the rate by a factor of ~18 and 5 M perchloric acid raising the rate by a factor of ~90.

With the activation parameters evaluated for the reaction of chromium(II) ion with chlorochromium(III) ion, one can make a direct comparison of these quantities with those evaluated for the reaction of mercury(II) ion with chlorochromium(III) ion. Espenson and Birk[22] evaluated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the latter reaction to be 18 kcal mol^{-1} and -5 cal mol^{-1} deg^{-1}, respectively, for solutions with ionic strength 1.0 M. Although the difference in ionic strength makes the comparison somewhat uncertain, the rather dramatic differences are not obscured by this uncertainty. The activation energy is much greater for the mercury(II) reaction, but the entropy of activation is much less negative. There is evidence that the reaction of mercury(II) with chlorochromium(III) ion produces pentaaquochromium(III) ion as an intermediate;[23] it seems that a reaction producing this unstable intermediate would have a high activation energy. In each of the reactions, however, the aquometal ion of charge 2+ (mercury(II) and chromium(II)) must lose a water molecule before forming the activated complex, so the differences of the values of $\Delta H^{\ddagger}$ also reflect differences in the enthalpy of formation of these species from the stable aquometal ions. Corresponding differences between the activation parameters for formation of the two analogous activation complexes $\{(H_3N)_5CoBrHg^{4+}\}^{\ddagger}$ and $\{(H_3N)_5CoBrCr^{4+}\}^{\ddagger}$ have been discussed by Ogard and Taube[24] and by Taube.[25]

(22) J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).

(23) S. P. Ferraris and E. L. King, *J. Am. Chem. Soc.*, **92**, 1215 (1970).

(24) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

(25) H. Taube, *Advan. Inorg. Chem. Radiochem.*, 1, 28 (1959).

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Exchange of Chromium between Chromium(II) and Fumaratochromium(III) and Related Reactions

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The reactions of chromous ion with fumaratopentaaquochromium(III), *cis*-fumaratoaquotetraamminecobalt(III), and *cis*-fumaratoaquobis(ethylenediamine)cobalt(III) have been studied. For the last complex the rate law has the form $-d[Cr^{2+}]/dt = (k_{-h}'[H^+]^{-1} + k_o + k_h'[H^+])[Cr^{2+}][Oxid]$, while for the first two complexes, the k_{-h}' and k_o terms suffice to express the variation of rate with $[H^+]$ in the range 0.1–1.0 M. The values of k_o at 25° for the three complexes, respectively, are ~3, 61, and 9.1 M^{-1} sec^{-1}. The relative insensitivity of rate to change in identity of the oxidizing agent is taken as indicating a stepwise mechanism for electron transfer. It is inferred that the activated complex corresponding to the k_{-h}' term is doubly bridged with OH^- and the adjacent carboxyl of the fumarate serving as bridging groups. The role of the proton in the k_h' term is interpreted as that of stabilizing the radical intermediate derived from the fumarate. This interpretation does not make obvious, however, why the k_h' term appears for one cobalt complex but not the other.

Comparisons[1] of the rate of reduction by chromous ion of isonicotinamidepentaamminecobalt(III) and isonicotinamidepentaaquochromium(III) have suggested that in these systems the electron transfers by a radical ion or stepwise mechanism. It seemed to us worthwhile to extend the comparison to other ligands featuring conjugated bond systems. We selected fumarate ion because considerable work has already been devoted to it with pentaamminecobalt(III) as the acceptor center[2-5] and because basic issues having to do not only with the mechanism of electron transfer but also with the configuration of the activated complex remain unresolved. Whereas with isonicotinamide as ligand, the latter issue can be settled by determining the identity of the immediate products of the reaction, with fumarate this direct method fails because the ligand is symmetrical. The ligand deserves attention also because the rate of reduction of acid fumaratopentaamminecobalt(III) by chromous ion shows a term first order in $[H^+]$ and the role of the proton in the activated complex is not understood. In making comparisons between acceptor centers we have not limited ourselves to studies with pentaaquochromium(III) but have extended the investigation to aquotetraamminecobalt(III) and aquobis(ethylenediamine)cobalt(III).

Experimental Section

Materials.—Stock lithium perchlorate solutions were prepared from two sources, commercial lithium perchlorate obtained from G. F. Smith Co. and that obtained by adding small portions of Baker Analyzed reagent grade lithium carbonate to 6 F perchloric acid solutions. The product obtained from both sources was recrystallized twice from aqueous solution before final dilution. An oxidizing component is often present in perchlorate solutions, but the conservation of chromous ion in the exchange experiments shows that this complication was not a factor in the present work.

Chromium(III) perchlorate was prepared by dissolving Mal-

(1) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).

(2) H. Taube, *ibid.*, **77**, 4481 (1955).

(3) R. T. M. Fraser, D. K. Sebera, and H. Taube, *ibid.*, **81**, 2906 (1959).

(4) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(5) J. K. Hurst and H. Taube, *ibid.*, **90**, 1178 (1968).

linckrodt Analytical reagent grade potassium dichromate (0.5 mol) in a solution of 350 ml of concentrated (70–72%) perchloric acid in 4500 ml of water. The potassium dichromate was reduced by slow addition of 180 ml (1.54 mol) of a 30% solution of hydrogen peroxide. After boiling to remove the excess hydrogen peroxide and reducing the volume to 1 l., the solution was cooled to 0°, and the precipitate of potassium perchlorate was filtered off. Solutions of chromous ion were obtained from chromium(III) perchlorate solutions by reduction with amalgamated zinc under a nitrogen atmosphere. Labeled chromium(II) perchlorate solutions were prepared as described by Deutsch.[6]

Fumaratopentaaquochromium(III) perchlorate was formed by reaction of fumaratopentaamminecobalt(III) with chromous ion. Fumaratopentaamminecobalt(III) perchlorate (0.06 mol), prepared by the method of Sebera and Taube,[4] was dissolved in 3 l. of water and 45 ml of 70–72% perchloric acid was added. After deoxygenating the solution by bubbling nitrogen through it for 1 hr, 46 ml of a solution 1.1 M in chromium(II) perchlorate and 0.1 F in perchloric acid was slowly added with stirring. The reaction mixture was kept under nitrogen for 10 min and then diluted to 5 l. The resulting solution was passed through an ion-exchange column. To minimize column hydrolysis the low-acid–low-temperature technique described by Deutsch[6] was used to elute the fumarate complex. An aliquot of the resulting solution, when diluted 25 times and passed through a new ion-exchange column in the same way as before, ran as a single band with no detectable formation of $Cr(H_2O)_6^{3+}$. The concentration of the complex in solution was assumed to be equal to the total chromium concentration.

