but this value is measured at pH 11 where hydroxide ion may interfere. (4) The stability constant for ring closure is 2.5×10^3, so that only 0.04% of $Ni(en)_3^{2+}$ can exist in solution with five nitrogens coordinated. (5) The results support the suggestion of the internal conjugate base mechanism.

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Reductions of *cis*- and *trans*-Diformatobis(ethylenediamine)cobalt(III) by Chromium(II). Doubly Bridging and Acid Catalysis[1a]

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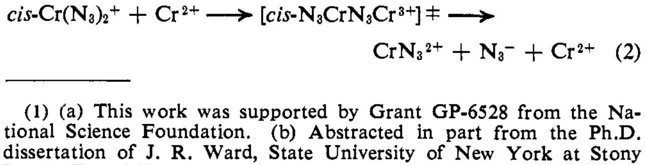
Abstract: The reductions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ by Cr^{2+} obey the rate laws $-d(\ln [cis\text{-}Co(en)_2(HCO_2)_2^+])/dt = k_0[Cr^{2+}]/(1 + Q[H^+])$ and $-d(\ln [trans\text{-}Co(en)_2(HCO_2)_2^+])/dt = (k_0 + k_1Q[H^+])[Cr^{2+}]$, respectively. At 25° and $[ClO_4^-] = 1.0\ M$, $k_0(cis) = 434 \pm 11\ M^{-1}\ sec^{-1}$, $k_0(trans) = 10.2 \pm 0.3\ M^{-1}\ sec^{-1}$, $Q(cis) = 0.44 \pm 0.07\ M^{-1}$, $k_1Q(trans) = 15.0 \pm 0.7\ M^{-2}\ sec^{-1}$. Protonation of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ is invoked to account for the observed kinetic patterns. Protonation of the *cis* complex decreases its reactivity toward chromium(II) reduction, whereas protonation of the *trans* complex increases its reactivity. Both the k_0 and k_1 paths for the *trans* complex proceed *via* inner sphere mechanisms with transfer of one formate ion from cobalt to chromium. The reaction of the *cis* complex proceeds *via* parallel singly and doubly bridged transition states with transfer of one and two formate ions, respectively, from cobalt to chromium. Various mechanistic details of these and related reactions are discussed.

The possibility that a doubly bridged transition state would provide a favorable pathway for electron transfer reactions was suggested long ago.[2] Early attempts to find evidence for this type of mechanism in the reactions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ and *cis*-CrF_2^+ with chromium(II) were unsuccessful.[3,4] In 1952, Snellgrove and King[5] provided the first conclusive evidence for a pathway involving a doubly bridged transition state: the dominant reaction that takes place when *cis*-$Cr(N_3)_2^+$ and Cr^{2+} are mixed is the exchange of chromium atoms between the two chromium species (eq 1). It was shown subsequently that, concomitant with the exchange reaction, but proceeding at a slower rate, a net reaction involving a singly bridged transition state (eq 2) was also important in this system.[6]



$$cis\text{-}Cr(N_3)_2^+ + {}^*Cr^{2+} \longrightarrow \left[cis\text{-}Cr \begin{matrix} N_3 \\ \\ N_3 \end{matrix} Cr^{3+} \right]^{\ddagger} \longrightarrow cis\text{-}{}^*Cr(N_3)_2^+ + Cr^{2+} \quad (1)$$

$$cis\text{-}Cr(N_3)_2^+ + Cr^{2+} \longrightarrow [cis\text{-}N_3CrN_3Cr^{3+}]^{\ddagger} \longrightarrow CrN_3^{2+} + N_3^- + Cr^{2+} \quad (2)$$

The factors governing the relative efficiencies of doubly and singly bridged paths are not apparent from the limited amount of data available, and a systematic study of a variety of systems featuring parallel singly and doubly bridged pathways seems to be called for. The report[7] that 69% of the chromium(III) produced in the chromium(II) reduction of *cis*-$Co(NH_3)_4(CH_3CO_2)_2^+$ has a unipositive charge (presumably *cis*-$Cr(OH_2)_4(CH_3CO_2)_2)^+$ encouraged the initiation of a study of the chromium(II) reductions of *cis*-dicarboxylatocobalt(III) complexes, and the results obtained with the *cis*-diformatobis(ethylenediamine)cobalt(III) complex are reported here.

In addition, because of the interest of the authors in the relative reactivities of *cis* and *trans* isomers in redox reactions,[8] the results obtained for the chromium(II) reduction of *trans*-diformatobis(ethylenediamine)cobalt(III) are also reported. The comparison of the kinetic behavior for the *cis* and *trans* isomers is of particular importance in the present system because formate ion is the conjugate base of a weak acid. For the analogous reactions of complexes containing basic ligands, namely *cis*- and *trans*-$CoA_4(CH_3CO_2)_2^+ + Cr^{2+}$ (A = NH_3 or $^1/_2$(en)[7,9,10] and *cis*- and *trans*-$Co(NH_3)_4(N_3)_2^+ + Fe^{2+}$,[11] contrasting kinetic behaviors have been reported; regardless of geometry, the diacetato complexes exhibit acid-catalyzed paths, whereas for the diazido system only the *trans* isomer exhibits an acid-catalyzed path. Consequently, the hydrogen ion de-

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[1] (a) This work was supported by Grant GP-6528 from the National Science Foundation. (b) Abstracted in part from the Ph.D. dissertation of J. R. Ward, State University of New York at Stony Brook, Feb 1969.

[2] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954);

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Table I. Electronic Spectral Data for Formatoamine–Cobalt(III) Complexes

Complex	λ, nm[a]	A, M^{-1} cm^{-1} [b]	Ref
cis-$Co(en)_2(HCO_2)_2^+$	501, 362, 224[c]	128, 85.0, 1.8×10^4 [c]	*d*
	501, 362, 224[e]	128, 84.3, 1.8×10^4 [e]	*d*
trans-$Co(en)_2(HCO_2)_2^+$	540, 453, 357, 233	51.4, 30.6, 66.5, 1.6×10^4	*d*
$Co(NH_3)_5(HCO_2)^{2+}$	501, 349, 232 (sh)	66.5, 54.4, 1.3×10^4	*d*
	503, 352	58.9, 44.7	*f*
	503, 351	69.2, 55.0	*g*

[a] Wavelengths for absorption maxima. [b] Molar absorptivities at absorption maxima. [c] From $[Co(en)_2CO_3](ClO_4)$ and formic acid. See text. [d] This work. [e] From $[Co(en)_3CO_3](ClO_4)$, perchloric acid, and sodium formate. See text. [f] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951). [g] K. Kuroda, *Nippon Kagaku Zashi*, **82**, 1481 (1961).

pendences of the *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reactions have been investigated in detail.

Experimental Section

Materials. Chromium(II) perchlorate stock solutions were prepared by reduction of chromium(III) perchlorate with amalgamated zinc. Lithium perchlorate and sodium perchlorate were prepared by neutralization of standard perchloric acid solutions with anhydrous lithium carbonate and anhydrous sodium carbonate, respectively. Sodium oxalate (Baker Analyzed Reagent), used in the standardization of potassium permanganate solutions, was dried at 105° for 3 hr. The cation exchange resins Dowex 50W X-8 and X-2 (50–100 mesh) were purified by pretreatment with warm alkaline hydrogen peroxide. Triply distilled water was used to prepare all of the solutions.

