Table III. Summary of Excited-State Reactivity of *trans*-$Co(CN)_4(SO_3)(X)^{n-}$

Excitation (type)	Irradiation wavelength, nm[a]	Comment
$d_{xz}, d_{yz} \rightarrow d_{z^2}$ (ligand field)	436, 366	Labilizes *z* axis. Affects π-donor ligands least, σ donors have intermediate lability, and π acceptors are much more reactive than in the ground state. Found: dramatic increase in lability of the π acceptor $-SO_3^{2-}$ on the *z* axis
$d_{xy} \rightarrow d_{x^2-y^2}$ (ligand field) and $SO_3^{2-} \rightarrow$ Co(III) (L → M CT)	313[b]	For ligand field excitation: equatorially localized. Found: lower quantum yields for disappearance implicating facile decay directly to ground state without reaction For L → M CT: Precursor to either redox chemistry or substitution
$SO_3^{2-} \rightarrow$ Co(III) (L → M CT)	254	Precursor to either redox chemistry or substitution. Found: modest yields of Co(II) and higher substitution yields than in 313-nm photolysis

[a] Both irradiation and absorption bandwidths are too broad to yield pure excitations. [b] For $X = SO_3^{2-}$ this irradiation wavelength corresponds closely to the L → M CT absorption maximum while for $X = OH^-$ or OH_2 this excitation is mixed d-d and L → M CT absorption.

its position in the spectrochemical series[17] and its strong trans-labilizing power in cyanocobaltate(III) complexes.[10,14] The most significant reaction associated with ligand field excitation is the loss of sulfite, consistent with the prediction of a greatly weakened Co(III) $-SO_3$ bond upon *depopulation* of π-bonding orbitals (d_{xz}, d_{yz}) *and population* of d_{z^2} σ*. In the ground-state loss of sulfite from either the aquo or hydroxo complex does not occur except under vigorous conditions.

The general decrease in reaction quantum yields upon 313-nm irradiation implicates a third excited state which gives less efficient reaction and/or incomplete internal conversion to the lower lying excited states. Nonradiative decay from this state must occur directly to the ground state. These observations could be accommodated satisfactorily by involving the lowest excited state arising from the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation.

A summary of the key points above appears in Table III. The two ligand field states and the L → M CT state account for all of the results. As with the $Co(CN)_5(X)^{n-}$ complexes,[5] the ligand field excited-state substitution reaction apparently proceeds primarily *via* a dissociative mechanism since added SO_3^{2-} suppresses the rate of sulfite substitution. The five-coordinate species produced *via* photolysis of *trans*-$Co(CN)_4(SO_3)_2^{5-}$ may be the same as that produced in the thermal dissociation.[10] The fact that the photosubstitution is very efficient in strongly alkaline media even though the thermal reaction is apparently acid catalyzed[10] evidences the important changes in binding interactions upon ligand field excitation.

The $Co(CN)_4(OH_2)_2^-$ photoproduct is extremely thermally reactive as addition of Na_2SO_3 results in very rapid formation of *trans*-$Co(CN)_4(SO_3)_2^{5-}$. Spectral changes also occur upon addition of other nucleophiles and characterization of the products is in progress.

Registry No. *trans*-$K_5Co(CN)_4(SO_3)_2$, 37954-25-9; *trans*-$K_3Co(CN)_4(SO_3)(H_2O)$, 37954-26-0; *trans*-$K_4Co(CN)_4(SO_3)(OH)$, 37954-27-1.

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(17) The first ligand band for $Co(CN)_5(SO_3)^{4-}$ is at 332 nm as compared with 312 nm for $Co(CN)_6^{3-}$ and 345 nm for $Co(CN)_5(NCCH_3)^{2-}$.

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Acid-Catalyzed Aquations of *cis*- and *trans*-Dicarboxylatoaminecobalt(III) Complexes[1a]

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The loss of one carboxylate ligand from *cis*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3, C_2H_5, C_3H_7), *cis*-$Co(NH_3)_4(CH_3CO_2)_2^+$, *cis*-$Co(dipy)_2(CH_3CO_2)_2^+$, and *trans*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3) is catalyzed by H^+ in aqueous solutions. For all the complexes studied, except *trans*-$Co(en)_2(HCO_2)_2^+$, the observed rate constant $k_{obsd} = -d(\ln [complex])/dt$ has a functional dependence with respect to $[H^+]$ (at ionic strength 1.00 *M* maintained with $LiClO_4$) given by $k_{obsd} = k_2Q[H^+]/(1 + Q[H^+])$. For *trans*-$Co(en)_2(HCO_2)_2^+$, k_{obsd} varies linearly with $[H^+]$. The kinetic results are interpreted on the basis of rapid preequilibrium protonation of the carboxylate complexes followed by slow aquation of the protonated complexes. The reactions of the cis complexes proceed with retention of configuration, whereas the trans complexes produce both *cis*- and *trans*-aquocarboxylatoamine products. An oxygen-18 tracer study of the acid-catalyzed aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ demonstrates that quantitative Co-O bond breaking obtains in this reaction. The reactivity trends observed and the mechanism of these reactions are discussed.

Introduction

In connection with our studies of the reductions of *cis*- and *trans*-diformatobis(ethylenediamine)cobalt(III) by chromium(II)[2] and vanadium(II),[3] it became necessary to obtain fairly detailed information about the hydrolytic stability of the two cobalt complexes. The trans isomer proved to be relatively stable toward loss of one formate group, whereas the cis isomer underwent rapid aquation in acid solution. The reaction is acid catalyzed, and detailed kinetic studies[1c] showed a first-order dependence on $[H^+]$

at low values of $[H^+]$ and a less than first-order dependence at higher values of $[H^+]$. These results were interpreted on the basis of a rapid protonation preequilibrium followed by slow loss of one formate ligand from the protonated complex.[1c] In view of the importance of dissecting assisted aquations of metal complexes into their thermodynamic and kinetic contributions,[4] the kinetic studies were extended first to the *cis*-$Co(en)_2(CH_3CO_2)_2^+$ compound[1c] and later to the compounds *trans*-$Co(en)_2(HCO_2)_2^+$, *trans*-$Co(en)_2(CH_3CO_2)_2^+$, *cis*-$Co(NH_3)_4(CH_3CO_2)_2$, *cis*-$Co(dipy)_2(CH_3CO_2)_2^+$, *cis*-$Co(en)_2(C_2H_5CO_2)_2^+$, and *cis*-$Co(en)_2(C_3H_7CO_2)_2^+$.[1b] Moreover, the stereochemical changes accompanying some of these reactions have been established, and an oxygen-18 tracer study of the aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ has been performed. In the present paper, we present the results of our investigations. After our work was completed, the results of a kinetic and stereochemical study of the acid-catalyzed aquation of *cis*- and *trans*-diacetatobis(ethylenediamine)cobalt(III) were published.[5] After allowing for the difference in experimental conditions, there is substantial agreement between the overlapping portions of the two investigations.