trans-Dichlorobis(ethylenediamine)cobalt(III) perchlorate was obtained by a modification of the methods of Linhard and Stirn[7] and of Bailar.[8] Ethylenediamine (1.2 kg of a 10% solution) was added, with stirring, to a solution of 320 g of $CoCl_2 \cdot 6H_2O$ in 1 l. of water. A stream of air was passed through the solution for 10 hr, and, after the oxidation was complete, 700 ml of concentrated hydrochloric acid and 120 g of sodium perchlorate were added. The mixture was heated in a water bath until the brown precipitate formed was replaced by green crystals. After cooling to 0° the green crystals were filtered off, washed with cold water, and dried at 105°. *cis*-Fumaratoaquobis(ethylenediamine)cobalt(III) perchlorate was prepared by suspending carbonatobis(ethylenediamine)cobalt(III) perchlorate[7] (0.033 mol) in 50 ml of water. Concentrated perchloric acid (8 ml) was added and, after gas evolution had ceased, the solution was added to a mixture of 0.30 mol of fumaric acid and 0.22 mol of sodium hydroxide in 500 ml of water. The resulting solution was heated to 70° and kept at that temperature for 1 hr. The reaction mixture was then cooled to room temperature and 27 ml of concentrated perchloric acid was added. The precipitate of fumaric acid that formed was filtered off and the filtrate was diluted to 3 l. and passed through an ion-exchange column. The column was eluted with a solution 1.99 M in lithium perchlorate and 0.01 M in perchloric acid. The first of three bands eluted was identified as the *trans*-diacido complex (the assignment of structures is discussed below), the second as the desired *cis*-fumaratoaquobis(ethylenediamine)cobalt(III) complex, and the third band as the diaquo complex.

Despite several attempts to crystallize the desired complex, it was not possible to isolate it in the solid form. Hence its solutions as eluted were used for kinetic measurements, and the concentration of the complex was considered to be equal to the total cobalt concentration.

cis-Fumaratoaquotetraamminecobalt(III) perchlorate was prepared by suspending carbonatotetraamminecobalt(III)[9] (0.1 mol) in 100 ml of water and adding 23 ml of concentrated perchloric acid. After all effervescence had ceased, the solution was added to 200 ml of water containing 0.16 mol of sodium hydroxide and 0.11 mol of fumaric acid. The reaction mixture was kept at 70° for 1 hr (longer heating times lowered the yield because of the formation of an unidentified insoluble cobalt compound believed to be a polymeric species). After cooling the solution to room temperature, 6.5 ml of concentrated perchloric acid was added; the reaction mixture was then filtered and the components of the filtrate were separated by ion-exchange chromatography. The first of three bands eluted with a 1.3 F lithium perchlorate 0.2 F perchloric acid solution was identified as *trans*-difumaratoaquotetraamminecobalt(III) ion, and the third band, as the diaquo complex. The *cis*-fumaratoaquotetraamminecobalt(III) fraction was diluted 25 times and absorbed on a new ion-exchange column. Upon elution with a solution 0.8 F in lithium perchlorate and 0.2 F in perchloric acid, two components were obtained. The first one was not identified; the second one was identified as the *cis*-fumaratoaquotetraamminecobalt(III) ion.

Several attempts to recrystallize the *cis* isomer gave the same insoluble cobalt compound obtained when the reaction mixture was heated for more than 1 hr at 70°. Accordingly, the solutions of *cis* isomer, as eluted from the ion-exchange column, were used for kinetic measurements. As before, the complex concentration was considered to be equal to the total cobalt concentration.

Stock solutions of *cis*-fumaratoaquobis(ethylenediamine)cobalt(III), *cis*-fumaratoaquotetraamminecobalt(III), and fumaratopentaaquochromium(III) were kept at 0° for 10 days without noticeable aquation or isomerization.

Analyses.—The total chromium and perchlorate concentrations of solutions, as well as the acid concentration of solutions of complexes other than hexaaquochromium(III), were determined as described in the literature.[6]

The concentration of free acid in hexaaquochromium(III) solutions was determined by the method of King and Neptune,[10] and the total Co(II) and Co(III) concentrations were determined by Kitson's method.[11] The concentration of Cr(II) in a solution was assumed to be equal to the total chromium concentration of the solution from which it was made.

Apparatus and Methods.—All spectra were taken using a Cary Model 15 recording spectrophotometer.

Temperature control was obtained using two Forma-Temp refrigerated, constant-temperature baths. The temperature of the water in these two baths was held to ±0.1°.

The apparatus used to prepare and mix air-sensitive labeled Cr(II) solutions was as described in ref 6.

For the tracer experiments an approximate volume of labeled Cr(II) solution was added, by means of a syringe, to a known volume of stock fumaratopentaaquochromium(III) solution which had previously been mixed with a solution containing lithium perchlorate and perchloric acid, in the necessary amounts to give the desired ionic strength and acid concentration, and purged with oxygen-free nitrogen for at least 1 hr. A second syringe was used to take aliquots of the reaction mixture at different times, usually six in less than 2.5 min. The reaction was quenched by injecting each of these aliquots into a deoxygenated 0.01 F oxalatopentaamminecobalt(III) perchlorate solution.[6] The components of the quenched solution were separated by ion-exchange chromatography and the specific activity of the chelated oxalatochromium(III) complex, which corresponded to the specific activity of the Cr(II) ion in the reaction mixture, was determined. At the end of the exchange experiment a total chromium analysis was performed and from this and the known amount of fumaratochromium(III) used the exact amount of labeled Cr(II) added was calculated. Concentrations of Cr(II) and fumaratoaquochromium(III) ions ranged from 2.4×10^{-3} to 5.0×10^{-4} M, respectively.

Radioactive samples were counted on a Nuclear-Chicago Model No. 8785 analyzer–scaler coupled with a Nuclear-Chicago DS 202 (V) well-scintillation detector.

The reaction of chromium ion with *cis*-fumaratoaquobis(ethyl-

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[6] E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

[7] M. Linhard and G. Stirn, *Z. Anorg. Allgem. Chem.*, **268**, 116 (1952).

[8] J. C. Bailar, *Inorg. Syn.*, **2**, 222 (1946).

[9] G. Schlessinger, *ibid.*, **6**, 173 (1962).

