Hughes, "Chemical Statics and Kinetics of Solutions," Academic Press, London, 1971, p 62.