Experimental Section

Materials. The samples of *cis*- and *trans*-$[Co(en)_2(HCO_2)_2]ClO_4$ were the same ones used previously.[2,3] *cis*-$[Co(en)_2(CH_3CO_2)_2]ClO_4$ was prepared by the method of Kuroda and Gentile,[6] except that the evaporation to dryness was carried out in a vacuum desiccator at room temperature instead of in a water bath at 60°. The product was recrystallized twice from hot 95% ethanol. *Anal.* Calcd for $C_8H_{22}N_4CoClO_8$: C, 24.22; H, 5.59; N, 14.13. Found: C, 24.07; H, 5.75; N, 13.34. *trans*-$[Co(en)_2(CH_3CO_2)_2]ClO_4$ was prepared by the method of Linhard and Stirn.[7] The actual preparative scheme gives a product with no difficulty, but the recommended recrystallization from hot ethanol apparently causes isomerization and/or aquation. Therefore, the compound was recrystallized from warm (~35°) water. *Anal.* Calcd for $C_8H_{22}N_4CoClO_8$: C, 24.22; H, 5.59; N, 14.13. Found: C, 24.09, 24.19; H, 5.51, 5.58; N, 14.10, 14.21. The isomeric purity was determined by comparing the spectrum of the complex in 1.0 *M* $HClO_4$ and in 1.0 *M* $LiClO_4$. Since the cis isomer aquates rapidly in acid solution and the aquation is accompanied by an appreciable decrease in absorbance at 500 nm, a contamination of the trans compound by the cis isomer would be detected by the decrease in absorbance in 1.0 *M* $HClO_4$ as compared to 1.0 *M* $LiClO_4$. The observed values of the extinction coefficients at 500 nm were 38.2 ± 0.5 and 37.1 ± 0.5 M^{-1} cm^{-1} in $LiClO_4$ and $HClO_4$, respectively. Assuming that the change in extinction coefficient is caused by the aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$, we calculate that the fraction of cis isomer present in the sample of *trans*-$Co(en)_2(CH_3CO_2)_2^+$ is 2.9 ± 2.1%. *cis*-$[Co(en)_2(C_2H_5CO_2)_2](ClO_4)$ was prepared by the procedure of Linhard and Stirn.[7] *Anal.* Calcd for $C_{10}H_{26}N_4CoClO_8$: C, 28.26; H, 6.12; N, 13.19. Found: C, 28.29; H, 6.35; N, 13.31. *cis*-$[Co(en)_2(C_3H_7CO_2)_2]ClO_4$ was prepared by the method of Linhard and Stirn.[7] *Anal.* Calcd for $C_{12}H_{30}N_4CoClO_8$: C, 31.86; H, 6.64; N, 12.39. Found: C, 31.11; H, 6.61; N, 12.16. *cis*-$[Co(NH_3)_4(CH_3CO_2)_2]ClO_4$ was prepared by the method of Linhard and Weigel.[8] *Anal.* Calcd for $C_4H_{18}N_4CoClO_8$: C, 13.92; H, 5.22; N, 16.23. Found: C, 13.75, 13.84; H, 5.11, 5.17; N, 16.54, 16.74. *cis*-$[Co(dipy)_2(CH_3CO_2)_2]ClO_4$ was prepared by the procedure of Aprile and Maspero.[9] *Anal.* Calcd for $C_{24}H_{22}N_4CoClO_8$: C, 49.00; H, 3.74; N, 9.53. Found: C, 45.45, 45.32; H, 3.78, 3.68; N, 9.31, 9.45. *cis*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$ and *cis*-$Co(dipy)_2(CH_3CO_2)(OH_2)^{2+}$ were prepared *in situ* by adding perchloric acid of the desired concentration to solutions of the corresponding *cis*-diacetato complexes. *trans*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$ was prepared *in situ* by making use of the base hydrolysis of *trans*-$Co(en)_2(CH_3CO_2)_2^+$, followed by acidification. Twenty milliliters of a solution of the *trans*-diacetato complex 0.10 *M* in NaOH and 1.13 *M* in $LiClO_4$ was allowed to stand for 2 min at 40°. A 5-ml quantity of 0.90 *M* $HClO_4$ was then added. The resulting solution of *trans*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$ was contaminated by small amounts of *cis*- and *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ and *cis*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$.

The absorption spectra, measured with a Cary 14 recording spectrophotometer, of the complexes used in the present work are given in Table I.

The preparation of the lithium perchlorate solutions and the purification of the water have been described previously.[2,3] The ion-exchange resins were Dowex AG-50W from Bio-Rad Laboratories.

Analytical Measurements. Lithium perchlorate solutions were standardized by passing aliquots through Dowex AG-50W-X2 (H^+ form) ion-exchange columns and titrating the acid liberated. Carbon, hydrogen, and nitrogen analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., or by Galbraith Laboratories, Knoxville, Tenn.

Kinetic Measurements. The rates of reaction of the cis complexes were determined by continuous monitoring of the absorbance at the appropriate wavelength. For reactions with half-lives longer than 10 sec, a Cary 14 recording spectrophotometer was employed. A thermostated solution of the desired complex in water or lithium perchlorate was mixed with a lithium perchlorate–perchloric acid solution in a spectrophotometric cell of appropriate path length, and a recording of absorbance *vs.* time was obtained. Twelve to thirty data points were taken and fitted to the first-order kinetic equation $(A_t - A_\infty) = (A_0 - A_\infty)\exp(-k_{obsd}t)$ by means of a nonlinear least-squares program. A_0 and A_∞, the initial and final (*e.g.*, after 7–10 half-lives) absorbances, respectively, and k_{obsd}, the observed first-order rate constant, were taken as adjustable parameters. A_t is the absorbance at time *t*. The values of A_0, A_t, and A_∞ calculated by the computer were compared with the experimentally determined values, and, in general, agreement was within ±0.002 absorbance unit. For reactions with half-lives shorter than 10 sec, a stopped-flow apparatus[10] connected to an IBM 1800 computer was used.[3] First-order rate constants k_{obsd} were obtained as described previously.[3]

The rates of reaction of the trans complexes were obtained by a combined ion-exchange spectrophotometric method. The desired amount of an aqueous solution of the complex was added to a thermostated solution of the desired concentrations of perchloric acid and lithium perchlorate. Aliquots were withdrawn at periodic intervals, diluted with an equal volume of 1.0 *M* $NaClO_4$–0.03 *M* $HClO_4$, and then added to an ion-exchange column of Dowex AG-50W-X8 (100–200 mesh, sodium form) kept near 0°. The unreacted unipositive complex was eluted with 1.0 *M* $NaClO_4$–0.03 *M* $HClO_4$, whereas the dipositive reaction products remained in the ion-exchange column.[11] The concentration of the unreacted trans complex in the eluents was measured spectrophotometrically at 540 nm in a 10-cm cell. First-order rate constants were obtained graphically from plots of the logarithm of the absorbance at 540 nm (corrected for the 1.0 *M* $NaClO_4$–0.03 *M* $HClO_4$ blank) *vs.* time.