[10] E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

[11] R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

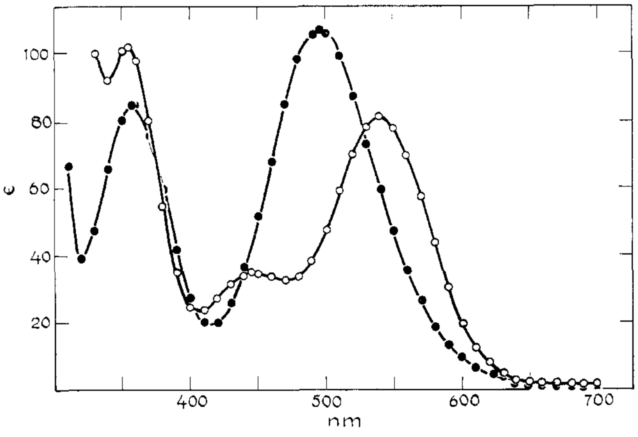

Figure 1.—Absorption spectra of *cis*-$(en)_2Co(H_2O)FuOH^{2+}$ (●) and *trans*-$(en)_2Co(FuOH)_2{}^+$ (○) in 0.1 M $HClO_4$ at 25° and μ = 1.50.

enediamine)cobalt(III) and *cis*-fumaratoaquotetraamminecobalt(III) ions was studied by the stopped-flow technique. The apparatus used was a modification[12] of the one designed by Sutin and coworkers.[13]

Results

Characterization of Species.—The fumaratopentaaquochromium(III) ion had been prepared before.[4,5]

As pointed out in the Experimental Section, when the reaction mixture for preparation of *cis*-fumaratoaquobis(ethylenediamine)cobalt(III) was passed through an ion-exchange column, three bands were obtained. The first of the three bands was readily eluted and gave a solution from which a solid crystallized. This solid was recrystallized from a diluted perchloric acid solution. It possessed the absorption spectrum characteristic of a *trans* isomer[14] (see Figure 1 and Table I). *Anal.* Calcd for $(C_2H_8N_2)_2Co(C_4H_3O_4)_2ClO_4$: C, 28.33; H, 4.37; Cl, 6.97; N, 11.01. Found C, 28.09; H, 4.60; Cl, 6.92; N, 11.09. On the basis of these results the ion eluted in the first band was taken to be *trans*-bis(bifumarato)bis(ethylenediamine)cobalt(III).

Table I

Absorption Characteristics of Bis(ethylenediamine)cobalt(III) Ions at 25°

Substituents	$\lambda_{max}{}^a$	ϵ^b	λ_{max}	ϵ	λ_{max}	ϵ	Ref
cis-$(H_2O)_2$	355	66.1			495	70.8	14
cis-$(H_2O)OAc^c$	360	77.6			498	100.0	14
cis-$(H_2O)FuOH^d$	360	84.9			498	106.7	This work
trans-$(H_2O)_2$	349	53.7	441	37.2	545	33.1	14
trans-$(H_2O)OAc$	355	66.1	445	32.4	543	51.3	14
trans-$(FuOH)_2$	354	102.3	445	35.3	539	81.9	This work

[a] Wavelengths in nm. [b] Extinction coefficients in M^{-1} cm^{-1}. [c] AcO represents the acetate ligand. [d] FuOH represents the fumarate ligand.

The second band, which was eluted at a rate corresponding to a +2 ion, showed an absorption spectrum similar to that of known *cis* isomers[14] (see Figure 1 and Table I). On this basis the second component was taken to be the *cis*-fumaratoaquobis(ethylenediamine)cobalt(III) ion. The possibility that this compound was *cis*-hydroxoaquobis(ethylenediamine)cobalt(III) can be ruled out because at the pH of the eluent, ~2, the diaquo complex, which has pK_a = 6.06, is overwhelmingly favored over the hydroxoaquo form.[15]

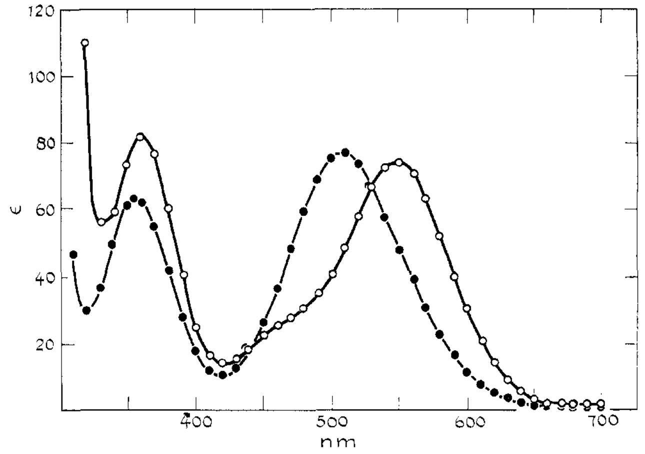

Figure 2.—Absorption spectra of *cis*-$(NH_3)_4Co(H_2O)FuOH^{2+}$ (●) and *trans*-$(NH_3)_4Co(FuOH)_2{}^+$ (○) in 0.1 M $HClO_4$ at 25° and μ = 1.50.

The same criterion was used to identify the products obtained in the preparation of *cis*-fumaratoaquotetraamminecobalt(III). The first band obtained in the ion-exchange separation gave a solution from which a solid crystallized. After recrystallization from aqueous perchloric acid, the elemental analysis was made. *Anal.* Calcd for $(NH_3)_4Co(C_4H_3O_4)_2ClO_4$: C, 21.04; H, 3.98; Cl, 7.76; N, 12.27. Found: C, 20.91; H, 3.98; Cl, 7.87; N, 12.25. The absorption spectrum was similar to that of a *trans* isomer[16] as can be seen in Figure 2 and Table II. These results led to the conclusion that the species contained in this band was the *trans*-bis(bifumarato)tetraamminecobalt(III) ion.

Table II

Absorption Characteristics of Tetraamminecobalt(III) Ions at 25°

Substituents	$\lambda_{max}{}^a$	ϵ^b	λ_{max}	ϵ	λ_{max}	ϵ	Ref
cis-$(H_2O)_2$	355	47			503	56	16
cis-$(H_2O)OAc$	355	50			510	67	16
cis-$(H_2O)FuOH$	355	63.2			509	76.4	This work
(*trans*-$OAc)_2$	363	66	470	25	550	62	16
(*trans*-$FuOH)_2$	361	81.3	468	27.6	547	73.6	This work

[a] Wavelengths in nm. [b] Extinction coefficients in M^{-1} cm^{-1}.

The second band, when passed through an ion-exchange column, again gave two components which were eluted at somewhat similar rates. The first component eluted was not identified; the second one gave the absorption spectrum expected for a *cis* isomer[16] (see Figure 2 and Table II) and was considered to be the *cis*-fumaratoaquotetraamminecobalt(III) ion. As before, the acidity of the eluent, in this case 0.2 M H^+, eliminated the possibility of the second band being the *cis*-hydroxoaquotetraamminecobalt(III) ion.

