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## Electron-Transfer Reactions of Ruthenium(III) Pentaammines with Chromium(II), Vanadium(II), and Europium(II)

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Kinetic measurements have been made on the reactions of Cr(II), V(II), and Eu(II) with pentaammineruthenium(III) complexes containing halide, aquo, and carboxylate ligands. With the exception of a possible significant contribution by outer-sphere paths to the reduction of the iodo and aquo complexes, the reactions with Cr(II) take place predominantly by inner-sphere mechanisms. The reactions with V(II) are in all cases so rapid that they cannot involve substitution by a bridging group into a normal coordination position of the reducing agent. Reactivities of corresponding Ru(III) and Co(III) complexes are compared and considered in relation to the electronic structure of the oxidizing metal ions. For most of the oxygen ligands, intermediates formed as a result of the electron-transfer reaction were detected. With Cr(II) as reductant, the intermediates are binuclear Ru(II)-Cr(III) ions. A comparison of the rate of aquation of the intermediate bridged by OH<sup>-</sup> and by a carboxylate ion leads to the conclusion that Cr(II), in reducing a carboxylate Ru(III) complex, attacks the oxygen not bearing the Ru(III) ion. The intermediates formed by V(II) and Eu(II) are identical, and it is concluded, therefore, that they are the Ru(II) complexes corresponding to the Ru(III) complexes which were reduced. Data on the rates of aquation of carboxylatopentaamine Ru(II) complexes are recorded, as are estimates of the proton affinities of these complexes.

### Introduction

The importance of comparing cobalt(III) and ruthenium(III) pentaammines in their reactivity toward reducing agents such as Cr<sup>2+</sup>(aq) has been noted previously.<sup>1,2</sup> The pentaammines of Co(III) and Ru(III) are similar in many respects but differ in that the  $e_g$  levels of Co(III) become occupied upon reduction, whereas in the reduction of Ru(III) the electron enters a  $t_{2g}$  orbital. In this study we report kinetic measurements on the reactions of Cr<sup>2+</sup>, V<sup>2+</sup>, and Eu<sup>2+</sup> with pentaammineruthenium(III) complexes containing halide, aquo, and carboxylate ligands.

### Experimental Section

**Reagents.**—Except where noted all chemicals were of reagent grade. All solutions were made up with doubly distilled water, the second distillation being from alkaline permanganate in an all-Pyrex still. The ionic strength and acidity of reaction mixtures were adjusted with lithium perchlorate and perchloric acid. Oxidant and reductant solutions were deoxygenated with a stream of nitrogen from which traces of O<sub>2</sub> had been removed by passing through a train of gas scrubbers containing chromous solution.

Solutions of chromous, vanadous, and europous perchlorates were prepared by zinc amalgam reduction of chromium(III), vanadyl, and europium(III) perchlorates. Reductant concentrations were measured by mixing with an excess of (NH<sub>3</sub>)<sub>5</sub>CoCl<sub>3</sub> and determining the concentration of the resulting cobalt(II) as the thiocyanate complex in 50% acetone-water.<sup>3</sup> Chromium(III) perchlorate solutions were prepared by reducing acidic solutions of either reagent grade potassium dichromate or chromic acid with hydrogen peroxide or formic acid, respectively. Both solutions gave identical results. Chromium content was determined spectrophotometrically as chromate.<sup>4</sup> Hydrogen ion in the chromium(III) stock solutions was determined by potentiometric titration with sodium hydroxide after complexing the

chromium(III) with oxalate.<sup>5</sup> Vanadyl perchlorate solutions were prepared from vanadyl sulfate and barium perchlorate, and total vanadium was determined by oxidizing to vanadate and titrating with iron(II).<sup>6</sup> Europium(III) perchlorate solutions were made up by dissolving europium(III) oxide in a known excess of perchloric acid. Europium content was determined as the reducing power after reduction by zinc amalgam.

In kinetic experiments for [H<sup>+</sup>] less than about 10<sup>-2</sup> M the reductant solution contained most or all of the acid of the reaction mixture. Provided the chromium(III), vanadyl, or europium(III) solution was carefully deoxygenated before the addition of zinc amalgam, negligible reduction of H<sup>+</sup> occurred during the 1.5–4 hr the solution and zinc amalgam were in contact. This is shown by the fact that kinetic results in this range of acidity were the same whether the reductant contained essentially all of the acid, or if up to 50% was initially in the oxidant solution. Barrett has shown by direct titration of Cr<sup>2+</sup> solutions with ethylenediamine that there is little loss of H<sup>+</sup> over zinc amalgam at higher [H<sup>+</sup>].<sup>7</sup>

(NH<sub>3</sub>)<sub>5</sub>RuCl<sub>3</sub> was prepared from (NH<sub>3</sub>)<sub>6</sub>RuCl<sub>3</sub> (Johnson, Matthey, and Co., Ltd.).<sup>8</sup> (NH<sub>3</sub>)<sub>5</sub>RuOH<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>, (NH<sub>3</sub>)<sub>5</sub>RuI(ClO<sub>4</sub>)<sub>3</sub>, and (NH<sub>3</sub>)<sub>5</sub>RuBr<sub>3</sub> were prepared from (NH<sub>3</sub>)<sub>5</sub>RuCl<sub>3</sub> as described in the literature.<sup>9,10</sup> (NH<sub>3</sub>)<sub>5</sub>RuCl<sub>3</sub> and (NH<sub>3</sub>)<sub>5</sub>RuBr<sub>3</sub> were converted to the perchlorate salts with AgClO<sub>4</sub>. The purity of the aquo- and halopentaammines was established by microanalysis and comparison of measured extinction coefficients with the published values.<sup>9,11</sup>

Ruthenium(III) complexes containing carboxylate ligands were prepared from (NH<sub>3</sub>)<sub>5</sub>RuCl<sub>3</sub> and buffer solutions of the carboxylic acid and its sodium or lithium salt. The sparingly soluble (NH<sub>3</sub>)<sub>5</sub>RuCl<sub>3</sub> was dissolved in a small amount of water with 2 equiv of silver trifluoroacetate. After removal of the silver chloride a 10–20-fold over-all excess of carboxylate buffer was added with sufficient dimethylformamide to keep the organic acid in solution. A catalytic amount of ruthenium(II) was

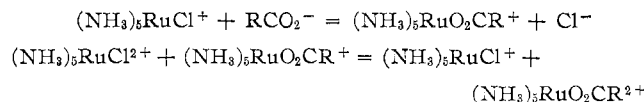
(1) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).(2) H. Taube in "Mechanisms of Inorganic Reactions," *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 118.(3) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).(4) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **46**, 414 (1952).(5) W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

(6) H. R. Grady in "Treatise on Analytical Chemistry," Vol. VIII, Part II, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, New York, N. Y., 1963, p 227.

(7) M. B. Barrett, Ph.D. Thesis, Stanford University, 1968.

(8) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, **4**, 1157 (1965).(9) H. Hartmann and C. Buschbeck, *Z. Physik. Chem. (Frankfurt am Main)*, **11**, 120 (1957).(10) K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, **227**, 237 (1936).(11) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

generated by swirling a mixture of the  $(\text{NH}_3)_5\text{RuCl}^{2+}$ -carboxylate buffer solution and a small amount of zinc amalgam in air. Equilibration was achieved in several minutes through the reactions



where R = H,  $\text{CH}_3$ ,  $\text{CF}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{OH}$ , or  $\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ . The zinc amalgam was then removed, and the perchlorate salt of the carboxylate complex was precipitated with saturated sodium perchlorate. The methylterephthalato complex was prepared only as the iodide salt by addition of a concentrated sodium iodide solution at this point.<sup>12</sup> The perchlorate salts were recrystallized from dilute sodium perchlorate. Details of the procedure for each complex can be found elsewhere.<sup>13</sup> When free from aquopentaammine, the perchlorate salts were quite stable at room temperature, and they could be stored at  $-10^\circ$  for at least several months without any apparent decomposition. *Caution!* The perchlorate salts of ruthenium amines are explosive and should be handled cautiously and only in small amounts.

The carboxylatopentaammineruthenium(III) complexes were characterized by elemental analysis and their visible and uv spectra. Microanalyses were performed by the Microanalytical Laboratory of the Stanford University Department of Chemistry, and spectra were recorded on a Cary Model 14 spectrophotometer. Analytical and spectral data are summarized in Tables I and II. The spectra of the formate, acetate, and trifluoroacetate complexes are similar to that of  $(\text{NH}_3)_5\text{RuOH}^{2+}$ , consisting of a single absorption maximum at about  $290\text{ m}\mu$  with  $\epsilon \sim 1.5 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$ . For the benzoate, *p*-hydroxybenzoate, and methylterephthalato complexes this band is found at about  $300\text{ m}\mu$  as a shoulder on more intense ( $\epsilon \sim 10,000\text{ M}^{-1}\text{ cm}^{-1}$ ) ligand transitions which remain essentially unaltered in the complexes. The main ruthenium(III) absorption for several complexes is asymmetric, and for the aquo complex a shoulder with  $\epsilon \sim 80\text{ M}^{-1}\text{ cm}^{-1}$  can be distinguished at about  $320\text{ m}\mu$ . The spectrum of the *p*-hydroxybenzoate complex has an additional band at  $400\text{ m}\mu$  ( $\epsilon\ 530\text{ M}^{-1}\text{ cm}^{-1}$ ) which disappears in basic solution with the appearance of a new band at about  $500\text{ m}\mu$  with slightly greater extinction. This change is reversible and probably corresponds to removal of the phenolic proton. A similar observation has been reported for *p*-hydroxybenzoatopentaamminecobalt(III).<sup>14</sup>

**Kinetic Experiments.**—All kinetic measurements were made with a stopped-flow apparatus similar to that of Dulz and Sutin.<sup>15</sup> The reactions were generally followed at the absorption maximum of the ruthenium(III) complex as given in Table II. The temperature was maintained to within  $\pm 0.1^\circ$ , and activation parameters were calculated from the equation

$$k = \frac{k_b T}{h} e^{-\Delta H^\ddagger/RT} e^{-\Delta S^\ddagger/R}$$

For reactions that obeyed second- or first-order kinetics, the measured transmittances were converted to absorbances and the rate constants were evaluated graphically. The determination of the rates of the reactions that proceeded by consecutive second- and first-order steps depended on the particular system. For the reaction of  $(\text{NH}_3)_5\text{RuOH}_2^{3+}$  with  $\text{Cr}^{2+}$  the complementary acid dependences of the two steps permitted each rate constant to be measured directly under conditions where the other step was immeasurably fast. Similarly, the rates of the two steps for the reaction of  $(\text{NH}_3)_5\text{RuO}_2\text{CH}^{2+}$  with  $\text{Cr}^{2+}$  were sufficiently different in a convenient concentration range that both rate constants could be evaluated directly in the

