CONTRIBUTION FROM THE MOBIL RESEARCH AND DEVELOPMENT CORPORATION,
CENTRAL RESEARCH DIVISION LABORATORY, PRINCETON, NEW JERSEY 08540

The Effect of Sodium Acetate on the Solvolysis of *trans*-Ditoluatobis(ethylenediamine)cobalt(III) Perchlorates in Acetic Acid

BY ARTHUR W. CHESTER

Received February 10, 1970

The kinetics of the solvolysis of *trans*-[$\mathrm{Co(en)_2(ArCO_2)_2}$]$\mathrm{ClO_4}$, with Ar = *o*- and *p*-tolyl, were examined spectrophotometrically at 84.5° in acetic acid as a function of added NaOAc. The product of the solvolysis was an equilibrium mixture of [$\mathrm{Co(en)_2(OAc)_2}$]$\mathrm{ClO_4}$ isomers. NaOAc retarded the solvolysis rate, as in the isomerization of *cis*-[$\mathrm{Co(en)_2(OAc)_2}$]$\mathrm{ClO_4}$. The rate retardation is attributed to formation of an acetate ion pair which is less reactive than the perchlorate ion pair initially present. The value of the equilibrium constant for the ion pair equilibrium *trans*-$\mathrm{Co(en)_2(ArCO_2)_2{}^+ClO_4{}^-} + \mathrm{OAc^-} \rightleftharpoons$ *trans*-$\mathrm{Co(en)_2(ArCO_2)_2{}^+OAc^-} + \mathrm{ClO_4{}^-}$ was calculated as 2500. The mechanism is discussed in terms of existing theories of base hydrolysis of cobalt ammines. The conjugate base mechanism (SN1CB) is virtually eliminated as the acetate ion should more easily abstract an amine proton than perchlorate, since acetate is more basic. However, the acetate ion pair is only about 20% as reactive as the perchlorate ion pair. It is proposed that the solvolysis involves solvent-assisted dissociation within the ion pairs.

The effect of sodium acetate (NaOAc) on the isomerization of diacetatobis(ethylenediamine)cobalt(III) perchlorate in acetic acid was previously reported.[1] The observed retardation of the isomerization rate by NaOAc was ascribed to the ion pair–ion pair equilibrium (1) for both isomers. The lower reactivity of the acetate ion pair is due to its structural similarity to a solvated free ion. The observed effect is the reverse of that usually observed in other solvents.[2-4]

$$\mathrm{Co(en)_2(OAc)_2{}^+ClO_4{}^-} + \mathrm{OAc} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{Co(en)_2(OAc)_2{}^+OAc^-} + \mathrm{ClO_4{}^-} \quad (1)$$

The present study concerns the effect of acetate on the solvolysis of complexes of the type *trans*-[$\mathrm{Co(en)_2(ArCO_2)_2}$]$\mathrm{ClO_4}$ in acetic acid. The Ar groups were chosen as *o*- and *p*-tolyl for the convenient spectroscopic characteristics of the complexes. The observed product of the solvolysis is the equilibrium mixture[1] of $\mathrm{Co(en)_2(OAc)_2{}^+}$, so that solvolysis occurs in two stages ((2), HOAc = acetic acid). The reactions are

$$trans\text{-}\mathrm{Co(en)_2(ArCO_2)_2{}^+} + \mathrm{HOAc} \xrightarrow{k_1} \mathrm{Co(en)_2(ArCO_2)(OAc)^+} + \mathrm{ArCO_2H} \quad (2a)$$

$$\mathrm{Co(en)_2(ArCO_2)(OAc)^+} + \mathrm{HOAc} \xrightarrow{k_2} \mathrm{Co(en)_2(OAc)_2{}^+} + \mathrm{ArCO_2H} \quad (2b)$$

formally analogous to hydrolysis in aqueous systems, and the addition of acetate (the lyate ion) could produce reactions analogous to base hydrolysis.