Tracer Experiments. In order to determine the position of bond breaking in the aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$, the reaction was carried out at 25° in oxygen-18-enriched water containing the desired amount of $HClO_4$ (~0.4 *M*). Following the completion of the reaction, the product *cis*-$Co(en)(CH_3CO_2)(OH_2)^{2+}$ and excess ClO_4^- were removed by adding dry Dowex AG-50W-X12 (200–300 mesh, K^+ form), cooling to 0°, and then filtering. The filtrate, containing the acetic acid released in the aquation, was treated as described by Llewellyn and O'Connor[12] to obtain silver acetate. The silver acetate was decomposed thermally in a vacuum line,[12] and the CO_2 released (produced in ~40% yield) was chromatographed on a firebrick column. The 46/44 and 45/44 mass ratios in the CO_2 were measured

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Table I. Spectral Data for Carboxylatocobalt(III) Complexes

Compound	λ,[a] nm	ϵ,[b] M^{-1} cm^{-1}	Ref
cis-$Co(en)_2(HCO_2)_2^+$	501, 362	128, 85.0	*c*
	500, 362	127, 84.7	*d*
trans-$Co(en)_2(HCO_2)_2^+$	540, 453, 357	51.4, 30.6, 66.5	*c*
	539, 452, 352	51.3, 39.9, 66.7	*d*
cis-$Co(en)_2(CH_3CO_2)_2^+$	504, 361	155, 98.7	*c*
	504, 361	153, 97.4	*d*
	505, 360	151, 97.7	*e*
	504, 361	150, 95.5	*f*
trans-$Co(en)_2(CH_3CO_2)_2^+$	540, 450, 356	60.7, 29.1, 72.7	*c*
	540, 450, 356	60.7, 29.5, 73.8	*d*
	536, 448, 356	60.1, 29.0, 73.0	*f*
	540, 360	51.3, 67.6	*e*
cis-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$	495, 358	114, 80.7	*c*
	495, 359	112, 78.7	*d*
	498, 360	100, 77.6	*e*
cis-$Co(en)_2(C_2H_5CO_2)_2^+$	503, 361	139, 91.5	*d*
	505, 363	145, 81.3	*g*
cis-$Co(en)_2(C_3H_7CO_2)_2^+$	508, 360	146, 109	*d*
cis-$Co(NH_3)_4(CH_3CO_2)_2^+$	525, 365	113, 65.2	*d*
	522, 364	112, 64.3	*f*
	524, 366	102, 59.0	*g*
cis-$Co(dipy)_2(CH_3CO_2)_2^+$	509	115	*d*
	509	120	*h*
cis-$Co(dipy)_2(CH_3CO_2)(OH_2)^{2+}$	495	84.0	*d*
	495	83.2	*h*

[a] Wavelengths for absorption maxima. [b] Extinction coefficients at maxima. [c] Reference 1c. [d] Reference 1b. [e] V. Carunchio, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, 6, 2168 (1967). [f] Reference 6. [g] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, 264, 321 (1951). [h] Reference 9.

with a Consolidated Electronics Corp. (Model 21-201) mass spectrometer at Brookhaven National Laboratory.

Results

Preliminary Experiments. The spectral changes that occur in acidified solutions of *cis*-$Co(en)_2(HCO_2)_2^+$ and the quantitative estimation of the formic acid released demonstrate conclusively that the loss of the two formate ligands occurs in a stepwise manner. The first formate is released quite rapidly. Thus, the spectrum of a solution of *cis*-$Co(en)_2(HCO_2)_2^+$ in 0.20 M perchloric acid at 25° changes rapidly and after 20 min reaches a steady spectrum with maxima at 495 nm ($\epsilon = 107\ M^{-1}$ cm^{-1}) and 359 nm ($\epsilon = 73\ M^{-1}$ cm^{-1}). The formic acid released in this stage was determined by adding the resulting solution to a Dowex 50W-X8 (50-100 mesh, H^+ form) ion-exchange column. The cobalt(III) product is retained in the column, whereas the formic acid passes through. The eluent was collected, and the formic acid was titrated.[13] The number of moles of formic acid released per mole of cobalt(III) reactant was found to be 1.03 ± 0.1. The stoichiometry of the first stage is therefore given by eq 1. The geometry of the product could not be

$$cis\text{-}Co(en)_2(HCO_2)_2^+ + H^+ = cis\text{-}Co(en)_2(HCO_2)(OH_2)^{2+} + HCO_2H \quad (1)$$

established directly, since aquoformate complexes have not been synthesized independently. However, two indirect pieces of evidence appear to be quite convincing in justifying the isomeric assignment. First, in common with other *cis*-bis(ethylenediamine)cobalt(III) complexes, the product of reaction 1 exhibits only two ligand field bands, and the spectrum is extraordinarily similar to that of *cis*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$. Second, the vanadium(II) reduction of the product shows only one kinetic component, whereas two rates would have been anticipated for a mixture of two isomers.[14,15]

The loss of the second formate is considerably slower than that of the first. Solutions of *cis*-$Co(en)_2(HCO_2)_2^+$ in 1.0 M $HClO_4$ kept at 50° for 48 hr exhibit maxima at 492 nm (ϵ 75 ± 1 M^{-1} cm^{-1}) and 359 nm (ϵ 59 ± 1 M^{-1} cm^{-1}), in excellent agreement with the values expected[16,17] for an equilibrium mixture of *cis*- and *trans*-$Co(en)_2(OH_2)_2{}^{3+}$. The cobalt(III) products from the resulting solutions were removed by ion-exchange chromatography, and the formic acid was titrated. The number of moles of formic acid released per mole of cobalt(III) was found to be 1.92 ± 0.01. Therefore, the overall stoichiometry of the second stage is given by eq 2. During the second stage, some cis-trans

$$cis\text{-}Co(en)_2(HCO_2)(OH_2)^{2+} + H^+ = cis\text{- and } trans\text{-}Co(en)_2(OH_2)_2{}^{3+} + HCO_2H \quad (2)$$

isomerization of the aquoformate complex occurs, but both the isomerization and the second aquation are very slow compared to the first aquation, and, therefore, kinetic studies of reaction 1 can be carried out by conventional spectrophotometric methods.

The behavior of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ is entirely analogous to that of *cis*-$Co(en)_2(HCO_2)_2^+$. Loss of the first acetate is complete in *ca.* 1 min at 25° and 1.0 M $HClO_4$ and produces stereospecifically *cis*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$. The subsequent cis-trans isomerization and further aquation are extremely slow compared to the first stage, requiring *ca.* 7 hr and *ca.* 2 days, respectively, at 40° and 1.0 M $HClO_4$.

The loss of the first formate or acetate from *trans*-$Co(en)_2(HCO_2)_2^+$ or *trans*-$Co(en)_2(CH_3CO_2)_2^+$ is considerably slower than the corresponding reaction of the cis isomers, and subsequent isomerization and loss of the second formate or acetate interfere with the first reaction. Thus, repetitive scans in the 600-450-nm region of solutions of *trans*-$Co(en)_2(HCO_2)_2^+$ or *trans*-$Co(en)_2(CH_3CO_2)_2^+$ in 1.0 M $HClO_4$ at 50° show the occurrence of an isosbestic point at 540 nm for periods of *ca.* 1 hr, but then the isosbestic point is lost. Moreover, the absorbance at 492 nm first increases and then decreases. For example, the apparent extinction coefficient of a solution of *trans*-$Co(en)_2(HCO_2)_2^+$ in 1.0 M $HClO_4$ at 50° is 52 after 15 min, 71 after 46 min, 85 after 97 min, 91 after 172 min, 84 after 932 min, and 77 after 48 hr. These results clearly indicate the occurrence of at least two consecutive reactions. Since the ratio of *cis*- to *trans*-$Co(en)_2(CH_3CO_2)(OH_2)^{2+}$ produced by loss of one acetate from *trans*-$Co(en)_2(CH_3CO_2)_2^+$ is approximately equal to the equilibrium ratio (see below), the two overlapping reactions correspond to the stepwise loss of formate (or acetate) from the parent complex with eventual formation of the equilibrium mixture of *cis*- and *trans*-$Co(en)_2(OH_2)_2{}^{3+}$.[18] Under these circumstances, conventional spectrophotometric measurements to obtain the kinetics of disappearance of the trans complexes were precluded, and therefore the combined ion-exchange-spectrophotometric method described above was utilized.

