Metal ion catalyzed acid hydrolysis of acidopentaammine cobalt(III) complexes. Kinetics and mechanism of metal ion catalyzed hydrolysis of oxalato pentaamminecobalt(III) complex

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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 σ-donor and π-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.[18]

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$_4$) the values of the parameters of the rate equations are $k_0 = 0.78 \times 10^{-6}\ sec^{-1}$, $k_1 = 4.16 \times 10^{-6}\ sec^{-1}$, $k_2 = 7.5 \times 10^{-6}\ sec^{-1}$ M^{-1}, $K_1 = 1.49 \times 10^{-2}\ M$; for Al(III), $k_3 = 701 \times 10^{-6}\ sec^{-1}$, $K_2 = 38.1\ M^{-1}$; for Ga(III), $k_3 = 568 \times 10^{-6}\ sec^{-1}$, $K_2 = 516\ M^{-1}$; for In(III), $k_3 = 100 \times 10^{-6}\ sec^{-1}$, $K_2 = 140\ M^{-1}$; for Fe(III), $k_3 = 1450 \times 10^{-6}\ sec^{-1}$, $K_2 = 610\ M^{-1}$; for Mn(II), $k_3 = 4.6 \times 10^{-6}\ sec^{-1}$, $K_2 = 10\ M^{-1}$; for Co(II), $k_3 = 14.6 \times 10^{-6}\ sec^{-1}$, $K_2 = 25.2\ M^{-1}$; for Ni(II), $k_3 = 15.4 \times 10^{-6}\ sec^{-1}$, $K_2 = 51.5\ M^{-1}$; for Cu(II), $k_3 = 83.8 \times 10^{-6}\ sec^{-1}$, $K_2 = 148\ M^{-1}$; for Zn(II), $k_3 = 7.12 \times 10^{-6}\ sec^{-1}$, $K_2 = 38.9\ M^{-1}$. The formation of binuclear species $(NH_3)_5CoC_2O_4M^{(n+1)+}$ 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.[1,2] 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-

(1) H. Taube and D. K. Sebera, *J. Amer. Chem. Soc.*, **83**, 1785 (1961).
(2) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965).

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

We have shown in our earlier work[3] 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

$[(NH_3)_5CoC_2O_4H](ClO_4)_2$ was prepared by the method of Saffir and Taube.[4] The purity of the sample was checked by analysis of cobalt and oxalate. *Anal.* Calcd for $[(NH_3)_5CoC_2O_4H]$-$(ClO_4)_2$: Co, 13.63; $C_2O_4{}^{2-}$, 20.37. Found: Co, 13.6; $C_2O_4{}^{2-}$, 20.3. The molar extinction coefficient of $(NH_3)_5CoC_2O_4H^{2+}$ at 507 nm was found to be 73.8 as compared to 74.0 reported by Taube, *et al.*[5]

Stock solutions of Fe(III), Al(III), Ga(III), and In(III) perchlorates were prepared and the metal ion contents estimated as described earlier.[3] 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 $Zn(NH_4)PO_4$, 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 p*K* of $(NH_3)_5CoC_2O_4H^{2+}$. 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 $[(NH_3)_5CoC_2O_4H](ClO_4)_2$ was transferred into the flasks and the volume was made up with distilled water equilibriated 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

(3) A. C. Dash and R. K. Nanda, *Inorg. Chem.*, **12**, 2024 (1973).
(4) P. Saffir and H. Taube *J. Amer. Chem. Soc.*, **82**, 13 (1960).
(5) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

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* H_2SO_4 medium. The media of exchange were 0.2 *M* $HClO_4$ (Co(II), Ni(II), Cu(II)) and 0.1 *M* H_2SO_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* $KMnO_4$ 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_{obsd}) were calculated from the relationship

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

where V_t and V_∞ 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_∞. 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 $(NH_3)_5CoC_2O_4H^{2+}$. The ultraviolet spectrum of oxalatopentaamminecobalt(III) ion, in aqueous medium, is pH sensitive. Andrade and Taube[5] ascribed this behavior of the oxalato complex to its protonation equilibrium

$$(NH_3)_5CoC_2O_4H^{2+} \overset{K_1}{\rightleftharpoons} (NH_3)_5CoC_2O_4{}^+ + H^+ \tag{1}$$
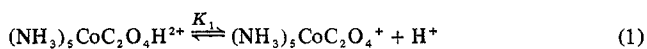
For such a system, it can be easily shown that