TABLE I  
ANALYTICAL DATA FOR  
CARBOXYLATOPENTAAMMINERUTHENIUM(III) COMPLEXES

		%	
		Calcd	Found
$(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CH})(\text{ClO}_4)_2$	C	2.8	2.9
	H	3.8	3.8
	N	16.3	16.3
	Cl	16.5	16.3
$(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CCH}_3)(\text{ClO}_4)_2$	C	5.4	5.5
	H	4.1	4.2
	N	15.8	15.8
	Cl	16.0	15.9
$(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CCF}_3)(\text{ClO}_4)_2$	C	4.8	5.0
	H	3.0	3.1
	N	14.1	14.3
	Cl	14.2	14.4
$(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CC}_6\text{H}_5)(\text{ClO}_4)_2$	C	16.6	16.1
	H	4.0	3.9
	N	13.8	13.6
	Cl	14.0	14.1
$(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CC}_6\text{H}_4\text{OH})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	C	15.6	15.6
	H	4.1	4.1
	N	13.0	13.2
	Cl	13.1	13.3
$(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2\text{CH}_3)_2$	C	17.5	17.6
	H	3.6	3.6
	N	11.3	11.3
	I	41.0	40.3

TABLE II  
SPECTRAL PROPERTIES OF PENTAAMMINERUTHENIUM(III) IONS

Ligand	$\lambda_{\text{max}}, \text{m}\mu$	$10^{-3}\epsilon, \text{M}^{-1}\text{ cm}^{-1}$
$\text{Cl}^-$	328	1.89
$\text{Br}^-$	398	1.82
$\text{I}^-$	540	2.1
$\text{H}_2\text{O}$ $\nabla$	268	0.73
$\text{OH}^-$	$\sim 295$	$\sim 1.5$
$\text{HCO}_2^-$	293	1.50
$\text{CH}_3\text{CO}_2^-$	295	1.61
$\text{CF}_3\text{CO}_2^-$	285	1.19
Benzoate	296	2.6
<i>p</i> -Hydroxybenzoate	300 sh	2.7
Methylterephthalate	286	5.6

same experiment. For most of the others it was necessary to obtain the specific rate for one step under limiting conditions and then evaluate the other under conditions where the two steps were competitive. The unknown rate constant, the effective extinction coefficient of the intermediate, and the time from mixing to the first observation were calculated as adjustable parameters in an iterative procedure that minimized the sum of the squares of the differences between the observed and calculated absorbances. The effective extinction coefficient for a reaction (over-all or elementary step) is defined by the equation  $\epsilon_{\text{eff}} = \sum \epsilon_r n_r - \sum \epsilon_p n_p$ , where the  $\epsilon_r$  and  $\epsilon_p$  are the molar extinction coefficients of the reactants and products, and  $n_r$  and  $n_p$  are their coefficients in the stoichiometric equation. Although no attempt was made to determine the complete spectrum of any of the intermediates, several of the reactions were followed at a second wavelength with results in satisfactory agreement with those at the absorption maximum of the ruthenium(III) complex.

The calculations were performed on the Burroughs B5500 computer at the Stanford University Computation Center. Up to 30 transmittance and time values, the initial concentrations of the reactants, the rate constant which was measured directly, and the effective extinction coefficient of the reactants were supplied to the program. The set of three parameters always gave a fit to the data well within experimental error.

(12) Methylterephthalic acid and lithium salt were provided by J. K. Hurst.

(13) J. A. Stritar, Ph.D. Thesis, Stanford University, 1967.

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

(15) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

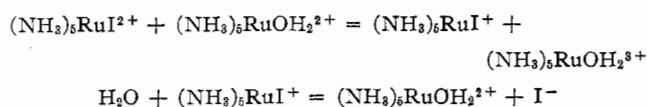
The calculated interval between mixing and the instant at which the flow halted was usually about 0.005 sec, and when the half-time for the initial absorbance change was sufficiently long (>20 msec), this interval could be taken as a constant. Both rate constants could then be treated as parameters, provided the half-times of the two steps were sufficiently different.

### Results

**Reactions of Halopentaammineruthenium(III) Complexes.**—When the reductant is in sufficient excess, the reactions of chloro- and bromopentaammineruthenium(III) with  $\text{Cr}^{2+}$  obey second-order kinetics

$$-\frac{d[\text{Ru(III)}]}{dt} = k[\text{Ru(III)}][\text{Cr}^{2+}]$$

However, the disappearance of iodopentaammineruthenium(III) when mixed with  $\text{Cr}^{2+}$  is strongly autocatalytic. Pseudo-first-order kinetic plots for this reaction deviate significantly from linearity after 1 half-life, even with a 160-fold excess of reductant. The autocatalytic behavior may be attributed to the catalytic aqution of  $(\text{NH}_3)_5\text{RuI}^{2+}$  through the reactions



For the first of these the rate constant was estimated as  $10^4 M^{-1} \text{sec}^{-1}$ , assuming the second to be the faster of the two. The specific rate of the reduction of  $(\text{NH}_3)_5\text{RuI}^{2+}$  by  $\text{Cr}^{2+}$  was taken from the initial slopes of the first-order kinetic plots.

The rate constant for the outer-sphere reaction of  $(\text{NH}_3)_5\text{RuOH}_2^{2+}$  and  $(\text{NH}_3)_5\text{RuBr}^{2+}$  was estimated as  $10^3 M^{-1} \text{sec}^{-1}$  from the curvature of kinetic plots when the initial  $[\text{Cr}^{2+}]/[\text{Ru(III)}]$  ratio was less than about 2. Otherwise kinetic plots for the reaction of  $(\text{NH}_3)_5\text{RuBr}^{2+}$  with  $\text{Cr}^{2+}$  were linear to well over 3 half-lives. For the reaction of  $(\text{NH}_3)_5\text{RuCl}^{2+}$  with  $\text{Cr}^{2+}$  kinetic plots were linear over the extent (85–95%) that the reaction was followed, even at initial  $[\text{Cr}^{2+}]/[\text{Ru(III)}]$  ratios as low as 1.6. In this case the reaction of  $(\text{NH}_3)_5\text{RuOH}_2^{2+}$  with the chloro complex is too slow (the specific rate was estimated by Endicott and Taube<sup>1</sup> as  $2 \times 10^2 M^{-1} \text{sec}^{-1}$ ) to compete with the reduction of the chloro complex by  $\text{Cr}^{2+}$ . There was a 27% decrease in specific rate for reduction of the chloro complex over the range  $0.31 \times 10^{-3} M \leq [\text{Cr}^{2+}] \leq 3.1 \times 10^{-3} M$ . On the basis of our data alone, however, this decrease cannot be regarded as significant relative to the rather large uncertainties encountered at half-times approaching the limit (0.005 sec) of the stopped-flow apparatus.<sup>16</sup>

(16) W. G. Movius and R. G. Linck (R. G. Linck, personal communication, University of California, San Diego, Calif., 1969) have observed a similar deviation from second-order kinetics for the reaction of  $(\text{NH}_3)_5\text{RuCl}^{2+}$  with  $\text{Cr}^{2+}$  in 0.1 M *p*-toluenesulfonic acid and a more pronounced effect in the reaction of *cis*-( $\text{NH}_3$ )<sub>4</sub> $\text{RuCl}_2^+$  with  $\text{Cr}^{2+}$ . Their data for the latter reaction indicate the rapid and reversible formation of an intermediate, presumably a Ru(II)–Cr(III) species, which then decays to the products. Our data for the reaction of  $(\text{NH}_3)_5\text{RuCl}^{2+}$  with  $\text{Cr}^{2+}$  are consistent with a similar mechanism with an equilibrium constant of  $\sim 120$  for formation of the intermediate and  $k \approx 270 \text{sec}^{-1}$  for its aqution. It should be noted that an intermediate has been observed in the reaction of  $(\text{H}_2\text{O})_5\text{RuCl}^{2+}$  with  $\text{Cr}^{2+}$ , having  $k$  for aqution as  $2 \text{sec}^{-1}$  at 25°. D. Seewald and N. Sutin, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M-005. A hydroxide-bridged

Experimental results for these reactions and those of  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$  with the chloro and bromo complexes are recorded in Tables III–V. For the latter reactions the reductant was maintained in large enough excess that second-order kinetics were obeyed throughout. Activation parameters for some of the reactions of the halopentaammines are listed in Table VI. The experimental uncertainties in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are estimated to be  $\pm 0.5 \text{kcal}$  and  $\pm 2 \text{eu}$ , respectively. The activation parameters for the reaction of the  $(\text{NH}_3)_5\text{RuCl}^{2+}$  with  $\text{Cr}^{2+}$  were evaluated at  $[\text{Cr}^{2+}] = 0.00051 M$ .

TABLE III  
RATE CONSTANTS FOR THE REACTIONS OF  
HALOPENTAAMMINERUTHENIUM(III) COMPLEXES WITH  
CHROMIUM(II) ( $[\text{H}^+] \approx$  IONIC STRENGTH = 0.11 M)

Halide	$10^3[\text{Cr}^{2+}]$ , M	$10^4[\text{Ru(III)}]$ , M	$10^{-3}k$ , $M^{-1} \text{sec}^{-1}$	Temp., °C	
Cl <sup>-</sup>	3.06	3.5	27.5	25.0	
	2.04	2.45	31	25.0	
	1.02	3.45	34.5	25.0	
	1.02	2.58	34 <sup>a</sup>	25.0	
	0.51	1.86	32.6	17.5	
			29.2	10.0	
		0.51	1.73	37.2	30.0
			32.7	15.0	
		0.51	1.92	35.7 <sup>b</sup>	25.0
		0.306	1.86	34.5 <sup>b</sup>	20.0
Br <sup>-</sup>			37.3	25.0	
			35.7	20.0	
	3.06	1.78	2.38	30.0	
			1.63	10.0	
	2.04	1.02	1.94	20.0	
			1.77	15.0	
		1.89	0.51	2.18	25.0
		0.95	0.49	2.11	25.0
		0.95	0.62	2.20 <sup>c</sup>	25.0
		0.95	0.66	2.20 <sup>c</sup>	25.0
I <sup>-</sup>	1.9	1.26	0.26	25.0	
	17.0	1.11	0.24	25.0	

<sup>a</sup>  $[\text{H}^+] = 5 \times 10^{-3} M$ . <sup>b</sup>  $[\text{NaCl}] = 5 \times 10^{-3} M$ . <sup>c</sup>  $[\text{H}^+] = 0.05 M$ .