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

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

(14) V. Carunchio, G. Illuminati, and G. Ortaggi, *ibid.*, **6**, 2168 (1967).

(15) V. Carunchio, G. Grassini-Strazza, G. Ortaggi, and C. Padiglione, *J. Inorg. Nucl. Chem.*, **27**, 841 (1965).

(16) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).

Further confirmation of the assigned structures for the cobalt(III) complexes was obtained from a study of the stoichiometry of the reaction and from kinetic measurements. The identification of the chromium-containing product as the fumarato complex indicated the presence of the fumarato ligand in the Co(III) complexes and the linearity of the rate plots demonstrated that only one Co(III) species was present in each of the stock solutions. Furthermore, the acid dependence found, which is characteristic of *cis*-aquo complexes, implied the presence of a water molecule *cis* to the fumarate ligand.

Stoichiometry.—Aquation of the reactants and/or the products, although thermodynamically favored, is expected to be so slow that it should not be a major reaction during the time the electron-transfer reactions take place. Hurst and Taube[5] have confirmed this for the case of fumaratopentaaquochromium(III). They found that for this complex the specific rate constant for acid hydrolysis at 45° and 1 *M* acid is 7.5×10^{-6} sec^{-1}. On the basis of the rate constants for acid hydrolysis for several amminecobalt(III) complexes[17] this is expected to be true also for the Co(III) complexes considered here and is confirmed by the study of the stoichiometry of the reactions.

For *cis*-fumaratoaquobis(ethylenediamine)cobalt(III) and *cis*-fumaratoaquotetraamminecobalt(III) stoichiometries were determined by analysis of the spent solutions for cobaltous ion and by determination of the amount of fumaratopentaaquochromium(III) formed. The latter was determined by separating the components of the reaction mixture using ion-exchange chromatography. It was found that at least 89% of the chromous ion, when the Co(III) complex was in excess, gave fumaratopentaaquochromium(III). Some aquation of the chromium product in the column is expected because a long column is needed for good separation of the species. As to stoichiometry with respect to cobalt, when the reactant in excess was chromous ion, 95% of the total cobalt was recovered as cobaltous ion.

The Chromium(II)–Fumaratopentaaquochromium(III) Isotope Exchange Reaction.—The McKay equation[18] was applied to the data obtained for the exchange process

$$Cr^{*2+} + CrFuOH^{2+} = Cr^{2+} + Cr^{*}FuOH^{2+} \qquad (1)$$

Assuming that the exchange reaction 1 follows the rate law

$$\text{rate} = k[Cr^{2+}][CrFuOH^{2+}] = kab \qquad (2)$$

then

$$k = \frac{-2.303 \log (1 - F)}{t(a + b)}$$

and k can be determined from the slope of a plot of log $(1 - F)$ *vs.* time with $(1 - F)$ taking the forms

$$1 - F = 1 - \frac{x}{x_\infty} \qquad (x_0 = 0)$$

$$1 - F = \frac{y_\infty - y}{y_\infty - y_0}$$

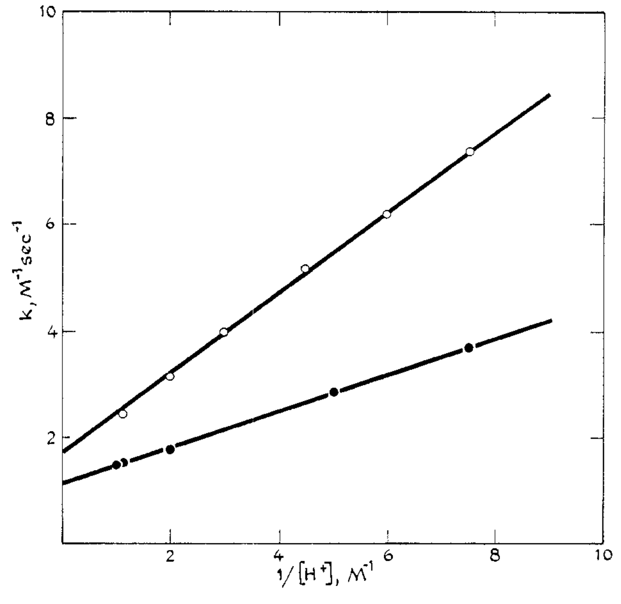

Figure 3.—Plot of specific rate constant for the Cr^{2+}–$Cr(H_2O)_5FuOH^{2+}$ isotope exchange reaction *vs.* $1/[H^+]$ at 0.5° (●) and 10.0° (○) and at $\mu = 1.00$.

where x and y stand for the specific activity, counts per minute per mole, of $CrFuOH^{2+}$ and Cr^{2+}, respectively, at time t.

The plots of log $(1 - F)$ *vs.* time fitted straight lines, as expected from eq 2. The values of k are summarized in Table III; comparison of the entries shows that the rate of exchange is indeed first order in each of $[Cr^{2+}]$ and $[CrFuOH^{2+}]$.

TABLE III

RATE DATA FOR THE Cr^{2+}–$CrFuOH^{2+}$ ISOTOPE EXCHANGE REACTION AT $\mu = 1.0$

$10^3[Cr^{2+}]$, *M*	$10^3[CrFuOH^{2+}]$, *M*	$[H^+]$, *M*	Temp, °C	k, M^{-1} sec^{-1}
0.99	1.20	0.133	0.5	3.71
0.94	0.80	0.200	0.5	2.99
0.80	2.40	0.200	0.5	2.62
0.95	0.80	0.200	0.5	2.85
1.82	0.80	0.200	0.5	2.93
2.03	1.61	0.200	0.5	2.86
1.45	2.00	0.500	0.5	1.78
1.96	2.00	0.900	0.5	1.52
0.80	2.40	1.000	0.5	1.49
0.44	0.40	0.133	10.0	7.39
0.65	0.70	0.167	10.0	6.20
0.71	0.70	0.222	10.0	5.19
1.10	0.90	0.333	10.0	3.98
1.46	1.00	0.500	10.0	3.15
2.01	2.00	0.900	10.0	2.59

In Figure 3 the values of k in Table III have been plotted against $1/[H^+]$ at two different temperatures. The straight lines obtained are consistent with the two-term rate law

$$\text{rate} = (k_0 + k_{-h}'[H^+]^{-1})[Cr^{2+}][CrFuOH^{2+}]$$

The values of k_0 and k_{-h}' at 0.5 and 10.0°, as well as the activation parameters calculated according to the absolute rate theory,[19] are summarized in Table

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[17] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 164.