Kinetics of Aquation of Cis Complexes. The results of the kinetic measurements for the loss of one carboxylate ligand from the complexes *cis*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3,

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[18] Titration of the formic acid released after 48 hr in 1.0 M $HClO_4$ at 50° yields a value of 1.97 ± 0.01 for the HCOOH:*cis*-$Co(en)_2(HCO_2)_2^+$ ratio.

Table II. Kinetics of Aquation of *cis*-$Co(en)_2(HCO_2)_2^{+\,a}$

	$10^3 k_{obsd}$,^{b} sec^{-1}		
$[H^+]$, *M*	15.5°	25.0°	34.8°
0.100	0.36 ± 0.03	1.11 ± 0.06	3.17 ± 0.13
0.200	0.65 ± 0.02	2.22 ± 0.06, 2.07^e	6.61 ± 0.01
0.400	1.30 ± 0.03	4.44 ± 0.15	12.4 ± 0.3
0.500		5.10 ± 0.02	
0.600	1.85 ± 0.03		18.1 ± 0.8
0.700	2.00 ± 0.04^c	6.68 ± 0.14	
0.800	2.21 ± 0.10	7.30 ± 0.20	21.5 ± 0.3
0.900	2.50 ± 0.02		
1.00	2.76 ± 0.14^d	8.62 ± 0.14^f	25.1 ± 0.2

[a] Measurements at 224 cm; ionic strength 1.00 *M* maintained with $LiClO_4$; [Co(III)] = (8–10) × 10^{-5} *M*. [b] Each entry represents the average of 2 measurements followed by the average deviation from the mean. [c] Average of three measurements. [d] Average of seven measurements. [e] Single measurement at 501 nm. [f] Average of five measurements.

Table III. Kinetics of Aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^{+\,a}$

	$10^2 k_{obsd}$,^{b} sec^{-1}		
$[H^+]$, *M*	15.5°	20.2°	25.0°
0.100	0.90 ± 0.03	1.55 ± 0.01	2.54 ± 0.08
0.200	1.49^c	2.59 ± 0.01	4.49 ± 0.14^d
0.400	2.00 ± 0.02	3.99^c	5.53^c
0.600	2.04^c	4.23 ± 0.07	6.62 ± 0.20
0.800	2.45 ± 0.05		7.25 ± 0.05
1.00	2.57 ± 0.11	4.81 ± 0.04	7.29^c

[a] Measurements at 224 nm; ionic strength 1.00 *M* maintained with $LiClO_4$; [Co(III)] = (8–10) × 10^{-4} *M*. [b] Each entry represents the average of two measurements followed by the average deviation from the mean. [c] Single measurement. [d] Average of three measurements.

C_2H_5, C_3H_7), *cis*-$Co(NH_3)_4(CH_3CO_2)_2^+$, and *cis*-$Co(dipy)_2(CH_3CO_2)_2^+$ are presented in Tables II-VI. It will be seen that the reactions are catalyzed by H^+, the dependence of the pseudo-first order rate constants, k_{obsd}, being first-order in hydrogen ion at low values of $[H^+]$, but less than first order at higher values. The functional dependence that best describes the observed variation of k_{obsd} with $[H^+]$ is given by eq 3. Values of k_2 and Q, obtained by nonlinear least-squares fitting of the experimental data to eq 3, are given in Table VII. Included in the table are the values extrapolated to 25° from the measurements of Dasgupta and Tobe.[5] Considering the differences in ionic strength (1.0 *M* *vs.* 2.0 *M*) and in medium ($LiClO_4$ *vs.* $NaClO_4$) between the two sets of data, the agreement is quite satisfactory.

$$k_{obsd} = \frac{k_2 Q[H^+]}{1 + Q[H^+]} \tag{3}$$

Kinetics of Aquation of *trans*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3). The results of the measurements of the rate constants for the aquation of the trans complexes are summarized in Table VIII. For R = CH_3 the dependence of k_{obsd} upon $[H^+]$ conforms to eq 3, and the values of k_2 and Q are (1.88 ± 0.48) × 10^{-3} sec^{-1} and 0.27 ± 0.09 M^{-1} at 40° and (5.9 ± 1.3) × 10^{-3} sec^{-1} and 0.38 ± 0.12 M^{-1} at 50°. The agreement between our measurements and those of Dasgupta and Tobe is satisfactory, after considering the different ionic media used in the two investigations.

For R = H, the dependence of k_{obsd} upon $[H^+]$ is linear, and therefore only values of k_2Q could be obtained. These values are (9.45 ± 0.07) × 10^{-5} and (4.10 ± 0.03) × 10^{-4} M^{-1} sec^{-1} at 40 and 50°, respectively.

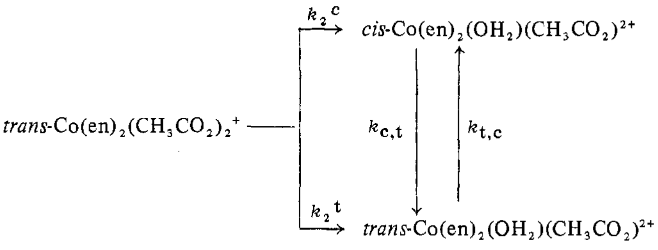
Table IV. Kinetics of Aquation of *cis*-$Co(en)_2(C_2H_5CO_2)_2^+$ and *cis*-$Co(en)_2(C_3H_7CO_2)_2^{+\,a}$

	$10^2 k_{obsd}$,^{b} sec^{-1}	
$[H^+]$, *M*	Propionate complex	Butyrate complex
0.00940	0.327 ± 0.027^c	0.285 ± 0.013
0.0470	1.54 ± 0.16	1.40 ± 0.03
0.0940	2.51 ± 0.07	2.30 ± 0.05
0.190	3.76 ± 0.15	3.22 ± 0.26^e
0.380	4.59 ± 0.05	3.85 ± 0.18
0.470	4.64 ± 0.13^d	4.16 ± 0.10^f
0.560	5.05 ± 0.69^c	4.12 ± 0.22, 4.27^g
0.750	5.09 ± 0.36^e	4.58 ± 0.26
0.940	4.97 ± 0.23^e	4.66 ± 0.15

[a] Measurements at 25° and ionic strength 1.00 *M* maintained with $LiClO_4$; wavelength of observation 225 nm; [Co(III)] = (4–5) × 10^{-5} *M*. [b] Each entry represents the average of four measurements followed by the average deviation from the mean. [c] Average of five measurements. [d] Average of eight measurements. [e] Average of six measurements. [f] Average of two measurements. [g] Single measurement at 250 nm.