The base hydrolysis of some *cis*- and *trans*-dibenzoato-[5] and dicarboxylatobis(ethylenediamine)cobalt(III)[6] perchlorates have been investigated at 25° in water and aqueous methanol under conditions such that [$\mathrm{OH^-}$] ≈ [complex]. The results were interpreted[6] as evidence for the SN1CB (conjugate base) reaction mechanism[7,8] ((3), en-H represents coordinated $\mathrm{NH_2CH_2CH_2NH^-}$). Other mechanisms have been proposed for the base hydrolysis of cobalt(III) ammines. Thus, Chan found that an ion-pair mechanism was consistent with data obtained with chloropentaamminecobalt(III) complexes in excess base[9] and Gillard[10] has proposed an electron-transfer mechanism involving transient reduction of cobalt(III) by hydroxide. It is of interest to consider the present results in the light of these mechanisms.

$$\mathrm{Co(en)_2(RCO_2)_2{}^+} + \mathrm{OH^-} \overset{K}{\rightleftharpoons} \mathrm{Co(en)(en\text{-}H)(RCO_2)_2} + \mathrm{H_2O} \quad (3a)$$

$$\mathrm{Co(en)(en\text{-}H)(RCO_2)_2} \xrightarrow{k} \mathrm{Co(en)(en\text{-}H)(RCO_2)^+} + \mathrm{RCO_2{}^-} \quad (3b)$$

$$\mathrm{Co(en)(en\text{-}H)(RCO_2)^+} + \mathrm{H_2O} \xrightarrow{\text{fast}} \mathrm{Co(en)_2(OH)(RCO_2)^+} \quad (3c)$$

Experimental Section

All chemicals were reagent grade. Sodium acetate was dried at 120° before use. Reagent grade acetic acid containing ~0.1% water was used as received. Acetic acid-d_1 and -d_4 were obtained from Merck Sharp and Dohme of Canada Ltd.

The *o*- and *p*-toluato complexes, *trans*-[$\mathrm{Co(en)_2(toluato)_2}$]$\mathrm{ClO_4}$, were prepared by refluxing stoichiometric quantities of the free acids with [$\mathrm{Co(en)_2CO_3}$]$\mathrm{ClO_4}$[11] overnight in 80% methanol. The solutions were stripped on a rotary evaporator and the solid recrystallized from 95% ethanol. *Anal.* Calcd for $\mathrm{C_{20}H_{30}N_4ClO_8Co}$: C, 43.62; H, 5.50; N, 10.18. Found: *ortho*, C, 43.45; H, 5.62; N, 10.01; *para*, C, 43.46; H, 5.41; N, 10.08.

Kinetics.—The solvolysis reaction was followed spectrophotometrically with equipment previously described.[1] Reaction solutions were prepared at room temperature from concentrated stock solutions of the complexes (*p*-toluato, 0.02 *M*; *o*-toluato, 0.01 *M*) and sodium acetate (0.1 and 1.0 *M*) in acetic acid. A 3-ml sample was placed in a 1-cm silica cell equipped with a glass

---

[1] A. W. Chester, *Inorg. Chem.*, **8**, 1584 (1969).

[2] M. L. Tobe, *Advan. Chem. Ser.*, **No. 49**, 7 (1965).

[3] M. L. Tobe, *Rec. Chem. Progr.*, **27**, 79 (1966).

[4] D. W. Watts, *ibid.*, **29**, 131 (1968), and references therein.

[5] F. Aprile, V. Caglioti, and G. Illuminati, *J. Inorg. Nucl. Chem.*, **21**, 325 (1961).

[6] V. Carunchio, G. Illuminati, and F. Mespero, *ibid.*, **28**, 2693 (1966).

[7] F. J. Garrick, *Nature*, **139**, 507 (1937).

[8] F. Basolo and R. G Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 177–193.

[9] S. C. Chan, *J. Chem. Soc., A*, 1124 (1966).

[10] R. D. Gillard, *ibid.*, *A*, 917 (1967).