Manipulations involving oxygen-sensitive solutions were carried out in an atmosphere of argon. The argon was purified by passing it over a BTS catalyst (B.A.S.F. Colors and Chemicals, Inc.). All other chemicals were reagent grade, and were used without further purification.

Preparation of Formatoamine–Cobalt(III) Complexes. The preparation of *cis*-diformatobis(ethylenediamine)cobalt(III) perchlorate was initially attempted by the method of Linhard and Stirn[12] starting with $[Co(en)_2CO_3](ClO_4)$. The molar absorbances of the material obtained were lower than expected, perhaps because of incomplete conversion of $Co(en)_2(OH_2)_2^{3+}$ to *cis*-$Co(en)_2(HCO_2)_2^+$. Linhard and Stirn give an alternate preparation of *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$ starting from $[Co(en)_2(OH_2)_2](ClO_4)_3$. Consequently, the material from the first preparation was assumed to be contaminated by the diaquo complex, and was converted to *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$ by the alternate method. *Anal.* Calcd for *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$: C, 19.55; H, 4.92; N, 15.20; Co, 15.99. Found: C, 18.46; H, 5.28; N, 15.53; Co, 15.89. A second batch of *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$ was prepared by treating 5 g of $[Co(en)_2CO_3](ClO_4)$ with 30% perchloric acid until the evolution of carbon dioxide ceased. Sodium formate (2.3 g) was added, and the mixture was evaporated to near dryness at 50°. The crude product was recrystallized from water, and the resulting crystals were washed with ethanol and ether, yield 3 g. *Anal.* Calcd for *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$: C, 19.55; H, 4.92; N, 15.20; Co, 15.99. Found: C, 18.75; H, 4.93; N, 14.49; Co, 15.73. As shown in Table I, the materials obtained by the two methods exhibit essentially identical electronic spectra.

trans-$[Co(en)_2(HCO_2)_2](ClO_4)$ was prepared and recrystallized following the procedure of Linhard and Stirn.[12] *Anal.* Calcd for *trans*-$[Co(en)_2(HCO_2)_2](ClO_4)$: C, 19.55; H, 4.92; N, 15.20; Co, 15.99. Found: C, 19.41; H, 5.16; N, 14.62; Co, 16.08. $[Co(NH_3)_5(HCO_2)](ClO_4)_2$ was prepared following the procedure of Linhard and Rau.[13] *Anal.* Calcd for $[Co(NH_3)_5(HCO_2)](ClO_4)_2$: C, 3.09; H, 4.16; N, 18.05; Co, 15.19. Found: C, 2.81; H, 4.26; N, 17.38; Co, 15.17. Electronic spectral data for these two complexes are included in Table I.

Preparation and Ion Exchange Separation of Formatoaquochromium(III) Complexes. Previous investigators have reported difficulties in recovering carboxylatopentaaquochromium(III) complexes absorbed on ion exchange resins by elution with acid.[14–16] Similar difficulties have been experienced here with the complexes $Cr(OH_2)_5(HCO_2)^{2+}$ and *cis*-$Cr(OH_2)_4(HCO_2)_2^+$. In order to obtain high recoveries of these complexes, it was necessary to use Dowex 50W X-2 in the sodium form, to elute the chromium(III) cations with sodium perchlorate solutions, and to carry out the ion exchange operation near 0°. In spite of these precautions, blank experiments indicated approximately 95% recovery of the complexes. Although the recoveries were somewhat less than quantitative, good separations of the complexes could be achieved. After various attempts, it was found that slow elution with 0.1 M sodium perchlorate–0.01 M perchloric acid cleanly separated *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ from $Cr(OH_2)_5(CHO_2)^{2+}$, and that $Cr(OH_2)_5(HCO_2)^{2+}$ was cleanly separated from $Cr(OH_2)_6^{3+}$ by elution with 0.5 M sodium perchlorate–0.05 M perchloric acid.

Formatopentaaquochromium(III) was prepared and isolated in solution in two ways. In the first method, 10 mg of $[Co(NH_3)_5(HCO_2)](ClO_4)_2$ was dissolved in 15 ml of water and 1 ml of 2.36 M perchloric acid at 0°. The solution was deaerated by bubbling argon for 20 min. A stoichiometric amount of chromium(II) was added, and the solution was allowed to stand for 30 min. The solution was added to a 15 × 1 cm column of Dowex 50W X-2 (50–100 mesh, sodium form) surrounded by ice. The resin was washed with 50 ml of 0.1 M sodium perchlorate–0.01 M perchloric acid, and then the $Cr(OH_2)_5(HCO_2)^{2+}$ ion was eluted with 0.5 M sodium perchlorate–0.05 M perchloric acid. Under these conditions, $Cr(OH_2)_5(HCO_2)^{2+}$ moves slightly faster than Co^{2+}, and therefore, the chromium(III) complex collected for identification contained no cobalt(II). The spectrum of the eluate was recorded, and aliquots were removed to determine the chromium content. In the second method, 21 ml of 97% formic acid was added to a solution containing 0.6 g of potassium dichromate, 3 ml of 11.8 M perchloric acid, and 21 ml of water. The resulting solution was allowed to stand at room temperature for 3 hr, and the color changed from orange to gray-purple, indicating reduction of chromium(VI) to chromium(III). The solution was diluted threefold, and the $Cr(OH_2)_5(HCO_2)^{2+}$ ion was isolated as before.

cis-Tetraaquodiformatochromium(III) was prepared in solution by the chromium(II) reduction of *cis*-$Co(en)_2(HCO_2)_2^+$. A solution containing 10–15 mg of *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$ in 20 ml of water was deaerated by bubbling argon for 20 min. One ml of 2.36 M perchloric acid was added, followed by the stoichiometric amount of chromium(II). After 1 min, the resulting solution was diluted threefold, and then added to a 15 × 1 cm column of Dowex 50 W X-2 (50–100 mesh, sodium form) surrounded by ice. The resin was washed with 50 ml of distilled water, and then the *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ ion was eluted (1 ml/min) with 0.1 M sodium perchlorate–0.01 M perchloric acid. The absorption spectrum was recorded, and aliquots were removed to estimate the chromium and formate contents.