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

where a = [complex]$_{total}$, E_1 and E_2 are the extinction coefficients of $(NH_3)_5CoC_2O_4{}^+$ and $(NH_3)_5CoC_2O_4H^{2+}$, respectively, l is the cell path length, and $\Delta d = E_1 al$ − 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.* $1/[H^+]$ plots. The acid dissociation constant of $(NH_3)_5CoC_2O_4H^{2+}$ 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 $HClO_4$ solutions over the acidity range 0.002–0.3 *M* at an ionic strength of 0.3 *M* adjusted with $NaClO_4$ wherever necessary. The pseudo-first-order rate constants for the aquation reaction

Table I. Effect of Temperature and Ionic Strength on the Acid Dissociation Constant of $(NH_3)_5CoC_2O_4H^{2+}$

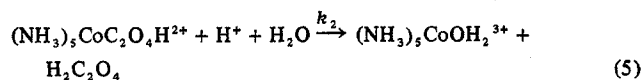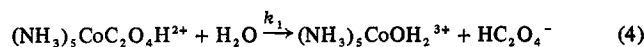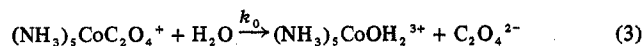| Ionic strength, M	$10^2 K_1$, M					
	25.0 (±0.1)°	28.0 (±0.1)°	35.0 (±0.2)°	45.0 (±0.5)°	66.1 (±0.1)°	70.0°
0	0.63 (±0.03)[a]	2.1[b]				
0.05		1.48 (±0.12)				
0.10		1.36 (±0.08)				
0.20		1.15 (±0.04)				
0.30	0.94 (±0.02)	1.03 (±0.04)	1.11 (±0.02)	1.27 (±0.03)	1.86 (±0.26)[c]	
1.0	0.88[d]			1.2[d]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

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

Table II. Rates of Aquation of the Oxalatopentaamminecobalt(III) Complex[a]

$10^2 [H^+]$, M	$10^6 k$, sec⁻¹							
	50.0 ± 0.1°		55.0 ± 0.1°		60.0 ± 0.1°		66.1 ± 0.1°	
	Obsd[b]	Calcd[c]	Obsd[b]	Calcd[c]	Obsd[b]	Calcd[c]	Obsd[b]	Calcd[c]
0.22							3.86 (±0.07)	3.86
1.2					3.85 (±0.08)	3.85	7.20 (±0.14)	7.17
2.0			2.82 (±0.05)	2.81	5.05 (±0.10)	5.04	8.73 (±0.23)	8.70
5.0	1.79 (±0.04)	1.79	3.62 (±0.07)	3.68	6.60 (±0.13)	6.63	11.4 (±0.2)	11.6
10.0	2.15 (±0.04)	2.14	4.42 (±0.09)	4.38	7.75 (±0.15)	7.78	14.4 (±0.3)	14.0
15.0	2.36 (±0.05)	2.39			8.71 (±0.17)	8.53	15.7 (±0.3)	15.7
20.0	2.64 (±0.05)	2.61	5.44 (±0.11)	5.33	9.14 (±0.18)	9.16	17.2 (±0.3)	17.1
25.0	2.85 (±0.05)	2.82	5.72 (±0.11)	5.75	9.65 (±0.19)	9.73	18.3 (±0.4)	18.5
30.0	2.99 (±0.06)	3.02	6.10 (±0.12)	6.16	10.3 (±0.2)	10.3	19.8 (±0.4)	19.7

Rates	50.0 ± 0.1°	55.0 ± 0.1°	60.0 ± 0.1°	66.1 ± 0.1°
$10^8 k_0 K_1$, sec⁻¹ M				4.98 (±0.98)
$10^6 k_0$, sec⁻¹	0.23 (±0.14)	0.78 (±0.18)	1.26 (±0.14)	2.67 (±0.12)
$10^6 k_1$, sec⁻¹	2.04 (±0.05)	4.16 (±0.06)	7.86 (±0.09)	13.8 (±0.7)
$10^6 k_2$, sec⁻¹ M⁻¹	3.7 (±0.2)	7.5 (±0.3)	9.7 (±0.4)	23.2 (±0.3)
$10^2 K_1$, M	1.40[d]	1.49[d]	1.59[d]	1.86 (±0.28)