[11] M. Linhard and G. Stirn, *Z. Anorg. Allg. Chem.*, **268**, 105 (1952).

stopper and allowed to attain thermal equilibrium at 84.5° for 10 min before absorbance readings were begun. The reactions were run for 90–100 min, since evaporation became noticeable after this time period. Infinite time samples were obtained in sealed ampoules as previously described;[1] the ampoules were heated at 84.5° for 2–3 days before A_∞ values were measured. Calculations were performed as before.[1]

Results and Discussion

The spectra of the *trans*-[Co(en)$_2$(toluato)$_2$]ClO$_4$ complexes in the visible region are very similar to the corresponding diacetato complexes. There is, however, a large spectral difference in the near-ultraviolet region due to the tail of charge-transfer bands in the ultraviolet region. The spectral changes during solvolysis are shown in Figure 1 for the *o*-toluato complex. The product spectrum (Figure 1, equilibrium curve) is identical with that of the equilibrium mixture of [Co(en)$_2$(OAc)$_2$]ClO$_4$ isomers observed previously.[1] The isosbestic point at ~19.4 kK indicates that the only observable species are the reactant and product; the mixed intermediate formed in (2a) is not observed. The same observations were made for the *p*-toluato complex.

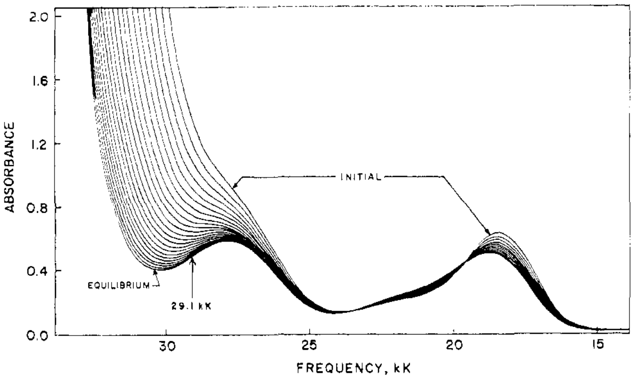


Figure 1.—Visible and near-ultraviolet spectra during the solvolysis of *trans*-[Co(en)$_2$(*o*-toluato)$_2$]ClO$_4$ in acetic acid at 84.5°. Spectra were recorded at 7.0-min intervals (scan time 2 min).

It was previously observed that an isosbestic point between *cis*- and *trans*-[Co(en)$_2$(OAc)$_2$]ClO$_4$ existed at 29.1 kK; thus measurements made at this frequency are independent of the isomer distribution of the product. The rate constants of the solvolysis were obtained from plots of ln $(A - A_\infty)$ *vs.* time at 29.1 kK. Plots for all runs were verifiably linear over the time period investigated. Due to evaporation, it was usually not possible to follow the reaction for more than 100 min, a period in general less than a reaction half-time. In a few trial experiments over longer time periods, no significant deviation from linearity was observed.

It has been observed by Carunchio, *et al.*,[12] that in the base hydrolysis of Co(en)$_2$X$_2^+$ complexes in water

$$\mathrm{Co(en)_2X_2^+} \xrightarrow{k'} \mathrm{Co(en)_2XOH^+} \xrightarrow{k''} \mathrm{Co(en)_2(OH)_2^+}$$

$k' \gg k''$ for *trans* isomers. For instance, when X$^-$ = Cl$^-$, k'/k'' = 5650; but for X$^-$ = OAc$^-$, k'/k'' = 40. Similar data are not available for benzoato or other carboxylato complexes, in that only k' was measured.[5,6] It is unlikely that k'/k'' would be much different from unity in acetic acid, where OH$^-$ is replaced by OAc$^-$ and X$^-$ = toluate, since acetate and toluate will differ only slightly as ligands, whereas OH$^-$ would differ significantly. In the present investigation, therefore, k_{obsd} is attributed to k_1 in (2a), particularly since only the initial phase of the reaction was experimentally observed.