[18] H. A. McKay, *Nature*, **142**, 997 (1938).

[19] W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 297.

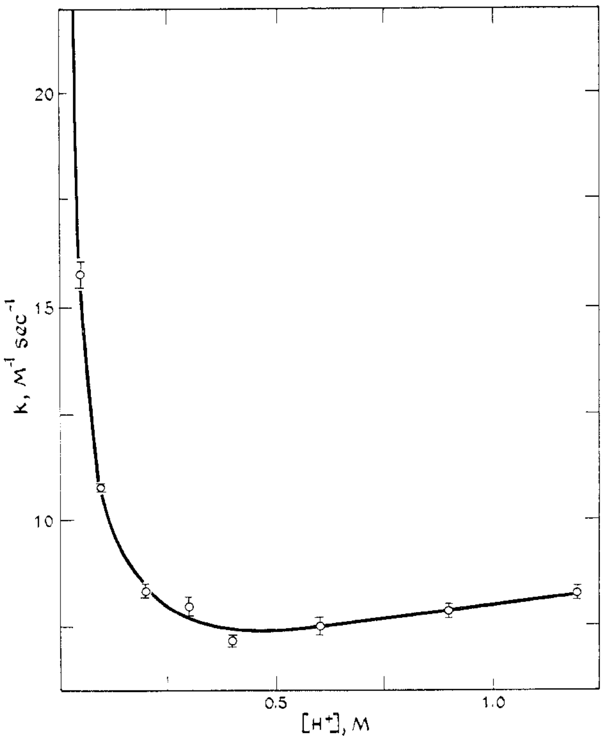

Figure 4.—Plot of specific rate constant for the Cr^{2+}-*cis*-$(en)_2Co(H_2O)FuOH^{2+}$ oxidation–reduction reaction *vs.* $[H^+]$ at 15.0° and μ = 1.50. The solid line is drawn using the rate constants for 15° shown in Table IV.

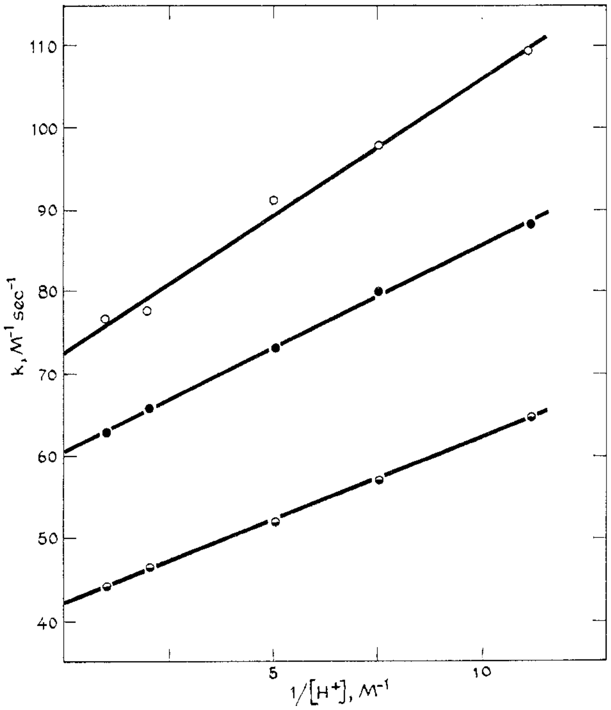

Figure 5.—Plot of specific rate constant for the Cr^{2+}-*cis*-$(NH_3)_4Co(H_2O)FuOH^{2+}$ oxidation–reduction reaction *vs.* $1/[H^+]$ at 15.0° (⊖), 25.0° (●), and 32.0° (○) and at μ = 1.50.

IV (at 20° the reaction was too fast to be measured by conventional techniques).

Reaction of Chromium(II) with *cis*-Fumaratoaquobis(ethylenediamine)cobalt(III).—This reaction, as well as that of Cr(II) with *cis*-fumaratoaquotetraamminecobalt(III), was studied by stopped-flow spectrophotometry.

The integrated rate law for a second-order reaction with different concentrations of reactants as given in ref 1 was used to determine the values of k (rate/$[Cr^{2+}][complex]$) for varying conditions, and the values are summarized in Table V. The first and third experiments of the table show that, at constant hydrogen ion concentration, the rate law is of the form: rate $= k[Cr^{2+}][Co(III)]$.

Figure 4 shows the variation of k with hydrogen ion concentration at 15°. Similar curves are obtained at 25 and 32°, and they fit the three-term rate law: rate $= (k_o + k_h'[H^+] + k_{-h}'[H^+]^{-1})\,[Cr^{2+}][Co(III)]$.

A least-squares computer program was used to calculate k_o, k_h', and k_{-h}' as well as the "best" curve from the data in Table V, the best curve being shown in Figure 4. In these calculations equal weight was given to all data points. These results and the activation parameters are summarized in Table IV.

Reaction of Chromium(II) with *cis*-Fumaratoaquotetraamminecobalt(III).—Table VI contains the specific rate constant k as a function of acidity and temperature for this system. A plot of k *vs.* $1/[H^+]$ gives a straight line (see Figure 5). The results in this case require only a two-term rate law: rate $= (k_o + k_{-h}'[H^+]^{-1})\,[Cr^{2+}][Cr(III)]$. The rate and energetic data for the reaction of Cr(II) with *cis*-fumaratoaquotetraamminecobalt(III) appear in Table IV.

Discussion

The nature of the isotope-exchange reaction between Cr(II) and fumaratopentaaquochromium(III) and the results obtained in the study of the stoichiometry of the reactions under consideration require that the several reactions proceed with complete transfer of the fumarate ligand to the primary coordination sphere of chromium. This necessarily means bridging by the anionic ligand, and indicates, moreover, that aquation of the reactants and the products is not important during the time in which the oxidation–reduction reactions take place.

The following scheme accommodates the observations

$$cis\text{-}R(H_2O)(FuOH)^{2+} + Cr^{2+} \xrightarrow{k_o} \text{products} \tag{3}$$

$$cis\text{-}R(H_2O)(FuOH)^{2+} + H^+ \overset{1/K_h}{\rightleftharpoons} cis\text{-}R(H_2O)(FuOH_2)^{3+} \tag{4}$$

$$cis\text{-}R(H_2O)(FuOH_2)^{3+} + Cr^{2+} \xrightarrow{k_h} \text{products} \tag{5}$$

$$cis\text{-}R(H_2O)(FuOH)^{2+} \overset{K_{-h}}{\rightleftharpoons} cis\text{-}R(OH)(FuOH)^{+} + H^+ \tag{6}$$

$$cis\text{-}R(OH)(FuOH)^{+} + Cr^{2+} \xrightarrow{k_{-h}} \text{products} \tag{7}$$

Known values of K_h and K_{-h} for several Co(III) and Cr(III) complexes[6,20–22] indicate that, in general, K_h is large and K_{-h} is small. There is no reason to expect the values for the complexes considered in this study to differ greatly from those reported and

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(20) Reference 17, p 32.