Stoichiometric Measurements. Stoichiometric experiments were designed to determine the amounts of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ and of $Cr(OH_2)_5(HCO_2)^{2+}$ produced in the chromium(II) reduction of *cis*-$Co(en)_2(HCO_2)_2^+$. The experiments were performed at $[ClO_4^-] = 1.0$ M (the conditions used in collecting the kinetic data) and constant temperature. Low acid concentrations were used in order to minimize the aquation of *cis*-$Co(en)_2(HCO_2)_2^+$ (prior to and during the reaction with chromium(II)) as well as that of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ (during elution from the resin). The desired amount of *cis*-$[Co(en)_2(HCO_2)_2](ClO_4)$ (usually 20–25 mg) was dissolved in an amount of lithium perchlorate solution such that subsequent addition to perchloric acid and chromium(II) would bring the total volume to 10 ml and the perchlorate concentration to 1.0 M. The solution was deaerated for 20 min at 0°, and then placed in a constant temperature bath at the desired temperature for 15 min. Previously deaerated perchloric acid was added, immediately followed by addition of the desired amount of chromium(II). After com-

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pletion of the reaction (30 sec), the solution was diluted to 100 ml with chilled triply distilled water, and then added to a 15 × 1 cm column of Dowex AG 50 W X-2 resin (50–100 mesh, sodium form) kept near 0° by a surrounding jacket of ice. Since the perchlorate ion concentration was 0.1 *M* after dilution, ions of charge +2 or higher were retained on the resin, but the unipositively charged *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ passed through the column. After the 100 ml of solution had percolated through the column, the column was rinsed with 100 ml of 0.1 *M* sodium perchlorate–0.01 *M* perchloric acid in order to ensure the quantitative removal of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ in the first fraction. The ion $Cr(OH_2)_5(HCO_2)^{2+}$ was then removed by elution with 200–250 ml of 0.5 *M* sodium perchlorate–0.05 *M* perchloric acid. Duplicate chromium analyses were performed in each fraction. The $Cr(H_2O)_5(HCO_2)^{2+}$ fraction contained cobalt(II) (which is also eluted with 0.5 *M* sodium perchlorate). Consequently, when this fraction was analyzed for chromium, cobalt hydroxide precipitated out. The precipitate was removed by centrifugation prior to the spectrophotometric measurements.

The stoichiometry of the chromium(II) reduction of *trans*-$Co(en)_2(HCO_2)_2^+$ was determined at 25° by the same procedure, except that chromium analyses were performed only on the fraction eluted with 0.5 *M* sodium perchlorate.

Kinetic Measurements. The rates of reaction of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ with chromium(II) were measured in a rapid flow apparatus constructed following the design of Dulz and Sutin.[17] The cobalt(III) solution contained the necessary amount of lithium perchlorate, but no perchloric acid since the acid-catalyzed aquation of *cis*-$Co(en)_2(HCO_2)_2^+$ is a relatively rapid process.[18] The chromium(II) solution contained the necessary amounts of perchloric acid and lithium perchlorate. Special flasks were designed[1b] to maintain the reactant solutions under a slight positive pressure of argon at all times. For all experiments the chromium(II) was in sufficient excess to ensure pseudo-first-order behavior. Four to six replicate measurements were carried out for each pair of reactant solutions at 270 nm. The photographs of the oscilloscope screen were enlarged, and the transmittance readings at 12 times during 3 half-lives were recorded. The readings were fit to the following equation

$$R = (1/B)[1 - (1 - R_0B)e^{-kt}] \qquad (3)$$

where *R* is the reading at time *t*, R_0 is the reading at time 0, *B* is a constant which depends on the gain in the oscilloscope and the offset calibration, and *k* is the measured first-order rate coefficient. The oscilloscope readings were fit to eq 3 using a nonlinear least-squares program.[19] R_0 and *k* were treated as floating parameters, and *R* and *t* were the dependent and independent variables, respectively.

Analytical Methods. Chromium(II) concentrations were determined by reaction with an excess of oxygen-free iron(III), followed by titration of the iron(II) produced with standard potassium dichromate.[20] The acid concentration of chromium(II) perchlorate solutions was determined by the procedure of King and Neptune[21] as modified by Thompson and Gordon.[22] Total chromium concentrations were determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide.[23] Cobalt was analyzed gravimetrically by conversion of the cobalt(III) complex to cobalt(II) sulfate.[24] Carbon, hydrogen, and nitrogen analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Analyses of formate in solutions of $Cr(OH_2)_5(HCO_2)^{2+}$ and *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ were carried out by treating aliquots with 1 *M* sodium carbonate solution to pH 8–10. Formate ion was released from the coordination sphere of chromium(III), and chromium(III) hydroxide precipitated. Perchloric acid was then added until the precipitate dissolved, and the resulting acidic solution was added to a 5 × 1 cm column of Dowex 50 W X-8 (50–100 mesh, hydrogen form). Chromium(III) was retained on the resin, and the effluent, containing formic acid, was analyzed by the procedure of Vogel.[25] Blank experiments with synthetic mixtures of sodium formate and $Cr(OH_2)_6^{3+}$ proved the method to be reliable to about 2%.

Instruments. Spectrophotometric measurements were carried out with a Cary 14 recording spectrophotometer. pH measurements were made with a Corning Model 12 Research pH meter. The least-squares computations were made on an IBM 7044 computer at the Stony Brook Computing Center.

Results

Preparation and Identification of $Cr(OH_2)_5(HCO_2)^{2+}$ and *cis*-$Cr(OH_2)_4(HCO_2)_2^{2+}$. The two previously unreported chromium(III) complexes $Cr(OH_2)_5(HCO_2)_2^{2+}$ and *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ were prepared in solution, separated by ion exchange chromatography, and identified by determining the formate to chromium ratios.

The monoformate complex was prepared by the inner-sphere reaction between $Co(NH_3)_5(HCO_2)^{2+}$ and Cr^{2+} (eq 4) which, in common with other chromium(II)

$$Co(NH_3)_5(HCO_2)^{2+} + Cr(OH_2)_6^{2+} + 5H_3O^+ = Co(OH_2)_6^{2+} + 5NH_4^+ + Cr(OH_2)_5(HCO_2)^{2+} \qquad (4)$$

reductions of carboxylatopentaamminecobalt(III) complexes,[14] features ligand transfer from cobalt to chromium. The same complex was also formed as a minor product in the reduction of chromium(VI) with an excess of formic acid.[26] The complex obtained by either method was absorbed on Dowex 50W X-2 (50–100 mesh, sodium form), and eluted with 0.5 *M* sodium perchlorate, a behavior which strongly suggests a dipositive charge for the ion. As shown in Table II, the samples obtained by the two different methods exhibit identical absorption spectra. The ratio of formate to chromium was 1.07 ± 0.02,[27] and it is concluded that the complex ion has the composition $Cr(OH_2)_5(HCO_2)^{2+}$.

Table II. Electronic Spectral Data for Formatoaquochromium(III) Complexes[a]

Complex	*A*, M^{-1} cm^{-1} [b]	*A*, M^{-1} cm^{-1} [c]
$Cr(OH_2)_5(HCO_2)^{2+}$ [d]	20.2 ± 0.1	21.1 ± 0.1
$Cr(OH_2)_5(HCO_2)^{2+}$ [e]	20.3 ± 0.1	20.9 ± 0.1
cis-$Cr(OH_2)_4(HCO_2)_2^+$ [f]	27.4 ± 0.1[g]	27.0 ± 0.1[h]

[a] Each entry is the average value for three independent preparations. [b] Molar absorptivity at 575 nm max. [c] Molar absorptivity at 412 nm max. [d] From $Co(NH_3)_5(HCO_2)^{2+}$–Cr^{2+} reaction. [e] From (Cr(VI)–HCO_2H reaction. [f] From *cis*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reaction. [g] Maximum absorption at 574 nm. [h] Maximum absorption at 413 nm.

The diformato complex was prepared by the reaction between *cis*-$Co(en)_2(HCO_2)_2^+$ and Cr^{2+} (eq 5) which

$$cis\text{-}Co(en)_2(HCO_2)_2^+ + Cr(OH_2)_6^{2+} + 4H_3O^+ = Co(OH_2)_6^{2+} + 2enH_2^{2+} + Cr(OH_2)_4(HCO_2)_2^+ \qquad (5)$$

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[26] The capture of ligands in the coordination sphere of chromium(III) formed by reduction of chromium(VI) appears to be a relatively common occurrence: L. S. Hegedus, B.S. Thesis, The Pennsylvania State University, 1965.