The effect of added NaOAc on the observed solvolysis rate constant is shown in Figure 2 for the p-toluato complex; the data for both the *o*- and *p*-toluato complexes are given in Table I. The observed retardation is similar to that observed in the isomerization of [Co(en)$_2$(OAc)$_2$]ClO$_4$.[1]

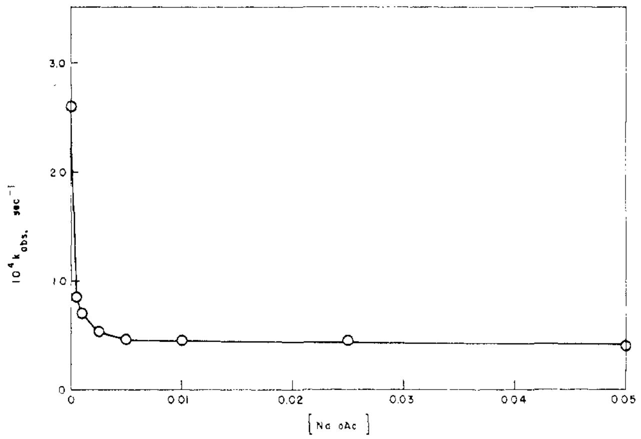


Figure 2.—The variation of the rate constant for the solvolysis of *trans*-[Co(en)$_2$(*p*-toluato)$_2$]ClO$_4$ with sodium acetate concentration at 84.5°.

TABLE I

THE EFFECT OF SODIUM ACETATE ON THE SOLVOLYSIS OF *trans*-[Co(en)$_2$(toluato)$_2$]ClO$_4$ IN ACETIC ACID AT 84.5°

[NaOAc], *M*	10^4k_{obsd}, sec^{-1} 0.01 *M* *p*-toluato	 0.005 *M* *o*-toluato
0.00	2.6 ± 0.3[a]	4.6 ± 0.1[b]
0.0005	0.85	1.3
0.0010	0.70	1.2
0.0025	0.53	1.1
0.0050	0.46	1.0
0.010	0.45	1.0
0.025	0.45	1.0
0.050	0.40	1.0
0.075	0.39	...
0.100	0.39	1.0
0.200	0.37	...
0.400	0.37	...

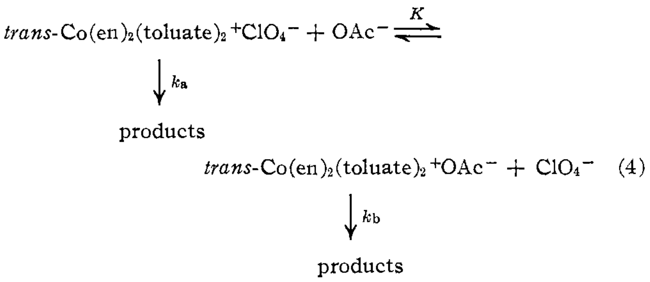
[a] Result of four rate determinations. [b] Result of three rate determinations.

The results above may be interpreted in a manner similar to that used for the isomerization of the diacetate,[1] *i.e.*, as an ion pair–ion pair equilibrium (4) in which an acetate ion pair is formed from the per-

---

[12] V. Carunchio, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, **6**, 2168 (1967).

chlorate ion pair present in the absence of NaOAc. Here k_a and k_b are the solvolysis constants for the



$$\begin{array}{ll} trans\text{-Co(en)}_2\text{(toluate)}_2{}^+\text{ClO}_4{}^- + \text{OAc}^- \overset{K}{\rightleftharpoons} & trans\text{-Co(en)}_2\text{(toluate)}_2{}^+\text{OAc}^- + \text{ClO}_4{}^- \\ \quad\downarrow k_a & \quad\downarrow k_b \\ \quad\text{products} & \quad\text{products} \end{array} \quad (4)$$

perchlorate and acetate ion pairs, respectively. With the assumptions and equations used previously,[1] the observed first-order rate constant is given by

$$k_{obsd} = \frac{k_a + k_b K' K_i^{1/2}[\text{NaOAc}]^{1/2}}{1 + K' K_i^{1/2}[\text{NaOAc}]^{1/2}} \quad (5)$$