(21) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

(22) A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc.*, *A*, 1504 (1967).

TABLE IV

RATE AND ENERGETIC DATA FOR THE REACTION OF CHROMIUM(II) WITH FUMARATOCHROMIUM(III) AND FUMARATOCOBALT(III) COMPLEXES

Complex	Temp, °C	k_o[a]	$\Delta H_o^{\ddagger}$[b]	$\Delta S_o^{\ddagger}$[c]	k_h'[d]	$\Delta H_h'^{\ddagger}$[b]	$\Delta S_h'^{\ddagger}$[c]	k_{-h}'[e]	$\Delta H_{-h}'^{\ddagger}$[b]	$\Delta S_{-h}'^{\ddagger}$[c]
$(NH_3)_5CoFuOH^{2+}$	1.9	0.48	6.7	−36	2.16	2.9	−45			
	14.3	0.75			2.76					
	25.1	1.32			3.48					
cis-$(NH_3)_4Co(H_2O)FuOH^{2+}$	15.0	42.3	5.1	−33				2.03	4.5	−42
	25.0	60.7						2.51		
	32.0	72.8						3.36		
cis-$(en)_2Co(H_2O)FuOH^{2+}$	15.0	5.42	7.4	−29	2.02	−2.2	−65	0.52	6.2	−38
	25.0	9.10			1.86			0.72		
	32.0	11.7			1.72			1.02		
$(H_2O)_5CrFuOH^{2+}$	0.5	1.13	6.3	−35				0.34	12.6	−15
	10.0	1.72						0.76		

[a] k_o in M^{-1} sec^{-1}. [b] Enthalpies of activation in kcal mol^{-1}. [c] Entropies of activation in eu. [d] k_h' in M^{-2} sec^{-1}. [e] k_{-h}' in sec^{-1}.

TABLE V

RATE DATA FOR THE CHROMIUM(II)–*cis*-FUMARATOAQUOBIS(ETHYLENEDIAMINE)COBALT(III) ELECTRON-TRANSFER REACTION AT μ = 1.5

$10^2[Cr^{2+}]$, M	10^3[Co(III)], M	$[H^+]$, M	Temp, °C	k,[a] M^{-1} sec^{-1}
2.50	5.00	0.600	15.0	7.4 ± 0.2
			25.0	11.5 ± 0.2
			32.0	14.4 ± 0.3
2.50	5.00	0.400	15.0	7.2 ± 0.1
			25.0	11.2 ± 0.2
			32.0	14.5 ± 0.2
2.00	3.00	0.600	15.0	7.5 ± 0.2
			25.0	11.6 ± 0.1
			32.0	14.6 ± 0.2
2.50	5.00	0.900	15.0	7.9 ± 0.2
			25.0	11.7 ± 0.1
			32.0	14.6 ± 0.2
2.50	5.00	0.200	15.0	8.4 ± 0.1
			25.0	13.1 ± 0.1
			32.0	17.4 ± 0.2
2.50	2.50	0.100	15.0	10.8 ± 0.1
			25.0	15.9 ± 0.3
			32.0	22.1 ± 0.8
2.50	5.00	0.300	15.0	8.0 ± 0.2
			25.0	12.1 ± 0.1
			32.0	14.9 ± 0.2
2.50	5.00	1.200	15.0	8.3 ± 0.2
			25.0	11.9 ± 0.2
			32.0	14.5 ± 0.2
2.50	2.50	0.050	15.0	15.7 ± 0.4
			25.0	25.9 ± 0.6
			32.0	34.6 ± 0.8

[a] Entries for rate constants are the mean values of at least three determinations.

TABLE VI

RATE DATA FOR THE REACTION OF CHROMIUM(II) WITH *cis*-FUMARATOAQUOTETRAAMMINECOBALT(III) AT μ = 1.5

$10^2[Cr^{2+}]$, M	10^3[Co(III)], M	$[H^+]$, M	Temp, °C	k,[a] M^{-1} sec^{-1}
2.50	9.00	0.500	15.0	46.6 ± 0.9
			25.0	66.0 ± 0.9
			32.0	78 ± 2
2.50	6.40	0.090	15.0	65 ± 2
			25.0	88 ± 3
			32.0	110 ± 3
2.50	6.50	0.200	15.0	52.1 ± 0.8
			25.0	73.1 ± 0.9
			32.0	91 ± 2
2.00	6.50	1.000	15.0	44.3 ± 0.7
			25.0	62.8 + 0.7
			32.0	76.8 ± 0.5
2.50	6.50	0.133	15.0	57.5 ± 0.9
			25.0	80 ± 1
			32.0	98 ± 2

[a] Entries for rate constants are the mean value of at least three determinations.

so, at least in the acid range 0.1–1.0 F, *cis*-$R(H_2O)FuOH^{2+}$ is the dominant form of the oxidant. If, as is entirely reasonable, reactions 4 and 6 are rapid equilibration steps, the rate law is

$$\text{rate} = (k_o + k_hK_h^{-1}[H^+] + k_{-h}K_{-h}[H^+]^{-1})[Cr^{2+}][cis\text{-}R(H_2O)FuOH^{2+}]$$

where [*cis*-$R(H_2O)FuOH^{2+}$] is tantamount to the total concentration of oxidant. The experimental parameters k_h' and k_{-h}' then are to be identified with $k_hK_h^{-1}$ and $k_{-h}K_{-h}$, respectively (for fumaratopentaaquochromium(III) and *cis*-fumaratoaquotetraamminecobalt(III) $k_h' \approx 0$).

Table IV shows a summary of the rate and energetic data obtained in the present work; the corresponding values for the chromium(II)–fumaratopentaamminecobalt(III) system are included for purposes of comparison.

The similarity of the values of the entropies and enthalpies of activation observed in Table IV for the k_o path suggests that for all four cases a common mechanism in which the electron transfer takes place through the fumarato ligand is operating.