The ratio of *cis*- to *trans*-$Co(en)_2(OH_2)(CH_3CO_2)^{2+}$ produced in the aquation of *trans*-$Co(en)_2(CH_3CO_2)_2^+$ was determined spectrophotometrically by measuring the absorbance at 492 nm for periods of time where substantial aquation and isomerization obtained, but loss of the second acetate was negligible (*ca.* 1 hr at 40°). The kinetic scheme (Scheme I) has been solved,[19] and therefore it is possible to calculate the absorbance as a function of time for various values of k_2^c/k_2^t using the known values of $k_2^c + k_2^t$ (4.03 × 10^{-4} sec^{-1} at 40° and $[H^+]$ = 1.00 *M*), $k_{c,t}$ (4.0 × 10^{-5} sec^{-1} at 40° and $[ClO_4^-]$ = 1.00 *M*), $k_{t,c}$ (1.64 × 10^{-4} sec^{-1} at 40° and $[ClO_4^-]$ = 1.0 *M*), and the extinction coefficients of *trans*-$Co(en)_2(CH_3CO_2)_2^+$, *trans*-$Co(en)_2(OH_2)(CH_3CO_2)^{2+}$, and *cis*-$Co(en)_2(OH_2)(CH_3CO_2)^{2+}$ (37.4, 29, and 112, respectively).[20] The calculated absorbances were indistinguishable from the experimental values (50 values taken at 1-min intervals) when k_2^c/k_2^t = 2.0. This value is quite sensitive to small errors in the parameters used, and we estimate, therefore, that the kinetically controlled fraction of *cis*-$Co(en)_2(OH_2)(CH_3CO_2)^{2+}$ produced in the aquation is 0.70 ± 0.10, in remarkable agreement with the value 0.70–0.80 reported previously.[5]

Scheme I



Oxygen-18 Tracer Studies of the Aquation of *cis*-$Co(en)_2$-

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[19] C. H. Bamford and C. F. H. Tipper, Ed., "Comprehensive Chemical Kinetics," Vol. II, Elsevier, Amsterdam, 1967, p. 31.

[20] The values of $k_{c,t}$ and $k_{t,c}$ were calculated from our measured values of the rate and equilibrium constants for isomerization in the *cis*-$Co(en)_2(OH_2)(CH_3CO_2)^{2+}$–*trans*-$Co(en)_2(OH_2)(CH_3CO_2)^{2+}$ system at 40.0°, $[HClO_4]$ = 0.10 *M*, and $[LiClO_4]$ = 0.90 *M*. Our rate constant $k_{iso} = k_{c,t} + k_{t,c}$ = (2.04 ± 0.01) × 10^{-4} sec^{-1} compares well with the value (2.6 ± 0.2) × 10^{-4} sec^{-1} measured by Dasgupta and Tobe[5] under somewhat different conditions. Our equilibrium constant is $Q_{iso} = k_{c,t}/k_{t,c}$ = 4.1 ± 0.5. The latter value was obtained from the apparent extinction coefficient at 495 nm of equilibrium mixtures of the isomers (96 M^{-1} cm^{-1}) and the values of the extinction coefficients of *cis*- and *trans*-$Co(en)_2(OH)_2(CH_3CO_2)^{2+}$ (112 and 29 M^{-1} cm^{-1}, respectively). Although at first glance our value of 4.1 for the equilibrium constant compares poorly with the value 3.0 reported by Dasgupta and Tobe[5] it must be recognized that the difference in percentage of cis complex at equilibrium is small (80% *vs.* 75%) and that a change in ±2% in the amount of cis complex at equilibrium results in an error of ±0.5 in the equilibrium constant.

Table V. Kinetics of Aquation of *cis*-$Co(NH_3)_4(CH_3CO_2)_2^+$ [a]

	$10^2 k_{obsd}$,[b] sec^{-1}	
$[H^+]$, M	25°	35°
0.00280		0.748 ± 0.027
0.00470	0.475 ± 0.004	1.29 ± 0.03
0.00940	0.942 ± 0.009	2.54 ± 0.18
0.0190		4.94,[e] 4.97[e,f]
0.0280	2.66 ± 0.01	
0.0470	4.18 ± 0.15	
0.100	7.44 ± 0.17	19.7 ± 0.4
0.200	12.9 ± 0.03	27.8 ± 0.8[c]
0.400	18.3 ± 0.03[c]	41.7 ± 0.2
0.500	18.9 ± 1.3[d]	43.6 ± 1.8
0.600	19.8 ± 0.2	49.8 ± 1.0
0.750	21.1 ± 0.5[d]	55.9 ± 0.3[c]

[a] Measurements at 280 nm with stopped-flow apparatus for $[H^+] \geqslant 0.100\,M$ and at 225 nm with Cary 14 spectrophotometer for $[H^+] < 0.100\,M$. Ionic strength 1.00 M adjusted with $LiClO_4$. [b] Each entry for $[H^+] < 0.100\,M$ is the average of four measurements followed by the average deviation from the mean. For $[H^+] \geqslant 0.100\,M$, each entry is the average of three independent stopped-flow measurements each of which is the average of three to five successive runs. [c] Average of two measurements. [d] Average of five measurements. [e] Single measurement. [f] Measurement at 260 nm.

Table VI. Kinetics of Aquation of *cis*-$Co(dipy)_2(CH_3CO_2)_2^+$ [a]

	$10^2 k_{obsd}$,[b] sec^{-1}	
$[H^+]$, M	25°	35°
0.00940	0.173 ± 0.005	0.529 ± 0.013
0.0470	0.790 ± 0.040	2.48 ± 0.04[c]
0.0940	1.48 ± 0.08[c]	4.71 ± 0.09
0.190	2.67 ± 0.03	8.33 ± 0.05[c]
0.280	3.48 ± 0.17	
0.470	4.82 ± 0.04	
0.500		15.2 ± 0.2[d]
0.560	5.11 ± 0.16	
0.600		17.1 ± 0.2[d]
0.750	5.83 ± 0.11	18.2 ± 0.2[d]
0.940	6.22 ± 0.12	

[a] Measurements at 280 nm; ionic strength 1.00 M maintained with $LiClO_4$. [b] Each entry is the average of four measurements followed by the average deviation from the mean. [c] Average of three measurements. [d] Average of two independent stopped-flow measurements each of which is the average of four successive runs.