where K_i is the ionization constant of NaOAc and $K' = K/[\text{ClO}_4^-]$. The constants derived[1] from (5) are $k_a = 2.6 \times 10^{-4}$ sec^{-1}, $k_b = 0.36 \times 10^{-4}$ sec^{-1}, $K'K_i^{1/2} = 240\ M^{1/2}$. For $K_i^{1/2} \approx 10^{-3}$ and $[\text{ClO}_4^-] \approx$ [complex] $\approx 10^{-2}$, K may be estimated as approximately 2500, in agreement with the values estimated for the corresponding equilibrium in the diacetato complex.[1]

The data for the *o*-toluato complex are insufficient for a plot according to (5), but the magnitude of the effect observed appears to be comparable to that of the *p*-toluato complex. The greater reactivity of the *o*-toluato complex will be discussed separately.[13]

The reasons for the lower reactivity of acetate ion pairs relative to perchlorate ion pairs in acetic acid have been discussed[1] and may be summarized briefly. Acetate ion pairs in acetic acid are structurally similar to free ions in that the solvent shell would be symmetrical, lacking one (delocalized) proton. Thus, in discussions of relative reactivity the acetate ion pair replaces the free ion in other treatments[2-4] and it becomes apparent that acetate ion pairs will react more slowly than, *e.g.*, perchlorate ion pairs.

The substitution mechanism within the perchlorate and acetate ion pairs in acetic acid may be discussed in terms of existing theories of base hydrolysis.[7-10] Chan's ion-pairing mechanism[9] in water is not inconsistent with the SN1CB mechanism. Basolo and Pearson[8] have pointed out that the conjugate base can be formed from the ion pair; indeed the proton extraction is probably more favorable in the ion pair. In spite of the similarity of Chan's interpretation to the present case, *i.e.*, ion pairs are the reactive species, there is a greater dissimilarity in that in acetic acid both ion pairs are reactive, while in water the free ion is apparently unreactive. In the SN1CB mechanism, the acetate ion pair should be more reactive, since OAc^- is significantly more basic than ClO_4^- and should more readily form the conjugate base in (3a). Since the acetate ion pair is the *less* reactive of the two (by a factor of approximately 5), the SN1CB mechanism is virtually eliminated in the case of acetic acid. The relevance of these experiments to aqueous base hydrolyses has already been discussed.[14]

The electron-transfer mechanism of Gillard[10] might have some relevance. In this mechanism, the outer-sphere anion transiently reduces the cobalt(III) to cobalt(II), with formation of an associated radical. This step is shown for the present case

$$\text{Co}^{\text{III}}(\text{en})_2\text{X}_2{}^+\text{Y}^- \rightleftharpoons [\text{Co}^{\text{II}}(\text{en})_2\text{X}_2]\text{Y}\cdot$$

where X = toluate and Y = ClO_4^- or OAc^-. If ClO_4^- is more easily oxidized than OAc^- to the corresponding radical, then this would be consistent with the observed greater reactivity of the perchlorate ion pair. However, the stability of a perchlorate radical, even associated with the complex ion, is questionable under the reaction conditions. The electron-transfer path seems unlikely in the present case.

A more reasonable mechanistic pathway is "solvent-assisted dissociation" (SAD).[1,15] The greater reactivity of the perchlorate ion pair indicates that the acetate ion in the acetate ion pair is not participating in nucleophilic attack but that both ion pairs interact with solvent molecules in the solvent sphere. The acetic acid molecule would partially enter the primary coordination sphere where it could be stabilized by hydrogen bonding[13] to the toluate carboxyl group and an amine group from ethylenediamine. The acetic acid proton would be transferred to the carboxyl group, producing labile toluic acid and an adjacent acetate ion.