Endicott and Taube have shown that the one-electron reduction product of the halopentaammineruthenium(III) complexes is  $(\text{NH}_3)_5\text{RuOH}_2^{2+}$  and have identified the chromium(III) product of the reaction of  $(\text{NH}_3)_5\text{RuCl}^{2+}$  with  $\text{Cr}^{2+}$  as  $\text{CrCl}^{2+}$ .<sup>11</sup> Since added NaCl does not appreciably catalyze the latter reaction, we may conclude that the rate term  $[(\text{NH}_3)_5\text{RuCl}^{2+}] \cdot [\text{Cr}^{2+}][\text{Cl}^-]$  is unimportant and that the  $\text{Cl}^-$  in the Cr(III) product is transferred from the Ru(III) complex *via* an inner-sphere mechanism.

From the well-known tendency of  $\text{Cr}^{2+}$  to react by inner-sphere paths when possible, it is tempting to conclude that the reactions of bromo- and iodopentaammineruthenium(III) with  $\text{Cr}^{2+}$  are also inner sphere, although the specific rate for the latter reaction is quite close to that for the outer-sphere reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  by  $\text{Cr}^{2+}$ .<sup>1</sup> The specific rates recorded are in any case upper limits on the rates *via* inner-sphere paths.

intermediate is accessible in this system and may be the cause of the difference in lability.

TABLE IV  
RATE CONSTANTS FOR THE REACTIONS OF  
HALOPENTAAMMINERUTHENIUM(III) COMPLEXES WITH  
VANADIUM(II) ( $[H^+] \approx$  IONIC STRENGTH = 0.11 M)

Halide	$10^3[V^{3+}]$ , M	$10^4[Ru(III)]$ , M	$10^{-3}k$ , $M^{-1} \text{ sec}^{-1}$	Temp, $^{\circ}C$
Cl <sup>-</sup>	4.8	1.92	2.5 <sup>b</sup>	25.0
	4.8	1.52	2.65 <sup>a,b</sup>	25.0
	2.4	1.84	3.03 <sup>a</sup>	25.0
	2.29	1.2	3.66	30.0
			3.05	25.0
	2.29	2.44	2.38	15.0
			3.48	30.0
	2.29	2.52	3.56	30.0
			2.83	22.0
	2.29	1.34	2.18	10.0
			2.38	16.5
	Br <sup>-</sup>	4.57	1.25	4.11
			4.70	20.0
4.57		1.25	5.75	30.0
			4.47	17.5
2.29		1.95	4.83	25.0
			3.64	10.0
2.29		1.92	5.10	25.0
			5.15	25.0

<sup>a</sup>  $[NaCl] = 5 \times 10^{-3} M$ . <sup>b</sup> Ionic strength 0.98 M.

TABLE V  
RATE CONSTANTS FOR THE REACTIONS OF  
HALOPENTAAMMINERUTHENIUM(III) COMPLEXES WITH  
EUROPIUM(II) ( $[H^+] \approx$  IONIC STRENGTH = 0.11 M)

Halide	$10^4[Eu^{2+}]$ , M	$10^4[Ru(III)]$ , M	$10^{-3}k$ , $M^{-1} \text{ sec}^{-1}$	Temp, $^{\circ}C$
Cl <sup>-</sup>	9.5	4.9	2.45	25.0
	4.24	1.69	2.36	25.0
Br <sup>-</sup>	7.4	2.49	1.34	25.0
			1.18	10.0
	3.7	1.01	1.36	30.0
			1.18	15.0
	37.0	2.12	1.05	10.0

The reactions of the chloro and bromo complexes with  $V^{2+}$  are too rapid ( $k > 10^3 M^{-1} \text{ sec}^{-1}$ ) to be preceded by substitution on vanadium(II) and must therefore be outer sphere.<sup>17</sup> The lability of  $Eu^{2+}$  and  $Eu^{3+}$  does not permit inner-sphere and outer-sphere mechanisms to be distinguished.

**Reaction of Aquopentaammineruthenium(III) with Chromium(II).**—At the absorption maximum of the ruthenium(III) complex (268  $m\mu$ ) the observed second-order rate constants (cf. Table VII) for the reaction of  $(NH_3)_5RuOH_2^{3+}$  with  $Cr^{2+}$  increase linearly with  $1/[H^+]$  as shown in Figure 1. Thus the reaction follows the rate law

$$-\frac{d[Ru(III)]}{dt} = (k + k'/[H^+])[Ru(III)][Cr^{2+}]$$

with  $k = (5 \pm 4) \times 10^2 M^{-1} \text{ sec}^{-1}$  and  $k' = (2.2 \pm 0.2) \times 10^2 \text{ sec}^{-1}$ . At 320  $m\mu$  where the spectrum of  $(NH_3)_5RuOH_2^{3+}$  has a weak shoulder, under conditions such that the half-life calculated from the results at 268  $m\mu$  should be less than 0.0013 sec, a decrease in absorbance

(17) (a) M. Orhanović, H. N. Po, and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968). (b) The specific rate for the substitution of water on  $V(H_2O)_6^{2+}$  is  $90 \text{ sec}^{-1}$  at  $25^{\circ}$ : M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

TABLE VI  
KINETIC PARAMETERS FOR REACTIONS OF HEXAAMMINE AND  
HALOPENTAAMMINE COMPLEXES OF COBALT(III)  
AND RUTHENIUM(III)

Reaction	$k$ , $M^{-1} \text{ sec}^{-1}$	Temp, $^{\circ}C$	$\Delta H^{\ddagger}$ , kcal mol <sup>-1</sup>	$\Delta S^{\ddagger}$ , eu	Ref
$V^{2+} + Co(NH_3)_6^{3+}$	$3.7 \times 10^{-2}$	25	9.1	-40	a
$Cr^{2+} + Co(NH_3)_6^{3+}$	$8.8 \times 10^{-3}$	25	14.7	-30	a
$V^{2+} + Ru(NH_3)_6^{3+}$	80	25	...	...	b
$Cr^{2+} + Ru(NH_3)_6^{3+}$	$2 \times 10^2$	25	...	...	b
$V^{2+} + Co(NH_3)_5Br^{2+}$	25	25	9.1	-22	c
$Eu^{2+} + Co(NH_3)_5Cl^{2+}$	$3.9 \times 10^2$	25	5.0	-30	c
$Eu^{2+} + Co(NH_3)_5Br^{2+}$	$2.5 \times 10^2$	25	4.7	-32	c
$Cr^{2+} + Co(NH_3)_5Cl^{2+}$	$6 \times 10^4$	25	...	...	d
$Cr^{2+} + Co(NH_3)_5Br^{2+}$	$1.4 \times 10^6$	25	...	...	d
$Cr^{2+} + Co(NH_3)_5I^{2+}$	$3 \times 10^6$	25	...	...	d
$Cr^{2+} + Ru(NH_3)_5Cl^{2+}$	$3.5 \times 10^4$	25	1.3	-33	e
$Cr^{2+} + Ru(NH_3)_5Br^{2+}$	$2.2 \times 10^3$	25	2.8	-34	e
$V^{2+} + Ru(NH_3)_5Cl^{2+}$	$3.0 \times 10^3$	25	3.8	-30	e
$V^{2+} + Ru(NH_3)_5Br^{2+}$	$5.1 \times 10^3$	25	2.8	-34	e
$Eu^{2+} + Ru(NH_3)_5Br^{2+}$	$1.3 \times 10^4$	25	1	-37	e

<sup>a</sup> A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).  
<sup>b</sup> J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964). <sup>c</sup> J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).  
<sup>d</sup> J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).  
<sup>e</sup> This work.

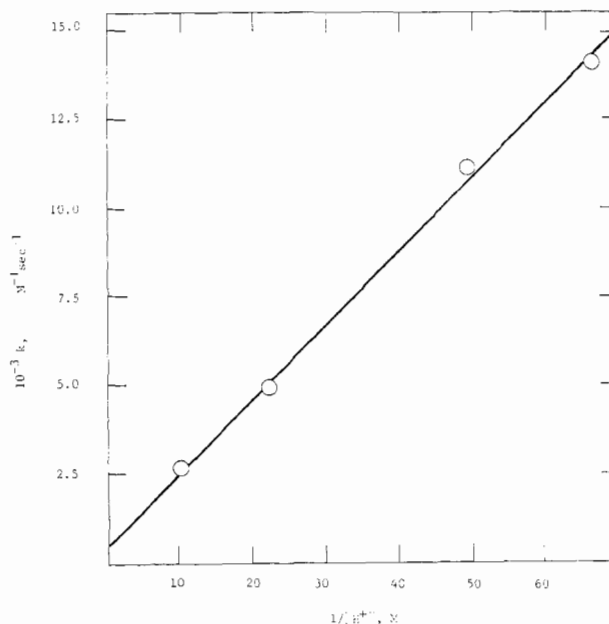


Figure 1.—Variation of  $k(268 m\mu)$  with  $[H^+]$  for the reaction of aquopentaammineruthenium(III) with chromium(II).

with a half-life greater than 0.015 sec is observed. When the calculated half-life was about 0.002 sec, the decrease in absorbance was preceded by a slight increase. Under these conditions the decrease in absorbance obeys first-order kinetics. The first-order rate constants are independent of  $Cr^{2+}$  and increase linearly with  $H^+$  (cf. Figure 2) according to the rate law

$$-\frac{d[Int]}{dt} = (k'' + k'''[H^+])[Int]$$

with  $k'' = 10.5 \pm 1.0 \text{ sec}^{-1}$  and  $k''' = (4.5 \pm 0.3) \times 10^3 M^{-1} \text{ sec}^{-1}$ . In the rate law Int represents the absorbing species being followed at 320  $m\mu$ . The extrapolated zero-time absorbances were proportional only to the total ruthenium concentration, giving an effective extinction coefficient for Int of  $540 M^{-1} \text{ cm}^{-1}$

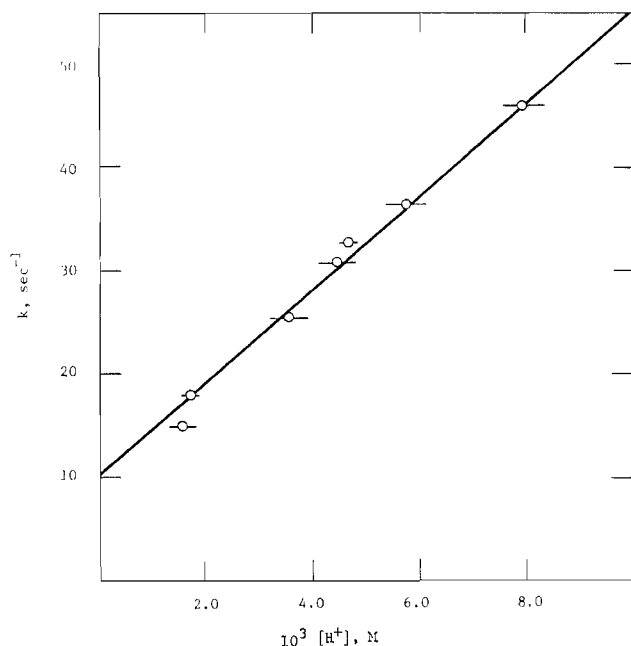


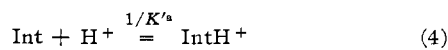
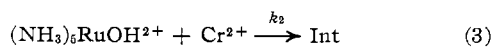
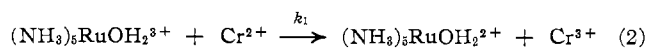
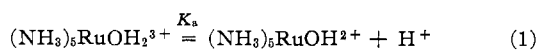
Figure 2.—Variation of  $k(320 \text{ m}\mu)$  with  $[\text{H}^+]$  for the reaction of aquopentaammineruthenium(III) with chromium(II).