[27] The excess of formate over chromium is attributed to aquation of the formate complexes during the ion exchange. During elution neutral formic acid will pass through the resin, whereas the chromium(III) species of higher charge will be retained in the resin. This will result in a high formate to chromium ratio.

Table III. Stoichiometry of the Chromium(II) Reduction of *cis*-$Co(en)_2(HCO_2)_2^+$ [a]

Co(III), mmoles	Cr(II), mmoles	$[H^+]$, *M*[b]	% *cis*-$Cr(OH_2)_4$-$(HCO_2)_2^+$	% $Cr(OH_2)_5$-$(HCO_2)^{2+}$	k_d/k_s[c]
0.132	0.147	0.065–0.01	82.8[d]	13.7[d]	6.4[d]
0.135	0.147	0.065–0.009	82.8[d]	11.5[d]	6.4[d]
0.146	0.113	0.065–0.017	85.1[d]	9.9[d]	8.6[d]
0.136	0.113	0.065–0.017	81.4[d]	13.2[d]	6.0[d]
0.063	0.077	0.039–0.013	79.7[e]	17.9[e]	5.2[e]
0.066	0.077	0.039–0.012	76.3[e]	21.1[e]	4.1[e]
0.064	0.077	0.039–0.012	71.0[f]	23.4[f]	3.0[f]
0.140[g]	0.147	0.20–0.13		94.6[f,g]	
0.123[g]	0.147	0.20–0.14		96.6[f,g]	

[a] Total volume 10 ml, $[ClO_4^-] = 1.0$ *M*. [b] Initial and final hydrogen concentrations; H^+ is consumed during the reaction by the ethylenediamine released. [c] Ratio of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ to $Cr(OH_2)_5(HCO_2)^{2+}$ produced in the reaction, corrected for loss of *cis*-$Cr(OH_2)_4$-$(HCO_2)_2^+$ during ion exchange. [d] At 0°. [e] At 15°. [f] At 25°. [g] Reactant is *trans*-$Co(en)_2(HCO_2)_2^+$.

proceeds in part by a doubly bridged transition state and features the transfer of two formate ligands from cobalt to chromium. For the identification of the complex, the reaction was carried out at low ionic strength, and the resulting solution was diluted (ionic strength <0.05) prior to absorption of the complex on Dowex 50W X-2 (50–100 mesh, sodium form). The complex was eluted with 0.1 *M* sodium perchlorate, a behavior that strongly suggests a unipositive charge for the ion. The ratio of formate to chromium was 2.19 ± 0.04,[27] and it is concluded that the complex ion has the composition $Cr(OH_2)_4(HCO_2)_2^+$. The *cis* geometry is assigned on the basis of the synthetic route that leads to the formation of this ion.

As seen in Table II, the ions $Cr(OH_2)_5(HCO_2)^{2+}$ and *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ exhibit, in common with other carboxylatoaquochromium(III) complexes, two absorption maxima in the vicinity of 570 and 410 nm. The molar absorptivities for the diformate complex are larger than those of the monoformate complex, but smaller than those of chelated carboxylato complexes.[28,29]

Stoichiometries of the Chromium(II) Reductions of ***cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$.** The reduction of *cis*-$Co(en)_2(HCO_2)_2^+$ by chromium(II) yields both *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ and $Cr(OH_2)_5(HCO_2)^{2+}$. The pertinent results are summarized in Table III. As indicated in the Experimental Section, in order to maximize the recovery of the two formatochromium(III) complexes, the ion exchange separation procedure was carried at low temperature and acidity. Although these precautions were fairly effective in leading to a relatively high total recovery (note that the sum of % *cis*-$Cr(OH_2)_4$-$(HCO_2)_2^+$ and % $Cr(OH_2)_5(HCO_2)^{2+}$ varies between 94.3 and 97.4 for the experiments reported in Table III), it cannot be concluded that the ratios of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ to $Cr(OH_2)_5(HCO_2)^{2+}$ *recovered* give a relatively accurate value of the ratio of the complexes *produced in the reaction.* Blank experiments demonstrate that approximately 5% of the diformato complex hydrolyzes during the separation, and therefore the % *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ recovered was corrected for the loss. The values of k_d/k_s listed in the last column of Table III were then calculated from the expression $C/100 - C$, where C is the % *cis*-$Cr(OH_2)_4(HCO_2)^+$ corrected for the 5% loss during separation. On the basis of these considerations, it is concluded that the values of k_d/k_s represent, as closely as can be ascertained, the ratio of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ to $Cr(OH_2)_5$-$(HCO_2)^{2+}$ produced in the reaction. It is seen that, within the relatively large experimental uncertainty, the values of k_d/k_s do not depend on whether the cobalt(III) or the chromium(II) is the limiting reagent (compare the first four entries of Table III). Furthermore, it is noteworthy that the values of k_d/k_s decrease with increasing temperature. The mechanistic implications of these results, as well as the significance of k_d and k_s will be discussed below.

Included in Table III (last two entries) are the stoichiometric results for the *trans*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reaction. As expected on the basis of geometric considerations, the sole formate-containing chromium(III) product of this reaction is $Cr(HCO_2)^{2+}$, and it is produced in nearly quantitative yield.

Kinetics of the Chromium(II) Reductions of ***cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$.** In order to simplify the data collected from the stop-flow measurements, the concentration of chromium(II) was greater than the concentration of cobalt(III) by at least a factor of 30. The concentration ranges used were $[Co(III)] = (1.7–3.1) \times 10^{-4}$ *M*, $[Cr^{2+}] = 0.0050–0.0394$ *M* for the *cis* complex; and $[Co(III)] = (0.90–1.4) \times 10^{-4}$ *M*, $[Cr^{2+}] = 0.010–0.040$ *M* for the *trans* complex. Under these conditions the disappearance of the cobalt(III) complex obeyed pseudo-first-order kinetics, and was governed by a pseudo-first-order rate coefficient k_p. The dependence of k_p upon chromium(II) concentration was not extensively investigated, but the measurements, summarized in Table IV, are seen to be consistent with the rate law

$$-d[Co(III)]/dt = k_2[Co(III)][Cr(II)] \qquad (6)$$

where $k_2 = k_p[Cr(II)]$.

Of major interest in the present work was the dependence of the second-order rate coefficients k_2 upon hydrogen ion concentration. For the *cis* complex the rate *decreases* with increasing hydrogen ion concentration (Table V), whereas for the *trans* complex the rate *increases* with increasing hydrogen ion concentration (Table VI). The hydrogen ion dependences have the form $k_2 = a/(1 + b[H^+])$ and $k_2 = c + d[H^+]$ for the *cis* and *trans* complexes, respectively.

Discussion

The results of the kinetic studies of the chromium(II) reduction of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ conform to the mechanism shown in eq 7.

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(28) D. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).

(29) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965).