[a] $\mu = 0.3$ M, [complex] = (2–3) × 10^{-3} M. [b] Average of four determinations at 60 and 66.1° and average of duplicate runs at 50 and 55°. The errors are the average deviations from the mean values. [c] Calculated from eq 6 using the best values of the rate and equilibrium parameters. [d] 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_{obsd}) of aquation of the complex (Table II): (i) k_{obsd} does not exhibit a simple first-order dependence on hydrogen ion concentration and (ii) a k_{obsd} vs. [H⁺] plot extrapolated to zero hydrogen ion concentration leads to a nonvanishing intercept. Consistent with our observation and as suggested by Andrade and Taube,[5] various paths of aquation of the oxalato complex, in the range of acidities studied, may be delineated as

$$(NH_3)_5CoC_2O_4^+ + H_2O \xrightarrow{k_0} (NH_3)_5CoOH_2^{3+} + C_2O_4^{2-} \quad (3)$$

$$(NH_3)_5CoC_2O_4H^{2+} + H_2O \xrightarrow{k_1} (NH_3)_5CoOH_2^{3+} + HC_2O_4^- \quad (4)$$

$$(NH_3)_5CoC_2O_4H^{2+} + H^+ + H_2O \xrightarrow{k_2} (NH_3)_5CoOH_2^{3+} + H_2C_2O_4 \quad (5)$$

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

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

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 $(NH_3)_5CoC_2O_4H^{2+}$. The intercept and slope of the straight-line plot of k_{obsd} vs. [H⁺] at [H⁺] = 0.15–0.3 M were taken to be k_1 and k_2, respective-

ly. Utilizing the rate data at [H⁺] < 0.15 M, $k_0 K_1$ and K_1 were computed from the straight-line plot of ($k_{obsd} - k_1 - k_2[H^+])[H^+]$ vs. k_{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 $\Sigma [(k_{calcd} - k_{obsd})/\sigma(k_{obsd})]^2$, where the sum is over all data points and $\sigma(k_{obsd})$ is the error of k_{obsd}. The values of the parameters calculated from the rate data at 66.1° have been given in Table II. When the pseudo-first-order rate constants at 50, 55, and 60° 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°) 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°. 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.[6] It is evident that k_{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

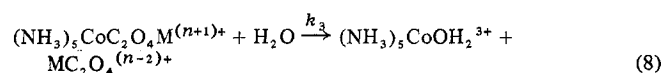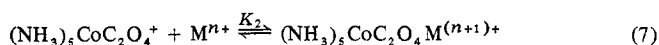(6) See paragraph at end of paper regarding supplementary material.

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

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

[a] Total concentration of the complex; R = $(NH_3)_5Co^{3+}$. [b] 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. [c] 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

$$(NH_3)_5CoC_2O_4^+ + M^{n+} \overset{K_2}{\rightleftharpoons} (NH_3)_5CoC_2O_4M^{(n+1)+} \quad (7)$$

$$(NH_3)_5CoC_2O_4M^{(n+1)+} + H_2O \overset{k_3}{\longrightarrow} (NH_3)_5CoOH_2^{3+} + MC_2O_4^{(n-2)+} \quad (8)$$

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

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

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° 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 $1/(k_{obsd} - k_{obsd}')$ vs. $1/[M^{n+}]$ at constant hydrogen ion concentration where $k_{obsd}' = k_{obsd}$ at $[M^{n+}] = 0$. 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 $[M^{n+}] = [M^{n+}]_{total}$ and $[H^+] = [HClO_4] + [complex]_{total}$ (since the complex was added in the form of $(NH_3)_5CoC_2O_4H^{2+}$). It may be mentioned that at 55 and 60°, the observed rate constant (k_{obsd}) at the highest concentration of Mn^{2+} (0.08 M) was only 15% higher than the acid hydrolysis rate constant for the oxalato complex in the absence of Mn^{2+} (Tables II and III). The values of K_2 for this system were estimated to be 15.3 (±1.4) at 28° and 18.6 (±11.9) at 66.1° (Tables V and VI). Utilizing an assumed value of $K_2 = 10$ at 55 and 60°, k_3 for 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 ith parameter of eq 6 or 9, is defined as $\sigma(x_i) = \pm A_{ii}^{1/2}$ where A_{ii} is the ith diagonal element of matrix A which is the inverse of the matrix H. The ith 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° (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 $(NH_3)_5$-$CoC_2O_4H^{2+}$ at various temperatures and ionic strengths have been summarized in Table I. From the values of K_1 at 28° and $\mu = 0.05-0.3 M$, it is evident that $(NH_3)_5CoC_2O_4H^{2+}$ ion