TABLE VII  
RATE CONSTANTS FOR THE REACTION OF  
AQUOPENTAAMMINERUTHENIUM(III) WITH CHROMIUM(II)  
AT 25° AND IONIC STRENGTH 0.1 M

$10^3[\text{Cr}^{2+}]$ , M	$10^3[\text{Ru(III)}]$ , M	$[\text{H}^+]$ , M	$k$
2.04	0.85	0.101	2,660 <sup>a</sup>
4.08	0.94	0.050	4,900 <sup>a</sup>
2.04	0.84	0.0223	11,100 <sup>a</sup>
1.02	0.74	0.0151	14,000 <sup>a</sup>
10.1	0.70	0.0076	46 <sup>b</sup>
15.2	0.66	0.0054	36.6 <sup>b</sup>
12.7	0.319	0.0045	32.6 <sup>b</sup>
10.1	0.74	0.0041	31.0 <sup>b</sup>
5.07	0.454	0.0032	25.5 <sup>b</sup>
5.07	0.239	0.0016	18.1 <sup>b</sup>
5.07	0.52	0.0013	15 <sup>b</sup>

<sup>a</sup> In  $M^{-1} \text{ sec}^{-1}$ ,  $\lambda$  268  $\text{m}\mu$ . <sup>b</sup> In  $\text{sec}^{-1}$ ,  $\lambda$  330  $\text{m}\mu$ .

For the results at the two wavelengths to be compatible with the fact that the products of the reaction are  $(\text{NH}_3)_5\text{RuOH}_2^{2+}$  and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ,<sup>1</sup> an intermediate must be postulated. The following mechanism describes our observations

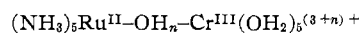


The form of steps 1–3 is common to many electron-transfer reactions between metal ions containing aquo ligands, and in particular the reaction of  $(\text{NH}_3)_5\text{Ru}^{3+}$

with  $\text{Cr}^{2+}$  is described by such a mechanism.<sup>18</sup> Steps 1–3 alone account for the behavior at 268  $\text{m}\mu$  if this wavelength is an isosbestic point for the intermediate and the products. Then if the absorbance at 320  $\text{m}\mu$  is due mainly to the intermediate, under our conditions only reactions 5 and 6 are observed. Since  $K_a[\text{H}^+] \ll 1$  in our experiments ( $K_a = 10^{-4.2}$ ),<sup>19</sup>  $k' = k_2K_a$  and  $k_2 = 3.5 \times 10^6 M^{-1} \text{ sec}^{-1}$ .  $k''$  and  $k'''$  correspond to  $k'_1$  and  $k'_2/K'_a$ , respectively.

Since electron transfer by an outer-sphere mechanism would give the products directly, the intermediate must contain both Ru(II) and Cr(III). Thus, detection of an intermediate verifies an inner-sphere path, at least for the reduction of the hydroxo complex. Reduction of the aquo complex may also produce an intermediate; the fact that only a small but strongly varying fraction of the over-all reaction went through the aquo path under our conditions while the effective extinction coefficient of the intermediate was constant demonstrates that step 2 alone cannot account for the formation of the observed intermediate.

Because coordinated  $\text{NH}_3$  does not act as a bridging ligand, the intermediate must have the structure



with  $n = 0, 1$ , or 2. The existence of similar ions is well documented, both as stable entities such as  $(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5^{5+20}$  and as intermediates in electron-transfer reactions.<sup>21</sup> In the present case the observed rate of decomposition is inconsistent with the usual substitution inertia of Cr(III) complexes and must therefore represent breaking of the ruthenium-oxygen bond.

The horizontal lines at each datum point in Figure 2 represent the change in acidity accompanying the decomposition of the intermediate assuming  $n = 1$ . Although in principle  $n$  could be determined from experiments with comparable initial Ru(III) and hydrogen ion concentrations, it is clear that the data of Table VII are inadequate for this purpose. However, the  $k'''$  term in the rate law implies  $n < 2$  for the dominant form of the intermediate, and comparison with  $(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5^{5+}$  for which  $\text{p}K_a = 7.8^{20}$  suggests that under our conditions  $n > 0$ . Thus we conclude that  $n = 1$ .

**Reactions of Carboxylatopentaammineruthenium(III) Complexes.**—The reactions of the carboxylatopentaammineruthenium(III) complexes with  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ , and  $\text{Eu}^{2+}$  provide support for the mechanism proposed for the reaction of  $(\text{NH}_3)_5\text{RuOH}_2^{3+}$  with  $\text{Cr}^{2+}$ . Of the reactions studied, only those of  $\text{Cr}^{2+}$  with the trifluoroacetato, benzoato, and methylterephthalato complexes obey second-order kinetics throughout the range of concentrations examined. The kinetic behavior of the

(18) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959).

(19) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

(20) W. K. Wilmarth, H. Graff, and S. T. Gustin, *J. Am. Chem. Soc.*, **78**, 2683 (1956).

(21) J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

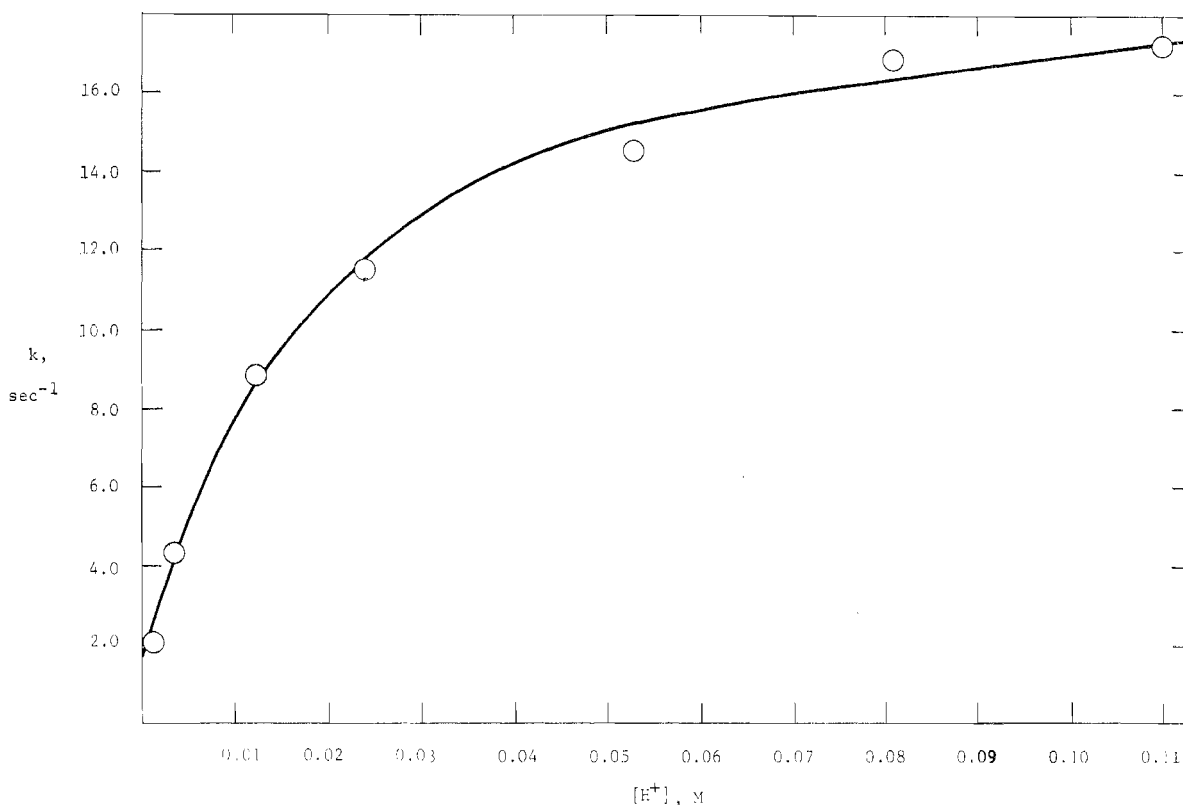
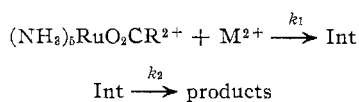


Figure 3.—Variation of  $k_2$  with  $[H^+]$  for the reaction of formatopentaammineruthenium(III) with europium(II).

others was that of consecutive second- and first-order reactions



Int represents an intermediate and  $\text{M}^{2+} = \text{Cr}^{2+}$  ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_4\text{OH}$ ), and  $\text{V}^{2+}$  or  $\text{Eu}^{2+}$  ( $\text{R} = \text{H}, \text{CH}_3, \text{CF}_3$ ). The rate constants  $k_1$  and  $k_2$  are defined by the equations

$$\begin{aligned} -\frac{d[\text{Ru(III)}]}{dt} &= -\frac{d[\text{M}^{2+}]}{dt} = k_1[\text{Ru(III)}][\text{M}^{2+}] \\ -\frac{d[\text{Int}]}{dt} &= \frac{d[\text{Ru(III)}]}{dt} + k_2[\text{Int}] \end{aligned}$$

Treatment of the kinetic data is described in the Experimental Section. Results of these experiments are listed in Tables VIII–X, and activation parameters for several of the reactions are given in Tables XI and XII. The precision of the rate constants which were measured directly is comparable to that for the reactions of the halopentaammineruthenium(III) complexes, but the scatter of the rates which were determined indirectly was somewhat greater.

The rate law for the formation of the intermediate suggests that this step involves the electron transfer. In the chromous and europous reactions the first step is too slow to be limited by substitution on the reductant, but in the vanadous reactions it is too rapid to involve substitution on  $\text{V}^{2+}(\text{aq})$ . Again we conclude that the vanadous reactions are outer sphere.

The intermediates in the reactions of the trifluoro-

acetato complex with  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$  decay at the same rate,  $5.4 \pm 0.1 \text{ sec}^{-1}$ , independent of ionic strength. The small difference in their effective extinction coefficients is probably an ionic strength effect as is observed for  $\text{Ru}(\text{NH}_3)_6^{2+}$ .<sup>22</sup> By contrast, only a lower limit of  $100 \text{ sec}^{-1}$  may be set on the rate of disappearance of any intermediate in the reaction of the trifluoroacetato complex with  $\text{Cr}^{2+}$ .