Table VII. Equilibrium and Kinetic Parameters for Protonation and Aquation of *cis*-Dicarboxylatocobalt(III) Complexes[a]

Complex	Q,[b] M^{-1}	k_2,[b] sec^{-1}
$Co(en)_2(HCO_2)_2^+$ [c]	0.36 ± 0.04	0.0324 ± 0.004
$Co(en)_2(CH_3CO_2)_2^+$ [d]	3.9 ± 0.4, 5.2[e]	0.095 ± 0.005, 0.079[e]
$Co(en)_2(C_2H_5CO_2)_2^+$	6.5 ± 0.5	0.063 ± 0.003
$Co(en)_2(C_3H_7CO_2)_2^+$	6.5 ± 0.5	0.055 ± 0.002
$Co(NH_3)_4(CH_3CO_2)_2^+$ [f]	3.3 ± 0.2	0.31 ± 0.01
$Co(dipy)_2(CH_3CO_2)_2^+$ [g]	1.9 ± 0.1	0.100 ± 0.003

[a] At 25° and ionic strength 1.00 M maintained with $LiClO_4$–$HClO_4$. [b] Defined by eq 3. [c] Values of Q at 15 and 35° are 0.32 ± 0.05 and 0.33 ± 0.06 M^{-1}, respectively. Values of k_2 at 15 and 35° are 0.0113 ± 0.0015 and 0.105 ± 0.016 sec^{-1}, respectively. [d] Values of Q at 15 and 20° are 4.1 ± 0.5 and 4.0 ± 0.5 M^{-1}, respectively. Values of k_2 at 15 and 20° are 0.0316 ± 0.001 and 0.0585 ± 0.006, respectively. [e] Ionic strength 2.0 M maintained with $NaClO_4$–$HClO_4$. Extrapolated to 25° from data in ref 5. [f] Values of Q and k_2 at 35° are 4.1 ± 0.4 M^{-1} and 0.68 ± 0.03 sec^{-1}, respectively. [g] Values of Q and k_2 at 35° are 1.8 ± 0.1 M^{-1} and 0.33 ± 0.01 sec^{-1}, respectively.

Table VIII. Kinetics of Aquation of *trans*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3)[a]

	$10^4 k_{obsd}$,[b] sec^{-1}			
	40°		50°	
$[H^+]$, M	R = H	R = CH_3	R = H	R = CH_3
0.100		0.58 ± 0.01	0.41 ± 0.01[c]	2.27 ± 0.05
0.200				4.42 ± 0.09
0.300		1.45 ± 0.03		6.08 ± 0.01
0.400			1.61 ± 0.03	
0.500		2.33 ± 0.02[c]	2.08[d]	9.44 ± 0.20
0.600	0.560 ± 0.004	2.64 ± 0.03[c]	2.40 ± 0.03	
0.800	0.769 ± 0.013	3.33 ± 0.03	3.38 ± 0.09[c]	14.3 ± 0.2
1.00	0.939 ± 0.007	4.03 ± 0.03[c]	4.08 ± 0.05[e]	16.3 ± 0.2

[a] Ionic strength 1.00 M maintained with $LiClO_4$. [Co(III)] = $7.7 \times 10^{-3}\,M$ for R = CH_3 and $1.6 \times 10^{-2}\,M$ for R = H. [b] Each entry is the average of two measurements followed by the average deviation from the mean. [c] Average of three measurements. [d] Single measurement. [e] Average of four measurements.

Table IX. Oxygen-18 Tracer Study of the Aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ [a]

Solvent	$10^3 R_{obsd}$[b]	$10^3 R_{calcd}$[c]	% Co–O bond breaking
7.89 g of enriched water + 2.00 ml of 2.02 M $HClO_4$	5.87	16.1	86.6
7.99 g of enriched water + 2.00 ml of 2.02 M $HClO_4$	5.50	16.2	89.8
5.98 g of unenriched water + 2.00 ml of 2.02 M $HClO_4$ + 6.08 g of enriched water[d]	4.91	10.6[e]	90.2

[a] 0.800 g of *cis*-$[Co(en)_2(CH_3CO_2)_2](ClO_4)$ dissolved in the specified solvent. The enriched water used contained 1.69% of $H_2{}^{18}O$. [b] Observed ratio of mass 46 to mass 44 peaks. [c] Calculated for 100% C–O bond breaking. This number is the sum of the ^{18}O isotopic composition of the solvent used and 2.04×10^{-3}, the natural abundance of oxygen-18. The value of R calculated for 0% C–O bond breaking is 4.29×10^{-3}. [d] The complex is dissolved in the water of normal isotopic composition and the perchloric acid, and *after* the aquation is complete, the enriched water is added. [e] Calculated if the acetic acid reached isotopic equilibrium with the solvent.

$(CH_3CO_2)_2^+$. The results of the tracer studies are summarized in Table IX.[21] The first two experiments, wherein the acid-catalyzed aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ was allowed to proceed in an oxygen-18-enriched solvent, demonstrate that there is little incorporation of solvent oxygen in the acetic acid produced and therefore that the reaction proceeds substantially by Co–O bond breaking. The slight incorporation of oxygen-18 in the acetic acid can be accounted for on the basis of the known rate of oxygen exchange between acetic acid and water.[12] A direct proof that the oxygen-18 is incorporated in the acid acetic *after* it is released from the coordination sphere of the cobalt(III) can be seen in the results of the third experiment in Table X. The aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ was allowed to proceed in water of normal isotopic composition, and *then* oxygen-18-enriched water was added. There is approximately 10% incorporation of oxygen-18 from the solvent in the acetic acid, and, therefore, when the results of the first two experiments are corrected for the exchange, it is concluded that the acid-catalyzed aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ proceeds quantitatively *via* Co–O bond breaking.

Discussion

The results of the kinetic studies of the acid-catalyzed aquations of *cis*- and *trans*-dicarboxylatoaminecobalt(III) complexes are readily interpreted on the basis of the mechanism postulated previously[22,23] to account for other acid-catalyzed aquations

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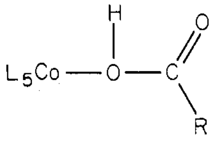
[21] The values reported in the table differ considerably from those reported in ref 1b. For example, the values of the % Co–O bond breaking reported originally were 83.8, 88.2, and 80.2 in the order reported in the table. There were a number of typographical and arithmetical errors in the values reported originally.

[22] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

$$\textit{cis-}\text{ or }\textit{trans-}\mathrm{Co(A)_4(RCO_2)_2}^+ + \mathrm{H}^+ \overset{Q}{\rightleftarrows} \textit{cis-}\text{ or }\textit{trans-}\mathrm{Co(A)_4(RCO_2)_2H^{2+}} \tag{4}$$

$$\textit{cis-}\text{ or }\textit{trans-}\mathrm{Co(A)_4(RCO_2)H^{2+}} \xrightarrow{k_2} \text{products} \tag{5}$$

According to this reaction sequence, the measured pseudo-first-order rate constant is given by eq 3, in agreement with the observed dependence of k_{obsd} upon $[\mathrm{H}^+]$. The kinetic results provide no direct evidence for the position of bond breaking (Co–O or C–O) or for the site of protonation (aryl or carbonyl oxygen). However, the oxygen-18-tracer results for *cis*-$\mathrm{Co(en)_2(CH_3CO_2)_2}^+$ and the stereochemical results for *trans*-$\mathrm{Co(en)_2(CH_3CO_2)_2}^+$ provide conclusive evidence that the reactions proceed by cobalt–oxygen bond breaking, and therefore these reactions must be viewed in the general context of substitution reactions of cobalt(III)-amine complexes.[24] In common with such reactions, the acid-catalyzed aquations of the carboxylate complexes are stereospecific for the cis complexes and are accompanied by substantial stereochemical changes in the case of the trans complexes.[24] However, in contrast with the small difference in reactivities between cis and trans isomers of chloro- and bromoaminecobalt(III) complexes (factors between 0.1 and 8), the reactivities of the cis dicarboxylate complexes are considerably higher than those of the trans isomers (factors of *ca.* 70 and 3 × 10^2 for formate and acetate, respectively). This result, coupled with the higher (by a factor of *ca.* 10) protonation constants of the cis complexes as compared to the corresponding trans isomers and with the similarity in rates and protonation constants between the trans isomers and the corresponding pentaammine complexes, points to the operation of a "special effect" in the case of cis isomers. The pertinent information is summarized in Table X. The patterns of relative basicities and reactivities can be rationalized if it is assumed that protonation of the trans and pentaammine complexes occurs at the acyl oxygen atom (I) whereas the proton is bound to two oxygen atoms (one of which, at least, is a carbonyl oxygen) of different carboxylate ligands in the cis complexes (II).[25] The stabilization brought about by the hydrogen-bonded structure in the cis complexes and the absence of such stabilization in the trans and pentaammine complexes accounts nicely for the higher basicity of the cis complexes.