Table IV. Chromium(II) Dependence of the *cis*-Co(en)$_2$(HCO$_2$)$_2$$^+$–Chromium(II) Reaction[a]

[Cr^{2+}], $M \times 10^3$	k_2, M^{-1} sec^{-1} $\times 10^{-2}$ [b]
5.00	4.13
9.84	3.99, 3.77, 4.37
19.7	4.04
39.4	3.84
19.9	2.63[c]
50.8	2.64[c]
20.2	16.1[d]
40.0	17.6[d]

[a] [Co(III)] = (1.7–3.1) × 10^{-4} M, [ClO$_4^-$] = 1.00 M, 25°, [H$^+$] = 0.200 M, LiClO$_4$ used as a supporting electrolyte. [b] Each entry is the average of four replicate measurements with the same pair of solutions. k_2 is defined by eq 6. [c] At 15°, [H$^+$] = 0.100 M. [d] Reactant is *trans*-Co(en)$_2$(HCO$_2$)$_2$$^+$; [H$^+$] = 0.500 M, 25°. The entry is the value of k_2.

Table V. Acid Dependence of the Chromium(II) Reduction of *cis*-Co(en)$_2$(HCO$_2$)$_2$$^+$ [a]

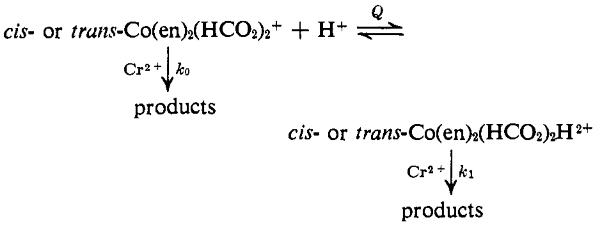
	k_2, M^{-1} sec^{-1} $\times 10^{-2}$ [b]		
[H$^+$], M	15°	25°	35°
0.050	2.80 (2.70)		5.20 (5.19)
0.100	2.64[c] (2.65)	4.15[d] (4.16)	
0.200	2.56 (2.55)	4.02[c] (3.99)	5.00 (4.97)
0.400	2.27 (2.38)	3.79[d] (3.69)	4.67 (4.71)
0.600		3.41[d] (3.43)	4.43 (4.48)
0.700	2.11 (2.16)		
0.800	2.08 (2.10)	3.36 (3.16)	4.34 (4.27)
0.900	2.15 (2.04)		
0.970	2.01 (2.00)	3.05[d] (3.04)	4.19[d] (4.11)

[a] [Co(III)] = (1.7–3.1) × 10^{-4} M, [Cr(II)] = 0.0050–0.0394 M, [ClO$_4^-$] = 1.00 M, LiClO$_4$ used as supporting electrolyte. [b] Unless specified otherwise, each entry is the average of four replicate measurements with the same pair of solutions. k_2 is defined by eq 6. Values in parentheses calculated using the parameters in Table VII. [c] Average of values in Table IV. [d] Average of eight replicate measurements with two independent pairs of solutions.

Table VI. Acid Dependence of the Chromium(II) Reduction of *trans*-Co(en)$_2$(HCO$_2$)$_2$$^+$ [a]

	k_2, M^{-1} sec^{-1} $\times 10^{-1}$ [b]		
[H$^+$], M	15°	25°	35°
0.100	0.82 (0.81)	1.18 (1.17)	1.51 (1.56)
0.200		1.34 (1.32)	
0.300	1.00 (1.02)		1.99 (1.95)
0.400		1.62[c] (1.62)	
0.500	1.24 (1.23)	1.68[d] (1.77)	2.55 (2.35)
0.700	1.43 (1.44)		2.57 (2.74)
0.880		2.35 (2.38)	
1.00	1.85[e] (1.74)		3.38[e] (3.34)

[a] [Co(III)] = (0.9–1.4) × $10^{-4}M$, [Cr(II)] = 0.010–0.040 M, [ClO$_4^-$] = 1.0 M, LiClO$_4$ used as supporting electrolyte. [b] Unless specified otherwise, each entry is the average of four replicate measurements with the same pair of solutions. k_2 is defined by eq 6. Values in parentheses calculated using the parameters in Table VII. [c] Average of values in Table IV. [d] Average of eight replicate measurements with two independent pairs of solutions. [e] [ClO$_4^-$] = 1.06 M.



$$\begin{array}{ccc} \textit{cis-}\text{ or }\textit{trans-}\mathrm{Co(en)_2(HCO_2)_2^+} + \mathrm{H^+} & \overset{Q}{\rightleftharpoons} & \textit{cis-}\text{ or }\textit{trans-}\mathrm{Co(en)_2(HCO_2)_2H^{2+}} \\ \mathrm{Cr^{2+}}\Big\downarrow k_0 & & \mathrm{Cr^{2+}}\Big\downarrow k_1 \\ \text{products} & & \text{products} \end{array} \qquad (7)$$

Equation 7 represents a rapid acid–base equilibrium governed by an equilibrium quotient Q. The second-order rate constants k_0 and k_1 correspond to the chromium(II) reductions of the nonprotonated and protonated diformato complexes, respectively. On the basis of this mechanism, the measured second order rate coefficients k_2 are related to Q, k_0, and k_1 by

$$k_2 = \frac{k_0 + k_1Q[\mathrm{H^+}]}{1 + Q[\mathrm{H^+}]} \qquad (8)$$

Different limiting forms of eq 8 obtain for the reactions of the *cis* and *trans* complexes.

Consider first the kinetic data for the *cis* complex (Table V). The observed decrease in rate with increasing hydrogen ion concentration suggests that substantial protonation of the complex obtains in the range of acidities studied, and that the protonated complex is unreactive. Under these conditions, eq 8 becomes $k_2 = k_0/(1 + Q[\mathrm{H^+}])$. This conclusion was put on a quantitative basis by first fitting the kinetic data of Table V to eq 8 using the nonlinear least-squares program. Best-fit values of k_1 were negative and had standard deviations larger than the values themselves.[30] Therefore, k_1 was set equal to 0, and the least-squares calculation repeated to obtain values of k_0 and Q. The results of these calculations are given in columns 2 and 5 of Table VII. By comparing the experimental values of k_2 (columns 2, 3, and 4 of Table V) with those calculated using the constants k_0 and Q (values in parentheses in columns 2, 3, and 4 of Table V), it is seen that the functional dependence of k_2 upon [H$^+$] closely obeys the equation $k_2 = k_0/(1 + Q[\mathrm{H^+}])$.[31]

Although the satisfactory agreement between experimental and calculated values of k_2 provides support for the proposed mechanism, it might be argued that the decrease in k_2 with increasing acidity does not represent a chemical effect, but rather a medium effect caused by replacement of H$^+$ for Li$^+$ as the acidity is increased. Independent evidence for the proposed protonation was obtained in a study of the acid-catalyzed aquation of *cis*-Co(en)$_2$(HCO$_2$)$_2$$^+$.[32] The acid dependence of the first-order rate coefficient for aquation has the form $k_1'Q[\mathrm{H^+}]/(1 + Q[\mathrm{H^+}])$. The values of Q obtained from the aquation studies are given in parentheses in column 5 of Table VII. The agreement between the two sets of values of Q obtained from systems that exhibit such radically different chemistry and kinetic behavior[33] is considered satisfactory, and provides strong evidence for the proposed protonation.