The rates of decomposition of the intermediates in the reactions of formato- and acetatopentaammineruthenium(III) with  $\text{Eu}^{2+}$  increase with  $[H^+]$  at lower acidities and reach limiting values for  $[H^+] > 0.1 \text{ M}$  (cf. Figures 3 and 4). The limiting rates and effective extinction coefficients of the intermediates in the vanadous reactions are similar to those of the europous reactions, and although measurements with  $\text{V}^{2+}$  were not extensive at lower acidities, a decrease in rate at lower  $[H^+]$  is observed with the formato complex. In the chromous reactions, however, the intermediates decay at rates which are independent of  $[H^+]$ .

That  $\text{Eu}^{2+}$  and  $\text{V}^{2+}$  generate the same intermediate is not unexpected. As a consequence of outer-sphere mechanisms for the  $\text{V}^{2+}$  reactions and the extreme lability of  $\text{Eu}^{2+}(\text{aq})$  and  $\text{Eu}^{3+}(\text{aq})$ , the carboxylato ruthenium(II) complexes must be the immediate products. Since the final ruthenium product is  $(\text{NH}_3)_5\text{RuOH}_2^{2+}$ , the carboxylatoruthenium(II) complexes must be the observed intermediates.

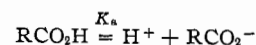
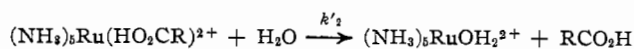
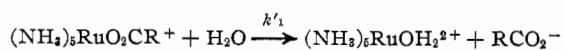
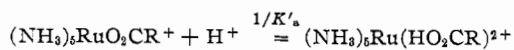
The aquation of the carboxylatoruthenium(II) com-

TABLE VIII  
 RATE CONSTANTS FOR THE REACTIONS OF CARBOXYLATOPENTAAMMINERUTHENIUM(III) COMPLEXES WITH CHROMIUM(II)<sup>a</sup>

Carboxylate	10 <sup>4</sup> [Cr <sup>2+</sup> ], M	10 <sup>4</sup> [Ru(III)], M	[H <sup>+</sup> ], M	10 <sup>-4</sup> k <sub>1</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>2</sub> , sec <sup>-1</sup> (λ, mμ)	10 <sup>-3</sup> ε <sub>int</sub> , M <sup>-1</sup> cm <sup>-1</sup> (λ, mμ)	Temp, °C	
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	0.306	2.06	0.005	2.8	(5.4)	1.3 (270)	10.0	
				2.6	(12.8)	1.3 (270)	17.5	
				3.2	(26.0)	1.2 (270)	25.0	
	0.51	2.76	0.005	2.7	(5.4)	1.4 (295)	10.0	
				2.7	(12.8)	1.5 (295)	17.5	
				3.2	(25.5)	1.3 (295)	25.0	
	0.51	2.81	0.103	2.4	(5.4)	1.5 (295)	10.0	
	1.02	1.92	0.107	2.5	5.4	1.5 (295)	10.0	
	2.04	3.00	0.100	2.9	5.5	1.4 (295)	10.0	
	5.1	1.68	0.010	...	5.4	...	10.0	
	10.2	1.46	0.060	...	12.6	...	17.5	
	8.2	2.81	0.070	...	25.0	...	25.0	
	4.1	2.26	0.090	...	26.0	...	25.0	
	4.1	1.26	0.39	...	28.0	...	25.0	
	HCO <sub>2</sub> <sup>-</sup>	2.04	2.00	0.004	...	2.4	...	25.0
...					1.12	...	17.5	
1.9		1.16	0.094	...	0.53	...	10.0	
0.57		0.87	0.105	16	0.55	...	10.0	
0.38		1.03	0.105	17	0.55	...	10.0	
0.306		2.21	0.005	19	0.55	...	10.0	
1.9		0.69	0.072	0.138	...	...	10.0	
0.95		0.53	0.077	0.135	...	...	10.0	
3.8		0.58	0.062	0.141	...	...	10.0	
2.04		1.53	0.002	0.149	...	...	17.5	
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	5.1	2.69	0.105	0.167	...	...	25.0	
				0.158	...	...	25.0	
				0.154	...	...	17.5	
	25.5	1.58	0.05	0.25 <sup>b</sup>	...	...	25.0	
	12.7	1.58	0.28	0.28 <sup>b</sup>	...	...	25.0	
	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	0.255	1.53	0.12	0.58	...	...	25.0
					0.58	...	...	25.0
		0.51	1.53	0.12	0.58	...	...	25.0
		1.02	1.6	0.115	0.55	...	...	25.0
		1.02	1.25	0.115	0.61	...	...	25.0
		5.1	1.60	0.088	0.53	...	...	25.0
		1.02	1.38	0.004	1.23 <sup>c</sup>	...	...	10.0
		1.02	1.43	0.50	1.44 <sup>c</sup>	...	...	20.0
		1.02	1.60	0.50	1.30 <sup>c</sup>	...	...	25.0
		1.02	1.60	0.50	1.55 <sup>c</sup>	...	...	15.0
HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup>	2.50	1.03	0.005	1.30 <sup>c</sup>	...	...	15.0	
				0.42	29	3.9 (300)	10.0	
				0.39	29	1.4 (410)	10.0	
CH <sub>3</sub> O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> <sup>-</sup>	2.39	2.62	0.104	0.40	28	1.2 (410)	10.0	
				0.50	...	...	10.0	
	2.55	0.517	0.10	0.65	...	...	10.0	
	2.55	0.559	0.10	0.63	...	...	10.0	
	2.55	0.553	0.10	0.725	...	...	20.0	
	1.28	0.597	0.10	0.695 <sup>d</sup>	...	...	10.0	
	1.28	0.597	0.10	0.72 <sup>d</sup>	...	...	18.0	
	1.53	0.626	0.10	0.675	...	...	10.0	
	0.51	0.55	0.50	0.665	...	...	10.0	
	1.02	0.555	0.37	1.20 <sup>b</sup>	...	...	10.0	
0.637	0.52	0.25	1.09 <sup>b</sup>	...	...	10.0		
1.59	0.68	0.12	0.955 <sup>b</sup>	...	...	10.0		
1.59	0.68	0.12	0.89 <sup>b</sup>	...	...	10.0		

<sup>a</sup> Ionic strength 0.12 M except where noted. The rate constants in parentheses were not measured in that experiment but were taken from other experiments for the calculation of the other rate constant and ε<sub>int</sub>. <sup>b</sup> Ionic strength 0.5 M. <sup>c</sup> Ionic strength 1.0 M. <sup>d</sup> [NaI] = 1.1 × 10<sup>-3</sup> M.

plexes, (NH<sub>3</sub>)<sub>5</sub>RuO<sub>2</sub>CR<sup>+</sup>, may be described by the mechanism



$K'_a$  is the dissociation constant of the coordinated carboxylic acid. According to this mechanism the rate law for the formation of (NH<sub>3</sub>)<sub>5</sub>RuOH<sub>2</sub><sup>2+</sup> is

$$\frac{d[(\text{NH}_3)_5\text{RuOH}_2^{2+}]}{dt} = \frac{k'_1 + k'_2[\text{H}]/K'_a}{1 + ([\text{H}^+]/K'_a)}[\text{Int}] = k_2[\text{Int}] \quad (7)$$

TABLE IX  
RATE CONSTANTS FOR THE REACTIONS OF  
CARBOXYLATOPENTAAMMINERUTHENIUM(III) COMPLEXES  
WITH VANADIUM(II)<sup>a</sup>

Carboxylate	10 <sup>2</sup> [V <sup>2+</sup> ], M	10 <sup>4</sup> [Ru- (III)], M	[H <sup>+</sup> ], M	10 <sup>-2</sup> k <sub>1</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>2</sub> , sec <sup>-1</sup>	10 <sup>-2</sup> ε <sub>Int</sub> , M <sup>-1</sup> cm <sup>-1</sup> (λ, mμ)
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	2.4	1.85	0.086	0.56 <sup>b</sup>	...	...
	4.8	1.6	0.071	0.52 <sup>b</sup>	...	...
	4.8	2.43	0.071	0.60 <sup>b</sup>	...	...
	2.4	2.13	0.21	1.2 <sup>c</sup>	...	...
	7.2	2.29	0.32	1.33	...	...
	12.0	1.88	0.39	(1.33)	20.0	2.1 (295)
	14.4	2.12 <sup>d</sup>	0.21	(1.33)	18.1	2.3 (295)
	19.2	3.04	0.08	(1.33)	16.8	1.0 (270)
	28.8	2.29	0.21	(1.33)	17.6	2.1 (295)
	28.8	2.29	0.22	(1.33)	17.4	2.2 (295)
HCO <sub>2</sub> <sup>-</sup>	0.60	0.60	0.105	4.1	...	...
	1.20	0.91	0.104	4.1	...	...
	6.0	2.12	0.069	(4.1)	16.7	1.35 (293)
	6.0	2.37	0.005	(4.1)	7.9	1.5 (293)
	9.0	2.12	0.30	(4.1)	17.6	1.5 (293)
	19.2	1.97	0.076	(4.1)	18.8	1.2 (285)
	19.2	1.97	0.076	(4.1)	18.8	1.2 (285)
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	9.0	0.975	0.46	2.88	(5.4)	1.2 (285)
	1.2	2.19	0.103	2.88	(5.4)	1.3 (285)

<sup>a</sup> Ionic strength 0.5 M and temperature 25°, except where noted. The rate constants in parentheses were not measured in that experiment but were taken from other experiments for the calculation of the other rate constant and ε<sub>Int</sub>. <sup>b</sup> Ionic strength 0.1 M. <sup>c</sup> Ionic strength 0.43 M. <sup>d</sup> Ru(III) as iodide salt.

where [Int] is the total ruthenium(II) carboxylate concentration. The saturation with respect to [H<sup>+</sup>] for R = H and CH<sub>3</sub> indicates complete conversion to (NH<sub>3</sub>)<sub>5</sub>Ru(HO<sub>2</sub>CR)<sup>2+</sup>, i.e., [H<sup>+</sup>]/K'<sub>a</sub> ≫ 1.

A least-squares fit of eq 7 to the experimental rate constants gives the solid lines in Figures 3 and 4. The calculated parameters for the acetato complex are k'<sub>2</sub> = 17.5 sec<sup>-1</sup> and K'<sub>a</sub> = 6.3 × 10<sup>-4</sup>. Since no more than 5% of the acetato complex was ever unprotonated under our conditions, only an upper limit of 5 sec<sup>-1</sup> is set on k'<sub>1</sub> and the uncertainty in K'<sub>a</sub> is rather large. K'<sub>a</sub> may be compared with 1.75 × 10<sup>-5</sup> for acetic acid and 3.25 for protonated acetatopentaquo-chromium(III).<sup>23</sup> For the formatoruthenium(II) complex k'<sub>1</sub> = 1.28 sec<sup>-1</sup>, k'<sub>2</sub> = 20.1 sec<sup>-1</sup>, and K'<sub>a</sub> = 2.02 × 10<sup>-2</sup>.