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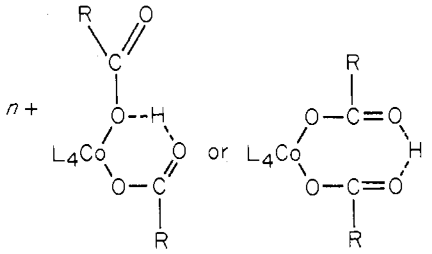


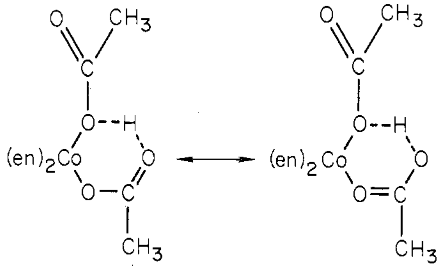
II

Table X. Protonation Constants of Carboxylatocobalt(III) Complexes and Rate Constants for Aquation of Protonated Carboxylato Complexes (25°, I = 1.0 M).

Complex	Q, M^{-1}	k_2, sec^{-1}
$\mathrm{Co(NH_3)_5(CH_3CO_2)^{2+}}$	0.25[a]	1.4×10^{-5} [b]
$\mathrm{Co(NH_3)_5(HCO_2)^{2+}}$	~0.02[c]	~2×10^{-4} [d]
cis-$\mathrm{Co(en)_2(CH_3CO_2)_2}^+$	3.9	9.5×10^{-2}
cis-$\mathrm{Co(en)_2(HCO_2)_2}^+$	0.36	3.2×10^{-2}
trans-$\mathrm{Co(en)_2(CH_3CO_2)_2}^+$	0.2[e]	3.2×10^{-4} [e]
trans-$\mathrm{Co(en)_2(HCO_2)_2}^+$	~0.02[c,e]	5.0×10^{-4} [c,e]

[a] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). [b] Calculated from the value of $Qk_2 = 3.6 \times 10^{-6}$ M^{-1} sec^{-1} obtained by extrapolating to 25° the data in ref 22. [c] Estimated assuming that the ratio of the protonation constants for acetate and formate complexes is 3.9/0.36, the observed ratio for the cis ethylenediamine system. [d] Calculated from the value of $Qk_2 = 4.0 \times 10^{-6}$ M^{-1} sec^{-1} obtained by extrapolating to 25° the data of K. Kuroda, *Nippon Kagaku Zasshi,* **82**, 1481 (1961). [e] Extrapolated to 25° from present data.

It must be noted that the argument based on the relative basicities of the isomers simply points to a hydrogen-bonded structure for the cis isomers and proton attachment to a single oxygen atom for the trans isomers and the pentaammine complexes but does not demand that the protonation sites be those specified in structures I and II. These protonation sites are inferred from arguments based on a comparison of the rates of aquation of complexes of cobalt(III) and chromium(III) containing a carbonyl oxygen in their coordination spheres with the rates of aquation of the protonated acetate complexes.[23,26,27] The comparison is particularly striking for the methyl acetate and acetic acid complexes of pentaamminecobalt(III). The rate constants for aquation are >0.02 and 1.4 × 10^{-5} sec^{-1}, respectively. If $\mathrm{CH_3}$ and H occupied equivalent positions in $\mathrm{Co(NH_3)_5(CH_3CO_2CH_3)^{3+}}$ and $\mathrm{Co(NH_3)_5(CH_3CO_2H)^{3+}}$, respectively, similar rates would be anticipated. Since the rates differ by at least three orders of magnitude and the methyl acetate ligand is bound to the cobalt(III) center *via* the carbonyl oxygen,[27] we infer that protonation of $\mathrm{Co(NH_3)_5(CH_3CO_2)^{2+}}$ (as well as of trans dicarboxylate complexes) occurs at the oxygen bound to the metal. Using the same argument, the extraordinarily high rates of aquation of the cis complexes and of the methyl acetate complex lead us to infer similar roles for H and $\mathrm{CH_3}$ in the respective complexes; that is, protonation of the cis complex leads to important contributions of resonance forms in which the oxygen bound to the metal has substantial carbonyl character, just as the adjacent oxygen of the methyl acetate complex, *i.e.*



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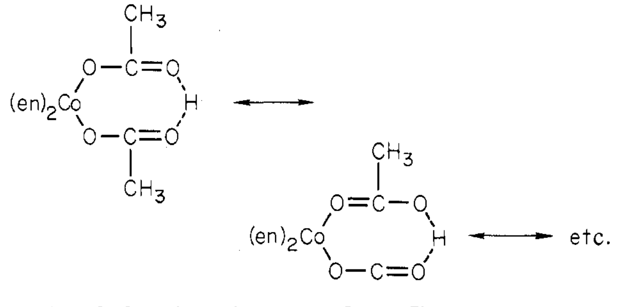

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[23] E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968).

[24] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 247.

[25] Whether the proton is bonded to the two carbonyl oxygens, as suggested previously, or to a carbonyl oxygen in one carboxylate and to an acyl oxygen in the other carboxylate (A. H. is indebted to Professor C. Springer for this suggestion) is not known. Experiments with molecular models suggest that either structure is feasible.

[26] R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

[27] J. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1174 (1968).

Thus, the increased carbonyl character (and attendant metal-oxygen bond weakening of the oxygen bound to the cobalt caused by protonation of the remote oxygen) is invoked to account for the high aquation rates of the cis complexes.

Turning to the trends in basicity and in reactivity of the cis complexes (see Table VII), it is apparent that the protonation constants of *cis*-diacetato complexes of $Co(en)_2{}^{3+}$, $Co(NH_3)_4{}^{3+}$, and $Co(dipy)_2{}^{3+}$ are in the narrow range 1.9–3.9, whereas the protonation of $Co(en)_2(HCO_2)_2{}^+$ is one order of magnitude smaller. These results indicate, not unexpectedly, that the basicities of the carboxylate complexes follow closely the basicity of the parent carboxylate ligands. With regard to trends in reactivity, it must be noted that the protonated acetate complexes aquate faster than the analogous formate complexes for *cis*-$Co(en)_2(RCO_2)_2{}^+$, whereas the opposite order obtains for *trans*-$Co(en)_2(RCO_2)_2{}^+$ and $Co(NH_3)_5(RCO_2)^{2+}$. Moreover, the *cis*-dipropionato and *cis*-dibutyrato complexes are intermediate in reactivity between diformato and diacetato complexes. These trends indicate the operation of opposing inductive and steric effects. In the case of the trans and pentaammine complexes, where steric interaction between the two carboxylate ligands is absent, the order of reactivity is determined by inductive effects: the more basic ligands are released at slower rates.[28] For the cis complexes, the order of reactivity based on inductive effects would be formate ≫ acetate > butyrate ~ propionate. The observed order acetate > propionate ~ butyrate > formate indicates that steric effects are important in determining the relative reactivity of formate and acetate complexes but that increasing the size of the alkyl group beyond methyl has little or no effect.