The properties of the entering acetic acid molecule would be more typical of the molecules in the solvent sphere (containing the anion of the ion pair) than of the bulk solvent. The rate of the proton transfer from acetic acid to toluate ion would be affected by the ionization constant of the entering solvent molecule. In the perchlorate ion pair, the solvent molecule would have properties similar to bulk solvent, since the ClO_4^- would be localized. In the acetate ion pair, however, the delocalization of the negative charge in the solvent sphere[1] would impart a partial negative charge to the entering solvent molecule, thus reducing its ionization constant. The SAD mechanism is thus consistent with the observation that $k_b < k_a$ in (5).

TABLE II

THE EFFECT OF DEUTERATION OF ACETIC ACID ON THE SOLVOLYSIS OF *trans*-[Co(en)$_2$(toluato)$_2$]ClO$_4$ AT 84.5°

	$10^4 k_{obsd}$, sec^{-1}	
Solvent	0.01 *M* *p*-toluato	0.005 *M* *o*-toluato
Acetic acid	2.6 ± 0.3	4.6 ± 0.1
Acetic acid-d_1[a]	2.1	2.7
Acetic acid-d_4[a]	2.0	3.2

[a] Duplicate determinations.

As a further test of the hypothesis that a lower solvent ionization constant would result in reduced

---

[13] A. W. Chester, *J. Inorg. Nucl. Chem.*, in press.

[14] A. W. Chester, *Chem. Commun.*, 865 (1969).

[15] Reference 8, pp 134–135. This mechanism has also been called SN2FS, for frontside attack.

solvolysis rates, the reaction was carried out in acetic acid-d_1 and -d_4. Acetic acid-d_4 has a $\mathrm{p}K_\mathrm{a}$ of 5.25, while the $\mathrm{p}K_\mathrm{a}$ of acetic acid is 4.75.[16] The results are shown in Table II; the observed reduction in rate is consistent with the above discussion.

Acknowledgments.—The author is indebted to Mr. A. W. Gerbig for his aid during this investigation and to Dr. R. H. Albert for useful discussions.

[16] "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Co., Cleveland, Ohio, 1966. Values are for 25° in water.

CONTRIBUTION FROM THE MOBIL RESEARCH AND DEVELOPMENT CORPORATION,
CENTRAL RESEARCH DIVISION LABORATORY, PRINCETON, NEW JERSEY 08540

Acetate Exchange of Diacetatobis(ethylenediamine)cobalt(III) Perchlorate in Acetic Acid

BY ARTHUR W. CHESTER

Received February 10, 1970

The kinetics of the acetate exchange of $[\mathrm{Co(en)_2(CH_3COO)_2}]\mathrm{ClO_4}$ with $\mathrm{CD_3COOD}$ were examined and compared with the *cis–trans* isomerization rates. The rates were measured by a pmr method based on an observed relative shift of the $\mathrm{CH_3}$ protons in the *cis* and *trans* isomers. The *cis* isomer exchanges more rapidly than it isomerizes, but the *trans* isomer appears to exchange at the isomerization rate. The proposed mechanism for isomerization involves a solvent-assisted, intramolecular isomerization *via* one transition state, with no acetate exchange with solvent.

The effect of added sodium acetate on the isomerization of *cis*-$[\mathrm{Co(en)_2(OAc)_2}]\mathrm{ClO_4}$[1] and the solvolysis of *trans*-$[\mathrm{Co(en)_2(toluato)_2}]\mathrm{ClO_4}$[2,3] in acetic acid has already been reported. The added acetate severely retarded the reaction rates and an ion pair–ion pair equilibrium in which a less reactive acetate ion pair is formed was proposed in order to explain the observed kinetics. It was further proposed that the reactions within the ion pairs occurred *via* a "solvent-assisted dissociation" pathway,[4] in which acetic acid partially bonds to the inner-sphere ligands and aids in their removal. In order to gain further insight into the mechanistic processes involved, the exchange of acetate ligands in *trans*-$[\mathrm{Co(en)_2(OAc)_2}]\mathrm{ClO_4}$ with solvent has been studied by a nuclear magnetic resonance technique.

Experimental Section

All chemicals were reagent grade. Acetic acid-d_4 (99.5%) was obtained from Merck Sharp and Dohme of Canada Ltd.