Hurst and Taube[5] have found that the values of k_o for $FuOH^-$, $FuOCH_3^-$, and $FuNH_2^-$ as ligands in pentaamminecobalt(III) complexes do not depend on the nature of the substituents on the remote end of the fumarato group. These results imply that the k_o path involves adjacent attack, and to the extent that this proposal is accepted, it can be assumed to apply also to *cis*-$(NH_3)_4Co(OH_2)FuOH^{2+}$, *cis*-$(en)_2Co(OH_2)FuOH^{2+}$, and $(H_2O)_5CrFuOH^{2+}$. The proposal, moreover, is supported by some of the effects observed in the present study.

Nordmeyer and Taube[1] have pointed out that the large (10^6 or greater) rates observed for the reduction of the pentaamminecobalt radical compared to the pentaaquochromium radical (k_{Co}/k_{Cr}) when F^- and OH^- are bridging ligands suggests that a resonance mechanism for electron transfer is operating. When isonicotinamide is the bridging ligand, k_{Co}/k_{Cr} is only 10. We note that when fumarate is the bridging ligand, k_{Co}/k_{Cr} measured by the rate of reduction of $(NH_3)_5CoFuOH^{2+}$ and $(H_2O)_5CrFuOH^{2+}$ is $\sim$0.4.

The fact that k_{Co}/k_{Cr} in this case is less than unity need be no cause for concern. In gauging the effect of changing from Co(III) to Cr(III) as electron acceptor *cis*-$(NH_3)_4Co(H_2O)FuOH^{2+}$ rather than $(NH_3)_5CoFuOH^{2+}$ should be compared to $(H_2O)_5CrFuOH^{2+}$. In Table VII a number of comparisons for aquocobalt and aquochromium are summarized, including the one of present interest. On the revised basis, the reduction of Co(III) over Cr(III) is favored by a factor of 20, and admitting a special role of water in the *cis* position and allowing for the statistical factor of 4, the ratio becomes 80. Even with this increased ratio, the rate of reduction by chromous ion through the acid fumarate ion by the k_o path is remarkably insensitive to the oxidizing power of the acceptor center, and it seems reasonable then to suppose that the k_o path for both centers involves a stepwise mechanism.

TABLE VII

COMPARISONS OF SPECIFIC RATES (k_o) OF THE REACTION OF Cr^{2+} WITH *cis*-AQUOTETRAAMMINECOBALT(III) AND PENTAAQUOCHROMIUM(III) COMPLEXES AT 25° AND $\mu = 1.0$

Ligand	Specific rates, M^{-1} sec^{-1} *cis*-$(NH_3)_4Co(H_2O)L$	Specific rates, M^{-1} sec^{-1} $(H_2O)_5CrL$	k_{Co}/k_{Cr}
OH^-	9×10^{6} [a]	0.7 [d]	1.3×10^{7}
OAc^-	47 [a]	$<10^{-4}$ [d]	$>4.7 \times 10^{5}$
$FuOH^-$	60.7 [b,c]	$\sim$3 [b]	$\sim$20

[a] Reference 16. [b] This work. [c] $\mu = 1.5$. [d] Reference 1.

A comparison of k_o for *cis*-$(NH_3)_4Co(H_2O)FuOH^{2+}$ and *cis*-$(en)_2Co(H_2O)FuOH^{2+}$ shows that the replacement of four ammonia molecules by two ethylenediamine molecules diminishes the reaction rate by a factor of about 7. A similar effect has been observed by Haim and Sutin[23] for the pair *cis*-$(NH_3)(en)_2CoNCS^{2+}$–$(NH_3)_5CoNCS^{2+}$ and by Fraser[24] for the pair $(en)_2(NH_3)CoSO_4^{+}$–$(NH_3)_5CoSO_4^{+}$.

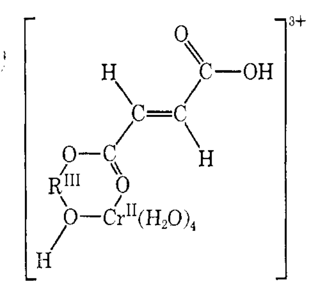
Little that is useful can be said about the factors affecting k_o when the data for $(NH_3)_5CoFuOH^{2+}$ and *cis*-$(NH_3)_4Co(H_2O)FuOH^{2+}$ are considered. If the adjacent attack mechanism is accepted, then we must reckon with the possibility that by changing the ligand *cis* to the bridging group we are changing its solvation requirements and, by doing so, changing the environment in the region where chromous ion attacks. It should be noted that in the system studied by Nordmeyer and Taube,[1] where remote attack has been demonstrated, the change from the pentaammine to the tetraammine is expected to have much less influence than in the present case.

The possibility must be considered that the k_o path for a complex having a water molecule in *cis* position involves an activated complex in which a proton has been transferred from a *cis*-water molecule to another position on the bridging group. For $(NH_3)_5CoFuOH^{2+}$, however, this possibility is excluded and, because it is highly improbable that the agreement in rates and activation parameters between $(NH_3)_5CoFuOH^{2+}$ and the rest of the complexes in Table IV is accidental, it is concluded that the proton in the *cis* water is not redistributed in the activated complex. In any event, the comparison of k_o for the Cr(III) complex and the tetraamminecobalt(III) complex on the basis discussed remains valid.

If adjacent attack for the k_o path is accepted as the most probable mechanism, as the evidence presented before suggests, it is remarkable that a pendant group such as the fumarate anion is so much more effective than the acetate anion in promoting reaction, particularly since neither is on the direct line for electron transfer. The same effect has been observed[25,26] with other conjugated bridging ligands, and it has been suggested that the conjugated pendant group lowers the energy of an unoccupied orbital of the lead-in carboxylate group and, hence, stabilizes the ion-radical intermediate.

We proceed now to a consideration of the term in the rate law which is inverse in $[H^+]$. Table IV shows that, except for $(NH_3)_5CoFuOH^{2+}$, each of the rate laws features a term of this kind. Similar rate laws have been obtained for other electron-transfer reactions including that of Cr(II) with $Cr(SCN)^{2+}$,[23] $Cr(H_2PO_2)^{2+}$,[27] $CrOAc^{2+}$,[6] and *cis*-$(NH_3)_4Co(H_2O)OAc^{2+}$.[21] This type of rate law can be taken to imply that in forming the activated complex a proton is lost from a *cis*-aquo group. That this path does not appear in the rate law for $(NH_3)_5CoFuOH^{2+}$ confirms the interpretation advanced because coordinated ammonia loses protons extremely slowly in acidic solution.