Table IV. Rates and Activation Parameters for the Acid Hydrolysis of $(NH_3)_5CoC_2O_4{}^{+}$ [a]

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

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

[a] 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^{-1} = 0.40 (35°), 1.20 (40°), 1.71 (45°), 7.8 (55°), 12.6 (60°), 26.8 (66.1°); $10^7 k_1$, sec^{-1} = 2.6 (35°), 7.0 (40°), 10.8 (45°), 41.0 (55°), 78.0 (60°), 140 (66.1°); $10^7 k_2$, sec^{-1} M^{-1} = 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°). [b] Assumed. [c] 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.[5]

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.*[5] (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[7] 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[8] have substantiated the proposed dissociative mechanism for the spontaneous aquation of $(NH_3)_5CoC_2O_4{}^{+}$ and $(NH_3)_5CoC_2O_4H^{2+}$.

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 $((NH_3)_5CoC_2O_4M^{(n+1)+})$ 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 $C_2O_4M^{(n-2)+}$, $C_2H_5C_2O_4M^{(n-1)+}$, and $(NH_3)_5CoC_2O_4M^{(n+1)+}$ 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 $C_2O_4{}^{2-} \gg (NH_3)_5CoC_2O_4{}^{+} > C_2H_5C_2O_4{}^{-}$. Presumably $(NH_3)_5CoC_2O_4{}^{+}$ 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

$$M^{n+} + A^{m-} \underset{}{\overset{K_{MA}}{\rightleftharpoons}} MA^{(n-m)+}$$

	log K_{MA}								
A^{m-}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Al^{3+}	Fe^{3+}	Ga^{3+}	In^{3+}
$C_2O_4{}^{2-}$	3.97^a	4.79^a	5.16^a	6.2^a	4.89^b	7^c	9.4,^{c} 7.6^d		
$C_2H_5C_2O_4{}^{-}$		1.0^e	1.1^e	1.9^e	1.1^e				
$(NH_3)_5Co$-$C_2O_4{}^{+}$	1.2^f	1.7^f	2.1^f	2.7^f	1.8^f	1.7^f	3.2^f	2.7^f	2.4^f

^{a} $\mu = 0$, 25°. A. McAuley, G. H. Nancollas, and K. Torrance, *J. Inorg. Nucl. Chem.*, 28, 917 (1966). ^{b} $\mu = 0$, 25°. C. E. Evans and C. B. Monk, *Trans. Faraday Soc.*, 66, 1491 (1970). ^{c} $\mu = 0$. J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, *Chem. Soc., Spec. Publ.*, No. 6 (1957). Estimated value for Al^{3+} (log β_2 = 13). ^{d} $\mu = 1$ M, 25°. E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 5, 1866 (1966). ^{e} $\mu_{cor} = 0.3$ M. G. L. Johnson and R. J. Angelici, *J. Amer. Chem. Soc.*, 93, 1106 (1971). ^{f} $\mu = 0.3$ M, 28°. A. C. Dash and R. K. Nanda, *J. Inorg. Nucl. Chem.*, in press.