Sodium acetate-d_3 was prepared by treating $\mathrm{NaHCO_3}$ in water with acetic acid-d_4 until the solution was slightly acidic. The solution was evaporated to dryness and the product dried at 120° overnight before use. Examination of the proton magnetic resonance spectrum of this compound in $\mathrm{D_2O}$ showed that $\mathrm{CH_3}$ peaks were absent.

cis- and *trans*-$[\mathrm{Co(en)_2(CH_3COO)_2}]\mathrm{ClO_4}$ were prepared as before.[1]

Proton magnetic resonance (pmr) spectra was determined on a Varian A-60 spectrometer at ambient temperature ($\sim$38°) with tetramethylsilane (TMS) as an external reference.

The kinetics of the isomerization of *trans*-$[\mathrm{Co(en)_2(CH_3COO)_2}]\mathrm{ClO_4}$ in acetic acid-d_4 were investigated by methods described previously.[1] First-order rate constants were determined from a least-squares plot of ln ($A_\infty - A$) *vs.* time. The absorbance increase was followed at 20.00 kK. The accuracy of these rate constants was severely limited by the small overall absorbance change (0.1–0.2 unit).

Measurement of Exchange Rates.—The pmr spectra of *cis*- and *trans*-$[\mathrm{Co(en)_2(CH_3COO)_2}]\mathrm{ClO_4}$ in $\mathrm{CD_3COOD}$ showed that the $\mathrm{CH_3}$ peak in the *trans* isomer was shifted 12–13 cps upfield from the *cis*-$\mathrm{CH_3}$ peak and that this effect could be used for measurement of the exchange rate of coordinated $\mathrm{CH_3COO^-}$ with $\mathrm{CD_3COOD}$ (*vide infra*). The exchange rate was followed by observing the decrease of the *trans* isomer $\mathrm{CH_3}$ peak with time (the *cis* isomer $\mathrm{CH_3}$ peak and the $\mathrm{CH_3}$ peak for free acetate occurred at the same chemical shift, so that no measurement of *cis*-acetate exchange could be made).

The exchange measurements were performed with a 0.05 *M* stock solution of *trans*-$[\mathrm{Co(en)_2(CH_3COO)_2}]\mathrm{ClO_4}$ in $\mathrm{CD_3COOD}$. The runs with added $\mathrm{NaO_2CCD_3}$ were performed on solutions prepared by adding a suitable amount of $\mathrm{NaO_2CCD_3}$ to a portion of the stock solution. Approximately 0.5-ml samples of the reaction solution were placed in nmr tubes, which were stoppered and partially submerged in a constant-temperature bath at the appropriate temperature (84.5°). Sample tubes were removed at suitable time intervals, quenched in ice immediately, and stored at room temperature (separate experiments verified that such solutions showed no change when stored for up to 1 month). The pmr spectrum of each sample was recorded and the integration was performed five times. The intensity of the *trans*-$\mathrm{CH_3}$ peak was calculated with reference to the $\mathrm{CH_2}$ (from ethylenediamine) peak intensity, *i.e.*, $R_\mathrm{t} = I(\textit{trans}\text{-}\mathrm{CH_3})/(\mathrm{CH_2})$. The final intensity was taken as the average of the five determined intensities for each time. First-order rate constants were calculated from plots of ln (R_t) *vs.* time by a least-squares calculation. Standard deviations of the slope were calculated as indicated previously.[1]

Results and Discussion

The pmr spectra of *cis*- and *trans*-$[\mathrm{Co(en)_2(CH_3COO)_2}]\mathrm{ClO_4}$ were consistent with previously reported spectra of *cis*- and *trans*-bis(ethylenediamine)cobalt-

---

[1] A. W. Chester, *Inorg. Chem.*, **8**, 1584 (1969).

[2] A. W. Chester, *Chem. Commun.*, 865 (1969).

[3] A. W. Chester, *Inorg. Chem.*, **9**, 1743 (1970).

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 134–135.