The absence of a hydrogen ion dependent path for the aquation of (NH<sub>3</sub>)<sub>5</sub>RuOCCF<sub>3</sub><sup>+</sup> is consistent with the reported behavior of the carboxylatopentaamine complexes of Co(III) and Rh(III).<sup>24</sup> For the trifluoroacetato complexes of these metals the aquation rates are virtually independent of [H<sup>+</sup>], but for the acetato complexes a rate term first order in [H<sup>+</sup>] is strongly developed. If K'<sub>a</sub>/K<sub>a</sub> and k'<sub>1</sub>/k'<sub>2</sub> are the same for formic and trifluoroacetic acids, the rate of aquation of (NH<sub>3</sub>)<sub>5</sub>RuO<sub>2</sub>CCF<sub>3</sub><sup>+</sup> is expected to increase by only 1% on increasing [H<sup>+</sup>] from 0.004 to 0.11 M.

Since the intermediates in the reactions of acetato- and formatoruthenium(III) with Cr<sup>2+</sup> are distinctly different from (NH<sub>3</sub>)<sub>5</sub>RuO<sub>2</sub>CH<sup>+</sup> and (NH<sub>3</sub>)<sub>5</sub>-RuO<sub>2</sub>CCH<sub>3</sub><sup>+</sup>, and since no intermediate was detected

TABLE X  
RATE CONSTANTS FOR THE REACTIONS OF  
CARBOXYLATOPENTAAMMINERUTHENIUM(III) COMPLEXES  
WITH EUROPIUM(II)<sup>a</sup>

Carboxylate	10 <sup>4</sup> [Eu <sup>2+</sup> ], M	10 <sup>4</sup> [Ru- (III)], M	[H <sup>+</sup> ], M	10 <sup>-2</sup> k <sub>1</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>2</sub> , sec <sup>-1</sup>	10 <sup>-2</sup> ε <sub>Int</sub> , M <sup>-1</sup> cm <sup>-1</sup> (λ, mμ)
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	4.50	2.13	0.205	...	16.9 <sup>c</sup>	...
	4.80	1.61 <sup>b</sup>	0.099	...	17.5	...
	4.10	1.60 <sup>b</sup>	0.099	...	16.7	...
	9.00	1.48 <sup>b</sup>	0.097	...	18.7	...
	2.38	1.56 <sup>b</sup>	0.103	...	17.5	...
	4.63	0.96	0.056	...	17.3	...
	4.63	1.69	0.0061	...	15.9	...
	6.95	1.79	0.0032	...	14.6	...
	9.25	1.17	0.0024	...	13.3	...
	9.25	1.19	0.0012	...	11.8	...
	8.65	3.00	0.097	...	4.9 <sup>d</sup>	...
	4.63	1.92	0.100	...	4.8 <sup>d</sup>	...
	0.37	0.333	0.105	1.7	...	...
	2.19	2.03	0.104	1.7	(17.5)	1.9 (295)
	0.925	0.66	0.105	1.5	(17.5)	1.8 (295)
HCO <sub>2</sub> <sup>-</sup>	4.62	1.53	0.0053	...	7.1 <sup>e</sup>	...
	9.25	2.31	0.111	...	17.2	...
	13.9	1.60	0.0815	...	16.8	...
	4.63	1.95	0.0553	...	14.5	...
	4.63	1.51	0.0249	...	11.5	...
	4.63	2.07	0.0128	...	8.8	...
	9.25	1.64	0.0035	...	4.3	...
	9.25	1.92	0.0012	...	2.1	...
	0.463	0.38	0.11	4.3	(17.3)	1.2 (293)
	9.25	1.26	0.004	...	5.4	...
	4.63	1.76	0.056	...	5.2	...
	9.25	1.55	0.11	...	5.35	...
	0.463	0.408	0.11	6.9	(5.3)	1.5 (285)

<sup>a</sup> Ionic strength 0.1 M and temperature 25°, except where noted. The rate constants in parentheses were not measured in that experiment but were taken from other experiments for the calculation of the other rate constant and ε<sub>Int</sub>. <sup>b</sup> Ru(III) as I<sup>-</sup> salt. <sup>c</sup> Ionic strength 0.41 M. <sup>d</sup> Temperature 10.0°. <sup>e</sup> Ionic strength 0.5 M.

TABLE XI  
RATE CONSTANTS FOR THE AQUATION OF  
PENTAAMMINERUTHENIUM(II) COMPLEXES,  
(NH<sub>3</sub>)<sub>5</sub>Ru<sup>II</sup>L, AT 25° AND IONIC STRENGTH 0.1-0.5 M

L	k, sec <sup>-1</sup>
HCO <sub>2</sub> <sup>-</sup>	1.28
HCO <sub>2</sub> H	20.1
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	<5
CH <sub>3</sub> CO <sub>2</sub> H	17.5 <sup>a</sup>
CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	5.3
(H <sub>2</sub> O) <sub>5</sub> Cr <sup>III</sup> OH-	(10.5 + 4.5) × 10 <sup>3</sup> [H <sup>+</sup> ]
(H <sub>2</sub> O) <sub>5</sub> Cr <sup>III</sup> OC(CH <sub>3</sub> )O-	25.5 <sup>b</sup>
(H <sub>2</sub> O) <sub>5</sub> Cr <sup>III</sup> OCHO-	2.4 <sup>c</sup>
(H <sub>2</sub> O) <sub>5</sub> Cr <sup>III</sup> OC(CH <sub>3</sub> )O-	>100
(H <sub>2</sub> O) <sub>5</sub> Cr <sup>III</sup> OC(C <sub>6</sub> H <sub>4</sub> OH)O-	29 <sup>d</sup>

<sup>a</sup> ΔH<sup>‡</sup> ≈ 14 kcal mol<sup>-1</sup>, ΔS<sup>‡</sup> ≈ 8 eu. <sup>b</sup> ΔH<sup>‡</sup> = 16.7 kcal mol<sup>-1</sup>, ΔS<sup>‡</sup> = 4 eu. <sup>c</sup> ΔH<sup>‡</sup> = 15.9 kcal mol<sup>-1</sup>, ΔS<sup>‡</sup> = -4 eu. <sup>d</sup> Temperature 10°.

in the reaction of (NH<sub>3</sub>)<sub>5</sub>RuO<sub>2</sub>CCF<sub>3</sub><sup>2+</sup> with Cr<sup>2+</sup> under conditions where (NH<sub>3</sub>)<sub>5</sub>RuO<sub>2</sub>CCF<sub>3</sub><sup>+</sup> would have been observed, we conclude that these reactions are inner sphere. The rates of the reactions of Cr<sup>2+</sup> with the benzoato, *p*-hydroxybenzoato, and methylterephthalato complexes are intermediate between those of the acetato and trifluoroacetato reactions, and their mech-

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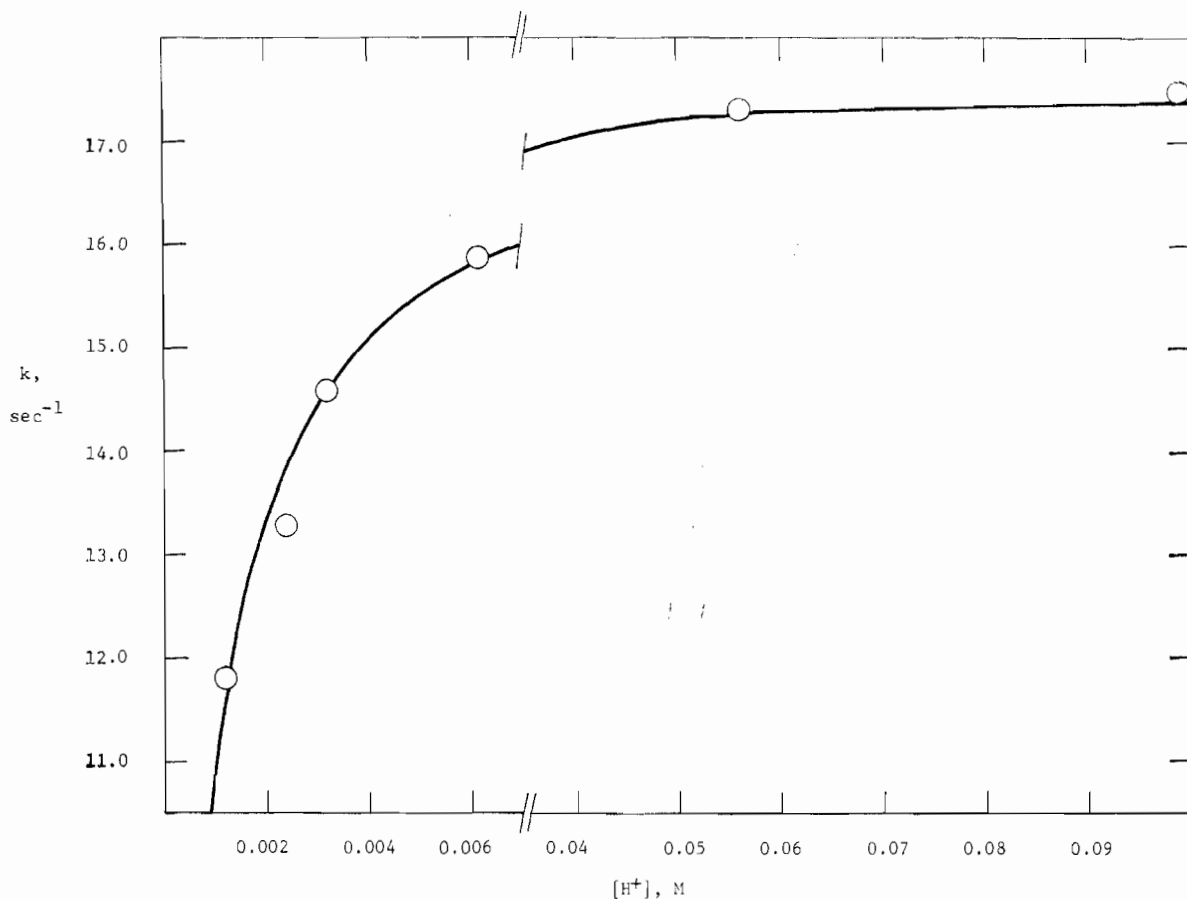


Figure 4.—Variation of  $k_2$  with  $[H^+]$  for the reaction of acetatopentaammineruthenium(III) with europium(II).