of aquation of the species $(NH_3)_5CoC_2O_4{}^+$ (k_0), $(NH_3)_5$-$CoC_2O_4H^{2+}$ (k_1), $(NH_3)_5CoC_2O_4M^{3+}$ ($k_{3(M^{2+})}$), and $(NH_3)_5$-$CoC_2O_4M^{4+}$ ($k_{3(M^{3+})}$) for which the leaving groups are $C_2O_4{}^{2-}$, $C_2O_4H^-$, C_2O_4M, and $C_2O_4M^+$, 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 $C_2O_4M^+ < C_2O_4M < C_2O_4H^- < C_2O_4{}^{2-}$. Thus it is apparent that the rate of aquation of $(NH_3)_5Co$-$C_2O_4{}^+$, $(NH_3)_5CoC_2O_4H^{2+}$, $(NH_3)_5CoC_2O_4M^{3+}$, and $(NH_3)_5$-$CoC_2O_4M^{4+}$ 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 monooxalato 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$^+$ ion (*i.e.*, k_1 and $1/K_1$) were fitted to the relationship log $k_3 = B + \beta$ log K_2. We obtained $B = -7.08$ (± 0.12) and $\beta = 1.46$ (± 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,[9] 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^{n+} ions, respectively, and $(r_c + d)$ is the distance of closest approach of the charge centers of $(NH_3)_5CoC_2O_4M^{(n+1)+}$ 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 α, 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
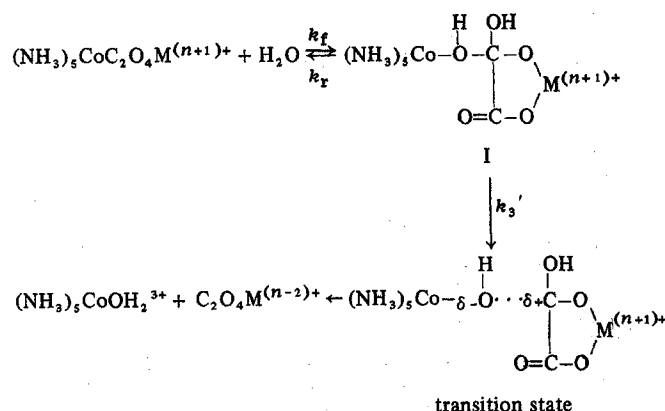
(9) E. A. Moelwyn-Hughes, "Chemical Statics and Kinetics of Solutions," Academic Press, London, 1971, p 62.

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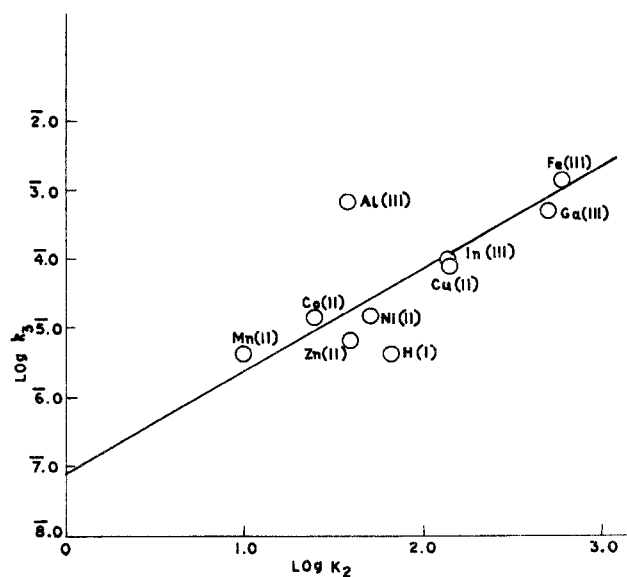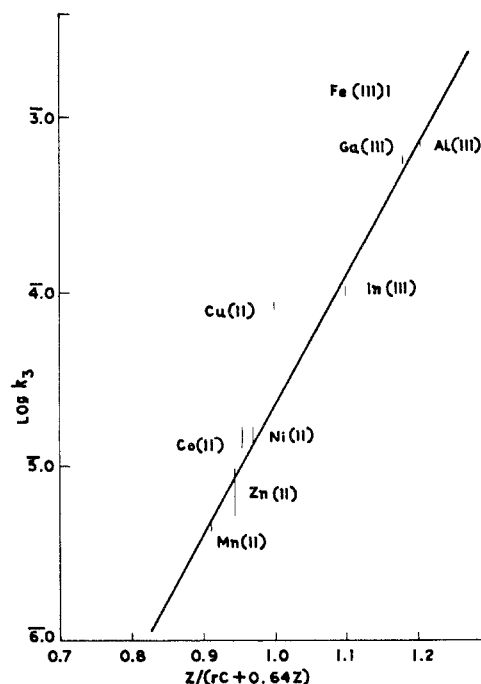
Figure 2. log k_3 *vs.* $Z/(r_c + 0.64Z)$ plot, 55°.