Turning to the chromium(II) reduction of *trans*-Co(en)$_2$(HCO$_2$)$_2$$^+$, the kinetic data of Table VI show that protonation of the *trans* complex enhances its reactivity toward reduction. The increase in rate is linear in hydrogen ion concentration, and therefore, on the basis of the proposed mechanism, it is concluded that, even at 1 M acid, $Q[\mathrm{H^+}] \leq 0.05$. Under these circumstances eq 8 simplifies to $k_2 = k_0 + k_1Q[\mathrm{H^+}]$. Values of k_0 and k_1Q were obtained by using the least-squares program, and the results of the calculations are given in columns 3 and 4 of Table VII. As can be seen by comparing the ex- of k_2 (columns 2, 3, and 4 of Table

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[30] For example, the data at 25° yielded k_0 = 422 ± 12, k_1 = −320 ± 1627, Q = 0.20 ± 0.53.

[31] It must be admitted, however, that a small contribution (k_1 ± 10 M^{-1} sec^{-1}) by the acid dependent path cannot be completely ruled out.

[32] J. R. Ward and A. Haim, in preparation.

[33] Note that the chromium(II) reduction is inhibited by acid, whereas the aquation is accelerated by acid.

Table VII. Rate Constants for Chromium(II) Reduction and Protonation Constants of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ [a]

t, °C	$k_0(cis)$, M^{-1} sec^{-1}	$k_0(trans)$, M^{-1} sec^{-1}	$k_1Q(trans)$, M^{-2} sec^{-1}	$Q(cis)$, M^{-1} [b]
15	275 ± 5	7.1 ± 0.1	10.3 ± 0.3	0.39 ± 0.04 (0.32 ± 0.05)
25	434 ± 11	10.2 ± 0.3	15.0 ± 0.7	0.44 ± 0.07 (0.36 ± 0.04)
35	526 ± 6	13.6 ± 1.0	19.8 ± 3	0.29 ± 0.03 (0.33 ± 0.06)

[a] $[ClO_4^-] = 1.0$ M. k_0, k_1, and Q are related to the measured second-order coefficient k_2 by eq 8. [b] Values in parentheses obtained from the acid-catalyzed aquation of *cis*-$Co(en)_2(HCO_2)_2^+$, ref 31.

Table VIII. Rate Constants and Activation Parameters for the Chromium(II) Reductions of Various Formatoamine–Cobalt(III) Complexes

Cobalt(III) complex	k, M^{-1} sec^{-1} (25°)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$Co(NH_3)_5(HCO_2)^{2+}$ [a]	7.2	8.3 ± 0.3	−27 ± 1
trans-$Co(en)_2(HCO_2)_2^+$ [b]	5.1 ± 0.3[c]	5.1 ± 0.2	−38.2 ± 0.8[c]
trans-$Co(en)_2(HCO_2)_2^+$ [d]	15.0 ± 0.7[e]	5.1 ± 0.4	−36 ± 1
cis-$Co(en)_2(HCO_2)_2^+$ [f]	50 ± 5[c]	7.9 ± 1	−25 ± 5[c]
cis-$Co(en)_2(HCO_2)_2^+$ [g]	334 ± 10	3.7 ± 1	−35 ± 4

[a] From ref 34. [b] Acid-independent path. [c] Corrected for the symmetry number factor. [d] Acid-dependent path. [e] This is the value of k_1Q in M^{-2} sec^{-1}. $k_1 \geq 300$ M^{-1} sec^{-1}; see text. [f] Singly bridged path. [g] Doubly bridged path.

VI) with those calculated using the best-fit values of k_0 and k_1Q (values in parentheses in columns 2, 3, and 4 of Table VI), the agreement is quite satisfactory.

The stoichiometric measurements of the *trans*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reaction at 25° and $[H^+] = 0.20$ M show nearly quantitative transfer of one formate group from cobalt(III) to chromium(II). Under these conditions, the ratio of the acid dependent (k_0) to the acid independent path ($k_1Q[H^+]$) is *ca.* 1:3. We conclude, therefore, that both pathways proceed *via* inner sphere transition states featuring a formate bridge between chromium and cobalt. There is an ambiguity regarding the location of the added proton for the transition state of composition $[Co(en)_2(HCO_2)_2CrH^{5+}]^{\ddagger}$, and this point will be discussed below.

The stoichiometric measurements of the *cis*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reaction show that both $Cr(HCO_2)^{2+}$ and *cis*-$Cr(HCO_2)_2^+$ are formed as primary products of the reactions. Since the kinetic measurements indicate that the protonated *cis*-$Co(en)_2(HCO_2)_2^+$ complex is unreactive, we conclude that reduction of the nonprotonated complex proceeds *via* parallel singly and doubly bridged transition states with transfer of one and two formate groups, respectively, from cobalt to chromium.

$$cis\text{-}Co(en)_2(HCO_2)_2^+ + Cr(OH_2)_6^{2+} + 5H_3O^+ \xrightarrow{k_s} Co(OH_2)_6^{2+} + 2enH_2^{2+} + HCO_2H + Cr(OH_2)_5(HCO_2)^{2+} \quad (9)$$

$$cis\text{-}Co(en)_2(HCO_2)_2^+ + Cr(OH_2)_6^{2+} + 4H_3O^+ \xrightarrow{k_d} Co(OH_2)_6^{2+} + 2enH_2^{2+} + cis\text{-}Cr(OH_2)_4(HCO_2)_2^+ \quad (10)$$

On the basis of this interpretation, the measured second-order rate coefficient $k_0(cis) = k_s + k_d$, where k_s and k_d are the second-order rate constants for reaction *via* singly and doubly bridged transition states, respectively. Since the ratio of *cis*-$Cr(OH_2)_4(HCO_2)_2^+$ to $Cr(OH_2)_5(HCO_2)^{2+}$ produced in the reaction is k_d/k_s (column 6 of Table III), a combination of the kinetic and stoichiometric measurements at various temperatures provides individual values of k_d and k_s and their corresponding activation parameters. The calculation was performed in three stages. First, the measured values of k_d/k_s at 0, 15, and 25° were fitted to the equation $k_d/k_s = \exp(\Delta H_s^{\ddagger} - \Delta H_d^{\ddagger})\exp(\Delta S_d^{\ddagger} - \Delta S_s^{\ddagger})$ by means of the nonlinear least-squares programs. The subscripts s and d refer to the kinetic parameters for the singly and doubly bridged pathways, respectively. Next, individual values of k_d and k_s were obtained from the measured k_0 values and the calculated k_d/k_s values at 15, 25, and 35°. Finally, the individual values of k_d and k_s were fitted to the transition state equation $k = (RT/Nh)e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S^{\ddagger}/RT}$. The results of these calculations are presented in Table VIII. The large standard deviations associated with the activation parameters reflect various experimental uncertainties as well as the accumulation of errors through the calculations. Included in Table VIII are the rate constants and activation parameters for the related reductions of *trans*-$Co(en)_2(HCO_2)_2^+$ and $Co(NH_3)_5(HCO_2)^{2+}$. It must be noted that the listed values of the rate constants and entropies of activation for the *trans*-$Co(en)_2(HCO_2)^{2+}$ (acid independent path) and *cis*-$Co(en)_2(HCO_2)^{2+}$ (singly bridged path) reactions are the symmetry corrected values.