TABLE XII  
KINETIC PARAMETERS FOR REACTIONS OF  
CARBOXYLTOPENTAAMMINE COMPLEXES OF COBALT(III)  
AND RUTHENIUM(III) WITH CHROMIUM(II)<sup>a</sup>

Oxidant	$k, M^{-1} \text{ sec}^{-1}$	$k_{rel}$	$\Delta H^\ddagger,$		$\Delta S^\ddagger,$	Ref
			Temp, °C	mol <sup>-1</sup> eu		
$A_5Co(O_2C_2F_3)^{2+}$	0.017	0.8	25	9.3	-33	<i>b</i>
$A_5Co(O_2CC_6H_4OH)^{2+}$	0.13	1.0	25	...	...	<i>c</i>
$A_5Co(O_2CC_6H_5)^{2+}$	0.15	1.2	25	9.0	-32	<i>b</i>
$A_5Co(O_2CC_6H_4CO_2CH_3)^{2+}$	0.17	1.3	25	...	...	<i>d</i>
$A_5Co(O_2C_2H_3)^{2+}$	0.27	2.1	25	7.0	-38	<i>b</i>
$A_5Co(O_2CH)^{2+}$	7.2	55	25	8.3	-27	<i>b</i>
$A_5Ru(O_2C_2F_3)^{2+}$	$1.4 \times 10^3$	0.4	10	1.3	-39	<i>e</i>
$A_5Ru(O_2CC_6H_4OH)^{2+}$	$4.0 \times 10^2$	1.0	10	...	...	<i>e</i>
$A_5Ru(O_2CC_6H_5)^{2+}$	$5.8 \times 10^2$	1.5	25	1.4	-35	<i>e</i>
$A_5Ru(O_2CC_6H_4CO_2CH_3)^{2+}$	$6.6 \times 10^2$	1.7	10	...	...	<i>e</i>
$A_5Ru(O_2C_2H_3)^{2+}$	$2.6 \times 10^4$	6.5	10	1	-34	<i>e</i>
$A_5Ru(O_2CH)^{2+}$	$1.7 \times 10^6$	43	10	...	...	<i>e</i>

<sup>a</sup> A refers to  $NH_3$ ;  $k_{rel}$  is rate relative to that of *p*-hydroxybenzoate complex. <sup>b</sup> Reference 7. <sup>c</sup> R. T. M. Fraser in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 287. <sup>d</sup> R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, **83**, 2242 (1961). <sup>e</sup> This work.

anisms are probably of the same type. It should be mentioned that reactions of  $Cr^{2+}$  and the corresponding cobalt(III) carboxylate complexes are all inner sphere<sup>2</sup> and that the relative rates of the Ru(III) and Co(III) reactions are quite similar (*cf.* Table XII).

Inner-sphere mechanisms require the observed intermediates to be  $\mu$ -carboxylato-ruthenium(II)chromium(III) ions. The magnitudes of the rates and

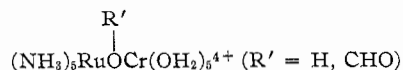
activation parameters (*cf.* Table XI) indicate that decomposition occurs by ruthenium(II) hydrolysis, resulting in transfer of the carboxylate ion to chromium. This conclusion was confirmed by spectrophotometric analysis of the products of the reaction of acetatopentaammineruthenium(III) with  $Cr^{2+}$ . At least 95% of the acetate from the ruthenium(III) complex is found in the chromium(III) product.

An intermediate would not be detected if its decomposition were faster than its formation as is probably the case in the reaction the trifluoroacetato complex with  $Cr^{2+}$ . It is somewhat surprising, however, that an intermediate was observed in the reaction of  $Cr^{2+}$  with the *p*-hydroxybenzoato complex and not with the closely related benzoato and methylterephthalato complexes. (The  $pK_a$ 's of the acids are 4.48, 4.19, and 3.80, respectively.) These complexes were followed at a single wavelength, and intermediates may have escaped detection on this account, but it is unlikely that each system has an isosbestic point for the intermediate and products where the other intermediates have large effective extinction coefficients. If, however, the intermediates containing the less basic benzoate and methylterephthalate ions decompose more than four times as fast as the *p*-hydroxybenzoato intermediate they would not have been detected under our conditions.

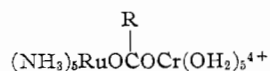
Although both the steric effect of the R group and

the inductive effect of Cr(III) will be important in the hydrolysis of the  $\mu$ -carboxylato-ruthenium(II)chromium(III), the twofold increase in rate for  $(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CH})\text{Cr}(\text{OH}_2)_5^{4+}$  relative to  $(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CH})^+$  leaves little room for a steric effect. On the other hand, the 10-fold increase in rate and more negative  $\Delta S^\ddagger$  for  $(\text{NH}_3)_5\text{Ru}(\text{O}_2\text{CCH}_3)\text{Cr}(\text{OH}_2)_5^{4+}$  relative to the  $\mu$ -formate complex is probably due to the steric effect of the methyl group.

The small steric effect for  $R = \text{H}$  permits comparison of the  $\mu$ -formate and  $\mu$ -hydroxo intermediates. If the two intermediates have similar structures



the rates of hydrolysis should parallel the basicity of  $\text{OR}'^-$  to some extent. The fact that the rate of hydrolysis is four times slower for  $R' = \text{CHO}$  than  $\text{H}$  although  $\text{HCO}_2^-$  is  $10^{10}$ -fold less basic than  $\text{OH}^-$  suggests that the metals are coordinated to different oxygens of the formate ion. Since the size of the  $R$  group should affect the accessibility of the oxygens about equally, the intermediates in the reactions of the other carboxylate complexes with  $\text{Cr}^{2+}$  should have similar structures



For  $R = \text{C}_6\text{H}_4\text{OH}$  or  $\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$  attack by the reductant at the polar group remote from the ruthenium center is possible. Rate measurements were made at an ionic strength of  $0.5 M$  on the reaction of the methylterephthalato complex with  $\text{Cr}^{2+}$  to try to demonstrate a first-order dependence on  $[\text{H}^+]$  that might be characteristic of such a mechanism.<sup>2</sup> Although a small increase (30%) in rate was noted from  $[\text{H}^+] = 0.12$  to  $0.50 M$ , the results are suspect due to the impurity of several of the reagents. Otherwise no evidence was obtained that would suggest attack by  $\text{Cr}^{2+}$  at any position other than the carbonyl oxygen of the coordinated carboxylate.

### Conclusions

**Hydrolysis of Ruthenium(II) Complexes.**—Kinetic parameters for the hydrolysis reactions of the ruthenium(II) complexes observed as intermediates are listed in Table XI. Where intermediates were not detected, lower limits on the aquation rates of the probable initial products may be estimated from the shortest half-times for which the electron-transfer reactions were followed. Thus, for example, we may conclude that the rate of aquation of  $(\text{NH}_3)_5\text{RuCl}^+$  is greater than  $100 \text{ sec}^{-1}$ .

Comparison of aquation rates of ruthenium(II) and cobalt(III) pentaammines is of interest since both are low-spin  $t_{2g}^6$ . The lower limit of 20 on the rate of loss of  $\text{Cl}^-$  relative to acetate from  $\text{Ru}(\text{II})$  is comparable to that for the corresponding  $\text{Co}(\text{III})$  complexes,  $k_{\text{Cl}^-}/k_{\text{CH}_3\text{CO}_2^-} = 10$ .<sup>24,25</sup> Likewise, the rates

of aquation of the carboxylate complexes reflect the basicity of the ligand to about the same extent. However, because the ruthenium(II) complexes are more readily protonated, the acid-catalyzed paths for the carboxylatoruthenium(II) complexes become important at lower acidities.

**Comparison of Ru(III) and Co(III) Electron-Transfer Reactions.**—Kinetic parameters for representative electron-transfer reactions of ruthenium(III) and cobalt(III) amines are listed in Tables VI and XII. The reactions of the ruthenium(III) and cobalt(III)<sup>2,26</sup> pentaammines with  $\text{Cr}^{2+}$  are inner sphere with the possible exceptions of the reactions of  $(\text{NH}_3)_5\text{RuI}^{2+}$  and  $(\text{NH}_3)_5\text{RuOH}_2^{3+}$ . Vanadous ion reacts with cobalt(III) pentaammines by both inner-sphere and outer-sphere mechanisms, the inner-sphere paths approaching substitution-limited rates,<sup>17,27</sup> while the  $\text{Ru}(\text{III})\text{-V}^{2+}$  reactions are outer sphere.

Since inner-sphere and outer-sphere paths cannot be distinguished directly in the europous reactions, indirect criteria based on reactivity patterns are often invoked.<sup>28,29</sup> For the  $\text{Ru}(\text{III})\text{-Eu}^{2+}$  reactions the pattern of relative rates is more or less intermediate between those of the outer-sphere vanadous and inner-sphere chromous reactions. In view of the Marcus theory,<sup>30</sup> this in itself is suggestive of inner-sphere mechanisms for the  $\text{Ru}(\text{III})\text{-Eu}^{2+}$  reactions.

Outer-sphere reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  by either  $\text{Cr}^{2+}$  or  $\text{V}^{2+}$ <sup>1,31</sup> is a factor of  $10^6$  faster than reduction of  $\text{Co}(\text{NH}_3)_6^{3+}$ ,<sup>32</sup> and for both  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Co}(\text{NH}_3)_6^{3+}$  the vanadous reaction is somewhat faster. A striking inversion in reactivity occurs in the reactions of the halopentaammines with  $\text{Cr}^{2+}$ . The reactions of the halocobalt(III) complexes<sup>33</sup> are a factor of  $10^{11}$  faster than the  $\text{Co}(\text{NH}_3)_6^{3+}\text{-Cr}^{2+}$  reaction and  $10\text{-}10^4$ -fold faster than the corresponding  $\text{Ru}(\text{III})$  reactions which show only modest increases in rate relative to the  $\text{Ru}(\text{NH}_3)_6^{3+}\text{-Cr}^{2+}$  reaction. The relative rates (chloro:bromo:iodo) are roughly  $10^2:10:1$  for the  $\text{Ru}(\text{III})$  reactions and  $1:2:5$  for the  $\text{Co}(\text{III})$  reactions. In contrast with their reactivities, the potentials of the  $(\text{NH}_3)_5\text{RuOH}_2^{2+,3+}$  and  $(\text{NH}_3)_5\text{CoOH}_2^{2+,3+}$  couples<sup>22,34</sup> are similar, and the relative affinities of  $(\text{NH}_3)_5\text{RuOH}_2^{3+}$  and  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$  for  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ <sup>11,29</sup> are about the same.