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 $(NH_3)_5Co^{3+}$ 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 $(NH_3)_5CoC_2O_4H^{2+}$. The tetrahedral intermediate, in turn, would undergo acyl cleavage with proton reorganization to yield $(NH_3)_5CoOH_2{}^{3+}$ and $C_2O_4M^{(n-2)+}$. 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

Scheme I

final products, respectively. k_f, k_r, and k_3' are expected to obey the Bronsted catalysis law ($k_i = G_i K_2^{\alpha_i}$). Positive catalytic effects of the metal ions are likely to be shown up in the hydration and dehydration steps.[10] The metal ions, on the other hand, would exert retarding influence on the acyl cleavage process (k_3') because of the unfavorable charge separation between the leaving groups in the transition state. These opposing effects of the metal ions on k_f/k_r and k_3' would have led to an inverse relationship between k_3 and K_2 (i.e., the log k_3 vs. log K_2 plot will have a negative slope) in contrast to our observation. In fact it has been shown in the Co(II)-, Ni(II)-, Cu(II)-, and Zn(II)-catalyzed acid hydrolysis of ethyl glycinate[11] that the log $k_{(H_2O)}$ vs. log $K_{(ME^{2+})}$ plot ($k_{(H_2O)}$ and $K_{(ME^{2+})}$ are the rate and stability constants of

(10) Y. Pocker and J. E. Meany, *J. Phys. Chem.*, **72**, 655 (1968).

(11) J. E. Hix, Jr., and M. M. Jones, *Inorg. Chem.*, **5**, 1863 (1966).

the 1:1 metal–ester complex) is linear with negative slope. From the above considerations, it is reasonable to think that the metal ion promoted acyl cleavage mechanism probably does not operate in the k_3 path.

Alternatively, the metal ions in their binuclear complexes will polarize the carboxyl group bound to $(NH_3)_5Co^{3+}$, weaken the Co–O bond, and promote its heterolytic cleavage. According to this mechanism, the transition state for the k_3 path will be highly polar as the leaving groups are $(NH_3)_5Co^{3+}$ and $C_2O_4M^{(n-2)+}$. k_3 is, therefore, expected to increase with increasing charge, decreasing basicity, and increasing thermodynamic stabilities of $C_2O_4M^{(n-2)+}$ species. The observed log k_3 vs. log K_2 and log k_3 vs. $Z/(r_c + \alpha Z)$ correlations are in accord with these generalizations. Co–O bond fission, therefore, appears to be rate determining in the metal ion catalyzed path of aquation of oxalatopentaamminecobalt-(III) complex. The activation enthalpies and entropies for the k_3 path agree, within experimental error, with the same for the k_0 and k_1 paths. As such it is not possible to make a reliable estimate of the energetic roles of the metal ions in the k_3 path of aquation of the oxalato complex.

Dinuclear Bridged d^8 Metal Complexes. I. Preparation and Structure of [RhCl(CO)L]₂ Compounds[1]

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The complex [RhCl(CO)(C$_2$H$_4$)]$_2$ provides a convenient starting material for the preparation of [RhCl(CO)L]$_2$ complexes where L = n-C$_3$H$_7$OPF$_2$, P(OCH$_3$)$_3$, P(C$_6$H$_5$)$_3$, P[N(CH$_3$)$_2$]$_3$, P(CH$_3$)$_2$C$_6$H$_5$, P(CH$_3$)$_3$, or P(C$_2$H$_5$)$_3$. Detailed infrared study has shown that the complex [RhCl(CO)(C$_2$H$_4$)]$_2$ exhibits two CO stretching frequencies and that the most probable structure is a double square plane ("cis" or "trans") with a bent configuration. Infrared and ^{1}H nmr data for the phosphine- or phosphite-substituted complexes suggest a similar structure but the planar configuration is not excluded. The ready displacement of ethylene from complexes Rh$_2$Cl$_2$(CO)(C$_2$H$_4$)$_3$ and Rh$_2$Cl$_2$(CO)$_3$(C$_2$H$_4$) by triphenyl phosphine or tertiary phosphite provides also a convenient route to complexes Rh$_2$Cl$_2$(CO)L$_3$ and Rh$_2$Cl$_2$(CO)$_3$L, respectively.

Introduction

When a tertiary phosphine L is allowed to react with di-μ-chloro-tetracarbonyldirhodium with an L/Rh ratio of <2, an equilibrium mixture of mononuclear species RhCl-(CO)$_{3-n}$L$_n$ (hereafter referred to as X$_n$) and dinuclear species Rh$_2$Cl$_2$(CO)$_{4-n}$L$_n$ (hereafter referred to as Y$_n$) is formed.[2] With careful control of the L/Rh ratio, infrared

and mass spectroscopic evidence for complexes Y$_1$ (L/Rh = 1/2) has been obtained;[3,4] isolation in the solid state of these complexes at present has not been achieved. However stable complexes Y$_2$ (L/Rh = 1), originally thought to be mononuclear of type X$_1$,[5–8] have been isolated;[2–4,9,10] for

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