Finally, it must be noted that in the earlier studies of the acid-catalyzed aquation of acetate complexes,[22,23] the proposed mechanism featured C–O bond breaking, whereas more recently[29] the mechanism involving metal-oxygen bond breaking was preferred.[30] Additional support for the latter mechanism is obtained from the results of calculations of the rates of formation of $Co(NH_3)_5(CH_3CO_2)^{2+}$ for the alternative Co–O and C–O bond rupture mechanisms. The equilibrium constant for reaction 6 can be calculated as

$$Co(NH_3)_5OH_2{}^{3+} + CH_3CO_2H \rightleftarrows Co(NH_3)_5(CH_3CO_2)^{2+} + H_3O^+ \qquad (6)$$

1.3×10^{-3} from the known dissociation constant of acetic acid (2.5×10^{-5} *M* at 25° and ionic strength 1.0 *M*) and the equilibrium constant for the anation of $Co(NH_3)_5OH_2{}^{3+}$ by acetate ion (the value is 5×10^2 M^{-1}).[31] Since the rate constant for the reverse of reaction 6 is known (3.6×10^{-6} M^{-1} sec^{-1} at 25°, extrapolated from values measured at higher temperatures),[22] the rate of the forward reaction in eq 6 is calculated as 4.5×10^{-8} M^{-1} sec^{-1}. This value is compatible with Co–O bond breaking since the rate of oxygen exchange between $Co(NH_3)_5OH_2{}^{3+}$ and water is 5.9×10^{-6} sec^{-1},[32] and the dissociative mechanism for pentaamminecobalt(III) complexes[33,34] requires that substitution be slower than water exchange. Moreover, the value of $Q^{\ddagger} = 0.003$ calculated[34] for the formal reaction 7 falls

$$[Co(NH_3)_5OH_2{}^{3+}]^{\ddagger} + CH_3CO_2H \rightleftarrows [Co(NH_3)_5(CH_3CO_2H)^{3+}]^{\ddagger} + H_2O \qquad (7)$$

in the range expected for the reaction of a neutral species. [Values of $Q^{\ddagger}$ for di- and uninegative species are in the ranges 2.5–2.8 and 0.1–0.4, respectively.[34]] Alternately, if one postulates that C–O bond rupture obtains, then the forward reaction in eq 6 would proceed *via* the sequence given by eq 8–10. Using $k_f = 4.5 \times 10^{-8}$ M^{-1} sec^{-1} for the forward

$$Co(NH_3)_5OH_2{}^{3+} \rightleftarrows Co(NH_3)_5OH^{2+} + H^+ \quad Q_8 \qquad (8)$$

$$CH_3CO_2H + H^+ \rightleftarrows CH_3CO_2H_2{}^+ \quad Q_9 \qquad (9)$$

$$Co(NH_3)_5OH^{2+} + CH_3CO_2H_2{}^+ \rightarrow Co(NH_3)_5(CH_3CO_2)^{2+} + H_3O^+ \quad k_{10} \qquad (10)$$

reaction in eq 6 and the values $Q_8 = 6.3 \times 10^{-7}$ *M*[35] and $Q_9 = 8 \times 10^{-7}$ M^{-1},[36] we obtain the value $k_{10} = k_f/Q_8Q_9 = 9 \times 10^4$ M^{-1} sec^{-1}. Assuming that the acid-catalyzed oxygen exchange[12] between CH_3CO_2H and water (rate law $k[CH_3CO_2H][H^+]$ with $k = 4.5 \times 10^{-4}$ M^{-1} sec^{-1} at 25°) proceeds by the mechanism[12] shown in eq 11, we calculate

$$CH_3CO_2H + H^+ \rightleftarrows CH_3CO_2H_2{}^+ \xrightarrow{H_2O^*} \text{slow exchange, } k_{11} \qquad (11)$$

a value of $k_{11} = 5.1 \times 10^2$ sec^{-1}. These calculations show that, if the C–O bond mechanism obtains, $CH_3CO_2H_2{}^+$ is more susceptible to attack by $Co(NH_3)_5OH^{2+}$ (eq 10) than by water (eq 11), the rate ratio being $\sim 2 \times 10^2$. Such discrimination in favor of $Co(NH_3)_5OH^{2+}$ seems implausible to us, and therefore we conclude that the acid-catalyzed aquation of $Co(NH_3)_5(CH_3CO_2)^{2+}$ proceeds with cobalt-oxygen bond rupture.

Registry No. *cis*-$Co(en)_2(HCO_2)_2ClO_4$, 14931-77-2; *trans*-$Co(en)_2(HCO_2)_2ClO_4$, 15091-45-9; *cis*-$Co(en)_2(CH_3CO_2)_2ClO_4$, 14240-81-4; *trans*-$Co(en)_2(CH_3CO_2)_2ClO_4$, 14931-78-3; *cis*-$Co(en)_2(C_2H_5CO_2)_2ClO_4$, 15091-46-0; *cis*-$Co(en)_2(C_3H_7CO_2)_2ClO_4$, 38127-88-7; *cis*-$Co(NH_3)_4(CH_3CO_2)_2ClO_4$, 14099-44-6; *cis*-$Co(dipy)_2(CH_3CO_2)_2ClO_4$, 10170-76-0; *cis*-$Co(en)_2(CH_3CO_2)(H_2O)^{2+}$, 24913-00-6; *cis*-$Co(dipy)_2(CH_3CO_2)(H_2O)^{2+}$, 20121-51-1; *trans*-$Co(en)_2(CH_3CO_2)(H_2O)^{2+}$, 21281-43-6; $Co(NH_3)_5(CH_3CO_2)^{2+}$, 16632-78-3; $Co(NH_3)_5(HCO_2)^{2+}$, 19173-64-9.

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(30) In retrospect, it seems that the Co–O bond breaking mechanism is more reasonable than the C–O bond breaking mechanism: the production of $Co(NH_3)_5OH_2{}^{3+}$ and CH_3CO_2H from $Co(NH_3)_5(CH_3CO_2H)^{3+}$ *via* Co–O bond rupture is energetically much more economical than production of $Co(NH_3)_5OH^{2+}$ and CH_3CO^+ or ($CH_3CO_2H_2{}^+$) *via* C–O bond scission.

(31) The value 5×10^2 was estimated using the rate constant for base hydrolysis of $Co(NH_3)_5(CH_3CO_2)^{2+}$ (7.0×10^{-4} M^{-1} sec^{-1} [28]), the linear free energy relation between rate constant for base hydrolysis, and the equilibrium constant for anation [W. E. Jones, R. B. Jordan, and T. W. Swaddle, *Inorg. Chem.*, 8, 2504 (1969)] and assuming that base hydrolysis of $Co(NH_3)_5(CH_3CO_2)^{2+}$ obeys the linear relation.

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