Since all the reactions listed in Table VIII proceed *via* inner sphere mechanisms, the variations in rates represent nonbridging ligand effects. The rate constants for the reactions of $Co(NH_3)_5(HCO_2)^{2+}$, *trans*-$Co(en)_2(HCO_2)_2^+$ (acid independent path), and *cis*-$Co(en)_2(HCO_2)_2^+$ (singly bridged path) span only one order of magnitude (5–50 M^{-1}sec^{-1}), an indication that the nonbridging ligand effect of formate ion (in either *cis* or *trans* positions) is quite modest. The reaction of *cis*-$Co(en)_2(HCO_2)_2^+$ *via* the doubly bridged pathway proceeds at a somewhat faster rate, and it is seen that the higher rate constant is associated with a smaller enthalpy of activation. Presumably this effect reflects a favorable enthalpy change for the formation of the precursor, doubly bridged binuclear complex.

By far, the most dramatic difference between the reactivities of the various formato complexes is related to the effect of acid on the reaction rates. The rates of reduction of $Co(NH_3)_5(HCO_2)^{2+}$, *cis*-$Co(en)_2(HCO_2)_2^+$, and *trans*-$Co(en)_2(HCO_2)_2^+$ are acid independent, acid inhibited, and acid catalyzed, respectively. As already noted, these trends can be understood by recognizing the extent and kinetic consequences of protonation for the various formato complexes. Thermodynamically, protonation in the range $[H^+] = 0.1$–1.0 M is unimportant for *trans*-$Co(en)_2(HCO_2)_2^+$ and $Co(NH_3)_5$-

$(HCO_2)_2^+$, but significant for *cis*-$Co(en)_2(HCO_2)_2^+$. Kinetically, protonation of *cis*-$Co(en)_2(HCO_2)_2^+$ (and presumably of $Co(NH_3)_5(HCO_2)^{2+}$) decreases its reactivity toward reduction, whereas protonation of trans-$Co(en)_2(HCO_2)_2^+$ increases its reactivity.

In this context it is noteworthy that protonation of $Cr(OH_2)(CH_3CO_2)^{2+}$ and $Co(NH_3)_5(CH_3CO_2)^{2+}$ has been recently demonstrated.[16,34] The equilibrium quotient for the reaction $Cr(OH_2)_5(CH_3CO_2)^{2+} + H^+ = Cr(OH_2)_5(CH_3CO_2H)^{3+}$ is 0.25 M^{-1} at 25° and ionic strength 4.0, and shows little or no temperature dependence in the range 25–55°. At 25° and ionic strength 1.0, an upper limit for the equilibrium quotient is 0.05 M^{-1}.[16] For the reaction $Co(NH_3)_5(CH_3CO_2)^{2+} + H^+ = Co(NH_3)_5(CH_3CO_2H)^{3+}$, the equilibrium quotient (25°) is 0.25 M^{-1} at ionic strength 1.0, and 2.2 M^{-1} at ionic strength 4.0.[34] The results obtained here on the protonation of *cis*-$Co(en)_2(HCO_2)_2^+$ ($Q \sim 0.4\ M^{-1}$ at 25° and $[ClO_4^-] = 1.0\ M$) show that the diformato complex is a slightly stronger base than $Co(NH_3)_5(CH_3CO_2)_2^{2+}$, and an appreciably stronger base (by at least a factor of 8) than $Cr(OH_2)_5(CH_3CO_2)^{2+}$. This conclusion is unexpected on the basis of the known relative basicities of free formate and acetate ions. It must be recognized, however, that the diformato complex has a positive charge smaller than that of the acetato complexes, and it might be argued on this basis that the relative base strengths of the carboxylato complexes is not unreasonable. However, this argument does not explain why *trans*-$Co(en)_2(HCO_2)_2^+$ ($Q < 0.05\ M^{-1}$, *vide supra*) is a weaker base than *cis*-$Co(en)_2(HCO_2)_2^+$. An additional factor to be considered is related to the site of protonation. In the case of $Cr(OH_2)_5(CH_3CO_2)^{2+}$ it has been suggested[16] that the dominant form of $Cr(OH_2)_5(CH_3CO_2H)^{3+}$ has the proton attached to the oxygen bound to chromium. For *cis*-$Co(en)_2(HCO_2)_2H^{2+}$, the authors are inclined to favor an internal hydrogen bonded structure with the proton attached to both carbonyl oxygens.[35] This suggestion is particularly attractive since it provides a simple rationalization not only for the trends in basicity of the various carboxylato complexes under consideration, but also, as discussed below, for the lack of reactivity toward chromium(II) reduction of the protonated *cis* diformato complex. For *trans*-$Co(en)_2(HCO_2)_2^+$, obviously the proton is attached to only one of the formate groups, but it is not known whether the proton binds to the carbonyl oxygen or the oxygen attached to cobalt.

In trying to understand the decrease in reactivity of *cis*-$Co(en)_2(HCO_2)_2^+$ upon protonation, the detailed mechanism *via* the singly and doubly bridged pathways must be considered. Two plausible modes of attack by chromium(II) can be envisaged:[36] attack at the carbonyl oxygen (remote) or attack at the oxygen bound to cobalt (adjacent). If we accept the suggestion of a hydrogen bonded structure for the protonated *cis* complex, its lack of reactivity *via* the doubly bridged pathway is readily accommodated whether remote or adjacent attack obtains. On the basis of remote attack, the effect can be ascribed to the tying up of the carbonyl oxygens and the consequent unavailability of these oxygen atoms for binding to the chromium(II). For the adjacent attack mechanism, an examination of molecular models indicates that with the carbonyl oxygens tied up by a proton, attack by chromium(II) at the two oxygen atoms bound to cobalt is sterically impossible. For the singly bridged pathway proceeding *via* remote attack, again the unavailability of the carbonyl oxygens can be invoked to account for the lack of reactivity of the protonated form. Adjacent attack at a single oxygen atom does not appear to be sterically hindered, but may be electronically unfavorable, perhaps because of the inductive effect of the proton on the carbonyl oxygens. We must conclude that the present results leave unanswered the important question of remote *vs.* adjacent attack for reduction of carboxylatocobalt(III) complexes.

Turning to the acid catalysis of the *trans*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reaction, it was indicated above that there is an ambiguity regarding the location of the added proton for the transition state of composition [*trans*-$Co(en)_2(HCO_2)_2CrH^{4+}]^{\ddagger}$: the proton could be attached to either the bridging or nonbridging formate ion. Since the reductions of carboxylatopentaamminecobalt(III) complexes where "special" effects[36] are absent exhibit no acid catalysis, it is concluded that the proton is attached to the nonbridging formate group. Since at 25° $k_1Q(trans) = 15.0\ M^{-2}\ sec^{-1}$ and $Q(trans) \leq 0.05\ M^{-1}$, the conclusion is that $k_1 \geq 300\ M^{-1}\ sec^{-1}$. The increase in reactivity on protonation (compare with the value $k_0(trans) = 10.2\ M^{-1}\ sec^{-1}$ at 25°) is then ascribed, as previously proposed,[11,37] to facilitation of the motion of the formate ion *trans* to the bridging group, and is taken to corroborate the suggestions[8] that stretching of the bond *trans* to the bridging group is an important feature of the activation process leading to electron transfer. Recent oxygen isotope fractionation studies in the Cr^{2+}–*trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ reaction support this view.[38]