The existence of a doubly bridged activated complex has been demonstrated unequivocally only for the reactions of Cr(II) with *cis*-$(H_2O)_4Cr(N_3)_2^{+}$ [28] and with diazidobis(ethylenediamine)cobalt(III),[29] but it is implicated on the basis of indirect evidence in the other reactions just referred to. It is reasonable then to suppose that a doubly bridged activated complex operates also in the case of the fumarate ligand



It is interesting again to make comparisons between the acetate ion and the fumarate ion as bridging ligands. Table VIII shows such comparisons. K_{-h} for a fumarate complex should not differ greatly from the value

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(23) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

(24) R. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).

(25) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **85**, 3706 (1963).

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(27) K. A. Schroeder and J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 2548 (1967).

(28) R. Snellgrove and E. L. King, *ibid.*, **84**, 4609 (1962).

(29) A. Haim, *ibid.*, **88**, 2324 (1966).

TABLE VIII

COMPARISONS OF SPECIFIC RATES (k_{-h}') OF THE REACTION OF Cr^{2+} WITH *cis*-$R(H_2O)L^{2+}$ AT 25° AND $\mu = 1.0$

R	Specific rates, sec^{-1}		$k_{-h}'(FuOH^-)/k_{-h}'(OAc^-)$
	$L^- = FuOH^-$	$L^- = OAc^-$	
$(H_2O)_4Cr$	$\sim 2.5^a$	$5.8 \times 10^{-4\,b}$	$\sim 4.3 \times 10^3$
$(NH_3)_4Co$	2.51^c	2.8^d	0.9
$(en)_2Co$	0.72	...	...

[a] This work; extrapolated from data at 0.5 and 10°. [b] Reference 6. [c] This work; $\mu = 1.5$. [d] Reference 21.

for the corresponding acetate complex and, therefore, the specific rate ratio $k_{-h}(FuOH^-)/k_{-h}(OAc^-)$ for the two processes

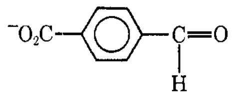
$$cis\text{-}R(OH)L^+ + Cr^{2+} \xrightarrow{k_{-h}} \text{products}$$

should be almost the same as the specific rate ratio $k_{-h}'(FuOH^-)/k_{-h}'(OAc^-)$.

From Table VIII it can be seen that when Co(III) is the oxidizing metal ion, it does not matter if fumarate or acetate is the bridging group, whereas in the case of Cr(III) as the oxidizing metal ion there is a sharp difference, the fumarate complex being 4.3×10^3 times faster than the acetato complex. This difference in behavior between chromium and cobalt is not unexpected. Even in the pentaammine series, reduction of Co(III) through OH^- is a very facile process with the second-order specific rate being[30] *ca.* 10^7. The values of k_{-h}' for the tetraammine and $(en)_2$ complexes would be of the same order of magnitude since the pK_2 values for the aquo acids are expected to be in the range of 6–7. By now considerable evidence has accumulated[31–33] to suggest that there is a ceiling[34–36] of *ca.* 10^7 M^{-1} sec^{-1} on the rate of reduction by chromous ion *via* an inner-sphere activated complex. Thus little assistance in the reduction act from the added bridging group is expected or required when Co(III) is reduced by Cr^{2+} through OH^-. However, Cr(III) is much less readily reducible than is Co(III), even through OH^- as a bridging group, and now the second bridging group can be expected to play a role in the reaction. It is likely that, here again, special electronic properties of the fumarate group are exploited, and in the case of Cr(III) as the acceptor center we are dealing with a radical-ion mechanism.

Any conclusions based on comparisons of rates for the Co(III) and Cr(III) complexes must allow for differences in the values of pK for the corresponding acids (this can be lower by 1 unit for Cr(III) compared to the Co(III) complexes) and for the statistical factor and, moreover, must recognize that though the values of k_{-h}' are not much different, $\Delta H_{-h}^{\ddagger}$ and $\Delta S_{-h}^{\ddagger}$ are quite different for the Co(III) and Cr(III) complexes. This alone points to a difference in mechanism, the rate for the Co(III) complexes being limited by the rate of readjustment in the coordination sphere of the reducing agent, whereas for the Cr(III) complexes it is limited by other factors.

Perhaps the most interesting reaction pathway is that involving an extra proton in the activated complex. This path, in the case of pentaamminecobalt(III), has been observed for $FuOH^-$, $FuOCH_3^-$, and $FuNH_2^-$ [4,5] ligands, and the sensitivity of rates to the nature of the remote substituent has been interpreted[5] as indicating reaction at least in part by remote attack. The k_h path is featured also for muconate as ligand[37] and most dramatically for[37,38]



$$^-O_2C{-}C_6H_4{-}\underset{\displaystyle H}{\overset{}{C}}{=}O$$

In considering the role of the proton, two distinct questions must be considered: (a) Where is it located in the activated complex? (b) What is its function? The fact that *p*-formylbenzoate shows a k_h term together with the fact that remote attack is involved[37,38] suggests that the proton is located on the adjacent carboxyl group. Its involvement at such a location has been interpreted[4] as improving conjugation between the two metal ion centers, an interpretation which is equivalent to invoking resonance transfer. However, its involvement can perhaps be more readily understood in terms of a stepwise electron-transfer process. Protonating the ligand can facilitate electron transfer from chromous ion to the ligand by lowering the energy of the unoccupied orbital which accepts the electron. This would help explain why the k_h path is not observed (upper limit, 0.1 M^{-2} sec^{-1}) for $(H_2O)_5CrFuOH^{2+}$. Reduction of Cr(III) by a fumarate radical ion is probably just marginally possible, and when the radical ion is stabilized by protonation, this path becomes insignificant compared to the others. We are at a loss, however, to understand why the k_h path is smaller for *cis*-$(NH_3)_4Co(H_2O)FuOH^{2+}$ (upper limit, 1 M^{-2} sec^{-1}) than for *cis*-$Co(H_2O)(en)_2FuOH^{2+}$ ($k_h = 1.9$ M^{-2} sec^{-1}).

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(34) It has been suggested[35] that the limiting rate measures the rate of substitution on $Cr(H_2O)_4(H_2O')_2^{2+}$. In view of the extraordinary lability[36a] of the water molecules in the axial positions and the demonstrated *trans* isotopic effect in the reduction of Cr(III) complexes,[36b] it seems likely to us that the rate-limiting step is the change in shape of the coordination sphere about Cr(II) from tetragonal to approximately octahedral.

(35) J. Halpern, as referred to by M. Green, R. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

(36) (a) C. W. Meredith, Ph.D. Thesis, University of California, Berkeley, Calif., 1965; (b) J. M. Dechant and J. B. Hunt, *J. Am. Chem. Soc.*, **89**, 5988 (1967); **90**, 3695 (1968).

(37) E. S. Gould, *ibid.*, **87**, 4720 (1965).

(38) A. Zanella, work in progress.