Another inversion in reactivity occurs in the reactions of the carboxylatopentaamine complexes with  $\text{Cr}^{2+}$ . The relative rates of the ruthenium and cobalt reactions are essentially the same, but the former are about  $10^5$ -fold faster (*cf.* Table XII). The rates relative to those for the respective hexaamine- $\text{Cr}^{2+}$  reactions, however, are still greater for cobalt. The reactivity

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pattern of the carboxylatopentaamminecobalt(III)-Cr<sup>2+</sup> reactions, hence the corresponding Ru(III)-Cr<sup>2+</sup> reactions, is determined by steric and inductive effects.<sup>35,36</sup> The fact that both the cobalt and ruthenium reactions are sensitive to these effects to the same extent suggests that the influence of the R group is limited to the formation constants for the binuclear Ru(III)-Cr(II) and Co(III)-Cr(II) ions, and that the structures of these ions are the same for both cobalt and ruthenium. Thus we conclude that carboxylate ions function as three-atom bridging groups for Co(III) as well as for Ru(III).

Comparison of the kinetic parameters listed in Tables VI and XII shows that the variations in specific rate are due mainly to differences in  $\Delta H^\ddagger$  whereas with several exceptions  $\Delta S^\ddagger$  is within 5 eu of -32 eu. If the electronic interaction between the acceptor orbital of the oxidant and the donor orbital of the reductant in the activated complex were less than about 0.5 kcal, the probability for electron transfer would be less than 1, resulting in a negative contribution to  $\Delta S^\ddagger$ . Since the activation entropies listed in Tables VI and XII are substantially constant, the corresponding probabilities cannot be very different. The interaction energies, however, are expected to be quite sensitive to whether the mechanism is inner sphere or outer sphere, the nature of the bridging group, and the electronic configuration of the oxidant and reductant. The fact that  $\Delta S^\ddagger$  is insensitive to these factors while the specific rates vary by a factor of 10<sup>11</sup> implies that in every case the interaction energy is  $\geq 0.5$  kcal, *i.e.*, the reactions are adiabatic.

The reduction of cobalt(III) amines requires either a change in spin multiplicity to give  $t_{2g}^5e_g^2$  cobalt(II) immediately or considerable tetragonal distortion to stabilize the configuration  $t_{2g}^6e_g^1$  initially. The fact that the experimental activation entropies show no evidence of a low probability associated with reduction of  $\text{Co}(\text{NH}_3)_6^{3+}$  suggests that the path of lowest  $\Delta G^\ddagger$  gives  $t_{2g}^6e_g^1$  cobalt(II) as the initial product. In any case outer-sphere reduction of  $\text{Co}(\text{NH}_3)_6^{3+}$  is expected to be slower than that of  $\text{Ru}(\text{NH}_3)_6^{3+}$  for which addition of a  $t_{2g}$  electron requires no prior spin change and only a symmetric expansion of the first coordination sphere.

Similarly, outer-sphere vanadous reactions are faster than outer-sphere chromous reactions. Apparently the more negative  $\Delta G^\circ$  for the latter are offset by the larger inner-sphere readjustments required to transfer an  $e_g$  electron from tetragonally distorted  $\text{Cr}^{2+}(\text{aq})$  than to transfer a  $t_{2g}$  electron from  $\text{V}^{2+}(\text{aq})$ .

The possibility of observing intermediates in the reactions of ruthenium(III) pentaammines is clearly the result of the relative substitution inertia of ruthenium(II), and the detection of intermediates in the Ru(III)-Cr<sup>2+</sup> reactions demonstrates that transfer of the bridging ligand in inner-sphere reactions of ruthenium(III) is incidental to electron transfer. The observation of similar intermediates in reactions of cobalt(III) pentaammines is precluded by the lability of cobalt(II). However, the breaking of the cobalt-bridging ligand bond in inner-sphere reactions with Cr<sup>2+</sup> may be essentially complete in the activated complex. Isotopic fractionation studies on the reaction of  $(\text{NH}_3)_6\text{CoOH}^{2+}$  with Cr<sup>2+</sup> demonstrate quite strong stretching of the Co-O but not the Co-N bonds in the activated complex,<sup>37</sup> and the initial product may well be five-coordinate  $t_{2g}^6e_g^1$  cobalt(II).

The readjustments in the chromium coordination sphere are complementary to those of the cobalt(III) complex since Cr<sup>2+(aq)</sup> is tetragonally distorted and the chromium(III) product is essentially octahedral. In an outer-sphere reaction these readjustments must occur independently in the two reactants. However, when the oxidant and reductant have an atom common to both their coordination spheres, the readjustments can be brought about by movement of the bridging atom or ion away from the cobalt toward the chromium center. At the same time interaction of the Co(III) and Cr(II)  $e_g$  orbitals *via* orbitals of the bridging atom may further stabilize the transition state.

These factors are less important in the reduction of Ru(III) complexes, leading to only modest increases in rate by inner-sphere paths. Stretching of the ruthenium-bridging ligand bond is not as important, and interaction of the Ru(III)  $t_{2g}$  and Cr(II)  $e_g$  orbitals *via* a single atom is expected to be less than the interaction between Co(III) and Cr(II)  $e_g$  orbitals. The overlap of the  $t_{2g}$  acceptor and  $e_g$  donor orbitals would be zero for a linear Ru-ligand-Cr configuration, but there probably is sufficient overlap for electron transfer when the Ru-ligand-Cr is angle only slightly less than 180°.

The relative rates of the reactions of the halopentaammineruthenium(III) complexes with Cr<sup>2+</sup> may parallel Ru(III)  $t_{2g}$ -halide  $p\pi$  overlap in the order Cl > Br > I, while the rates of the corresponding Co(III)-Cr<sup>2+</sup> reactions increase with decreasing Co(III)-halide bond strength and increasing Co(III)  $e_g$ -ligand  $\sigma$  overlap in the opposite order, I > Br > Cl > F. It has been noted that the relative insensitivity of the cobalt reactions to the different halide ions as bridging ligands may imply that the rates of these reactions approach the limit for substitution on Cr<sup>2+</sup>.<sup>33</sup>

Since the Ru(III)  $t_{2g}$  acceptor orbital can overlap directly with the carboxylate  $\pi$  system, the three-atom carboxylate group and halide ions are comparable bridging groups in the Ru(III)-Cr<sup>2+</sup> reactions. In the reactions of the carboxylatopentaamminecobalt(III) complexes with Cr<sup>2+</sup>, however, the complementary readjustments in the cobalt and chromium coordination spheres cannot be brought about as efficiently by the three-atom carboxylate group as changes in either the

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Co-O or Cr-O bond affect the other only indirectly. This factor and the decreased overlap of the Co(III) and Cr(II)  $e_g$  orbitals *via* the carboxylate  $\pi$  system make the carboxylate ions less effective than halide ions in the Co(III)-Cr<sup>2+</sup> reactions by a factor of about 10<sup>7</sup>.

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## Preparation and Stereochemistry of Bis-Chelate Chromium(II), Manganese(II), Iron(II), and Cobalt(II) Complexes of the Types M-O<sub>4</sub> and M-O<sub>2</sub>S<sub>2</sub>

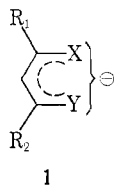
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A series of monomeric bis-chelate metal(II) complexes derived from the  $\beta$ -difunctional ligand **1** with X = Y = O and X = O, Y = S has been prepared and their stereochemistry has been established in the crystalline state and in solutions of noncoordinating solvents. The bis(dipivaloylmethanido) complexes Cr(dpm)<sub>2</sub> and Mn(dpm)<sub>2</sub> have been synthesized for the first time and are members of an extensive series of M(dpm)<sub>2</sub> complexes, M = Cr(II)-Zn(II), of known structure. Cr(dpm)<sub>2</sub> is shown to be planar. The monothio analogs Fe(Sdpm)<sub>2</sub> and Co(Sdpm)<sub>2</sub> have also been prepared. The former, like Fe(dpm)<sub>2</sub>, is tetrahedral but the latter is planar in the solid and exhibits a planar  $\rightleftharpoons$  tetrahedral equilibrium in chloroform solution, in contrast to the tetrahedral and planar structures of Co(dpm)<sub>2</sub> and bis(dithioacetylacetonato)cobalt(II), respectively, in both phases. Several other bis(monothio- $\beta$ -diketonato)cobalt(II) complexes are shown to be tetrahedral in both the solid and solution phases. Several stereochemical patterns of four-coordinate complexes which may be recognized from the results of this and other investigations are summarized.

### Introduction

In the course of investigating the stereochemistry of monomeric bis-chelate metal(II) complexes, we have utilized the  $\beta$ -difunctional ligand **1**. The advantage of this ligand system, as emphasized previously,<sup>2</sup> lies



in the relative synthetic ease by which the donor atoms or groups X and Y and the terminal substituents R<sub>1</sub> and R<sub>2</sub> can be varied. In order to clarify certain of the factors which govern the preferential stability of the planar and tetrahedral stereoisomers, we are currently engaged in an investigation of series of bis-chelate complexes of titanium(II) through zinc(II) derived from **1**. A particular advantage of **1** is that alterations in the donor atoms X and Y are unlikely to produce significant, purely steric effects on the relative stabilities of stereoisomers of a given metal ion, with the consequence that structural differences can be related to the electronic properties of various donor-atom sets as implicated in this ligand system. Further, ligands of this type are known or are potentially able to form complexes with a variety of divalent metal ions,

thereby allowing stereochemistry to be investigated as a function of the coordinated metal ion in series of complexes possessing constant ligand structure. This report is concerned with the preparation and stereochemistry of monomeric complexes having X = Y = O and X = S, Y = O.

Bis-chelate complexes of cobalt(II), nickel(II), copper(II), and zinc(II) derived from **1** with X = Y = O have been thoroughly investigated and important information concerning their electronic and structural properties has been collected.<sup>3</sup> These complexes, especially the acetylacetonates, are polymeric in the solid state and in solutions of noncoordinating solvents. Bulky terminal substituents tend to depress association but the only ligand which uniformly produces monomeric species is dipivaloylmethane (**1**, R<sub>1</sub> = R<sub>2</sub> = *t*-C<sub>4</sub>H<sub>9</sub>).<sup>4</sup> Hence, the series of complexes Fe(dpm)<sub>2</sub>,<sup>5,6</sup> Co(dpm)<sub>2</sub>,<sup>7,8</sup> Ni(dpm)<sub>2</sub>,<sup>9,10</sup> Cu(dpm)<sub>2</sub>,<sup>9,11</sup> and Zn(dpm)<sub>2</sub><sup>7</sup>

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(4) The following abbreviations of the ligand anions **1** are used throughout: acac, acetylacetonate; Sacac, monothioacetylacetonate; SacSac, dithioacetylacetonate; bzac, benzoylacetonate; Sbzac, thiobenzoylacetonate; dpm, dipivaloylmethanide; Sdpm, monothiodipivaloylmethanide; Sdbm, monothiodibenzoylmethanide.

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