The hydrogen ion effects found in the present system conform to those previously observed in the *cis*- and *trans*-$Co(NH_3)_4(N_3)_2^+$–Fe^{2+} system,[11,37] but contrast, in part, with those reported for the *cis*- and *trans*-$Co(en)_2(CH_3CO_2)_2^+$–Cr^{2+} reactions.[10] The hydrogen ion dependences of the second-order rate constants reported for the diacetato complexes are (25°) $5[H^+]$ and $4 + 13.5 \cdot [H^+]$ for the *cis* and *trans* complexes, respectively. The results for the *trans* diacetato complex parallel those for the *trans* diformato complex, but disagreement exists for the *cis* isomers. It must be stated, however, that the reported[10] rates and rate law for *cis*-$Co(en)_2(CH_3CO_2)_2^+$ may be incorrect. The rate of the acid-catalyzed aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ has been measured in this laboratory,[32] and, at 25° and $[H^+] = 0.2$–$0.6\ M$ (the range used in the reduction studies), the half-lives for aquation are found to be in the range 10–15 sec. From the reported rate constants and concentrations in the measurements of the *cis*-$Co(en)_2(CH_3CO_2)_2^+$–Cr^{2+} reaction,[10] the half-lives for reduction are estimated to be in the range 10–20 sec. Clearly, under the conditions chosen for the reduction studies, appreciable aquation is taking place, and doubt is therefore cast on the validity of the reported rates.

Finally, it is pertinent to consider some further details of the mechanism of inner sphere electron transfer reac-

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(34) M. B. Barrett, *Dissertation Abstr.*, **29**, 2333-B (1969).

(35) One of the authors (A. H.) is indebted to Professor Henry Taube for this suggestion.

(36) H. Taube, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D.C., 1965, p 107.

(37) A. Haim, *J. Amer. Chem. Soc.*, **86**, 2352 (1964).

(38) M. J. DeChant and J. B. Hunt, *ibid.*, **90**, 3695 (1968).

tions.[39] In the radical ion mechanism, the bridging ligand is first reduced to a radical which subsequently reduces the oxidizing metal center to which it is coordinated. In the resonance transfer or exchange mechanism, the bridging ligand acts merely as a mediator, and no radical ion intermediate is formed. Nordmeyer and Taube[40] have argued that in the radical ion mechanism the reduction of the ligand is rate determining, and consequently the nature of the metal ion center in the oxidant should not affect appreciably the reaction rate. In constrast, for the resonance mechanism the identity of the oxidizing metal center is quite important in determining the reaction rate. On this basis, they suggested that a possible test to distinguish between the radical ion and exchange mechanisms involves a comparison of the rate of chromium(II) reduction of $Co(NH_3)_5L^{n+}$ and the rate of chromium(II) exchange with $Cr(OH_2)_5L^{n+}$. For $L^- = F^-, Cl^-, OH^-$, and NCS^-, the ratios of the rate constant for reduction to the rate constant for exchange are larger than 3×10^4, and it was suggested that the exchange mechanism obtains. For L = isonicotinamide, the ratio is ~10, and the radical ion mechanism was favored.[40] A similar comparison can be made by considering the rate of reduction of *cis*-$Co(en)_2(HCO_2)^{2+}$ *via* the singly bridged pathway (eq 9) with the rate of the chromium(II) catalyzed dissociation of *cis*-$Cr(OH)_2(HCO_2)_2^+$ (eq 11). A

$$cis\text{-}Cr(OH_2)_4(CHO_2)_2^+ + Cr^{2+} + H_3O^+ \longrightarrow Cr(OH_2)_5(HCO_2)^{2+} + Cr^{2+} + HCO_2H \quad (11)$$

preliminary measurement of the rate constant k_{11} for reaction 11 has been carried out in this laboratory. At 25° and $[HClO_4] = 0.10\,M$, $k_{11} \sim 5 \times 10^{-4}\,M^{-1}\,sec^{-1}$. Since the rate constant k_s for reaction 9 is $100\,M^{-1}\,sec^{-1}$, it is concluded that $k_s/k_{11} \sim 5 \times 10^5$. Using this ratio as a diagnostic of mechanism, it appears that the chromium(II) reductions of the formatoaminecobalt(III) complexes proceed by the resonance transfer mechanism.

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[39] P. George and J. S. Griffith in "The Enzymes," Vol. 1, Academic Press, New York, N. Y., 1959, p 347.

[40] F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

Donor Properties of Positively Charged Ligands. Pseudotetrahedral Transition Metal Complexes Containing a Monoquaternized Tertiary Diamine

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Abstract: The halide salts, $(L^+)X$, of the monoquaternized diamine, L = 1,4-diazabicyclo[2.2.2]octane, react under anhydrous conditions with the halides of the divalent transition metals, Mn(II) to Zn(II), forming crystalline compounds of the stoichiometry $MX_2 \cdot (L^+)X$. On the basis of their electronic and vibrational spectra, magnetic susceptibilities, and X-ray powder diffraction patterns, these compounds are formulated as the high-spin, four-coordinate complexes $[M(L^+)X_3]$, having a pseudotetrahedral stereochemistry with C_{3v} symmetry. These crystalline complexes containing a positively charged ligand coordinated to a (positively charged) metal ion are remarkably stable, and the various factors contributing to their stability are discussed.

This work is part of a general study on the donor properties of positively charged ligands,[1] in particular monoquaternized diamines. The cation formed by monoquaternizing a diamine still has a donor nitrogen atom capable of coordination, and if this cation ligates to a metal ion, the resulting coordination compound will have the novel feature of containing two or more centers of positive charge, the central metal ion and the quaternized N atom of the ligand(s). In the presence of anions with poor donor properties, such as the perchlorate, complex cations of unusually high ionic charge can be formed; for example, $[Ni(L^+)_6]^{8+}$ if L^+ is a monoquaternized ethylenediamine.[2] With anions of moderate to good donor properties, such as the halides, both the cation ligand and the anions can coordinate, and the unusual metal ion to anion ratio resulting from the presence of the positive charge on the ligands may favor the formation of uncharged (or low-charged) complex species of uncommon stoichiometry and geometry. Furthermore, the electronic configuration of the central metal ion may be indirectly affected by the presence of a positive charge on the amine ligand(s), since this positive charge has a marked effect on the basicity of the N-donor atom.

It is known that the basicity of a diamine generally decreases by less than 2 pK_a units upon monoquaternization if the nitrogen atoms are separated by two or more $-CH_2-$ groups; but if the nitrogen atoms are closer the effect is much more pronounced. For example, upon monoprotonation the pK_a of $NH_2(CH_2)_8NH_2$ decreases[3] from 10.9 to 10.1, that of $NH_2(CH_2)_2NH_2$ decreases[3] from 9.97 to 6.97, and that of hydrazine, H_2N-NH_2, decreases[4] by a factor of 9 pK_a

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[1] J. V. Quagliano and L. M. Vallarino, "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz, Switzerland, 1966, Verlag Helvetica Chimica Acta, Basel, Switzerland, 1966, pp 216–218.

[2] J. V. Quagliano, J. T. Summers, S. Kida, and L. M. Vallarino, *Inorg. Chem.*, 3, 1557 (1964).

[3] E. J. Shepherd and J. A. Kitchener, *J. Chem. Soc.*, 2448 (1956).

[4] G. Schwarzenbach, *Helv. Chim. Acta*, **19**, 178 (1936).