solvolysis rates, the reaction was carried out in acetic acid-d_1 and -d_4. Acetic acid-d_4 has a pK_a of 5.25, while the pK_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.

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

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The kinetics of the acetate exchange of $[Co(en)_2(CH_3COO)_2]ClO_4$ with 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 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*-$[Co(en)_2(OAc)_2]ClO_4$[1] and the solvolysis of *trans*-$[Co(en)_2(toluato)_2]ClO_4$[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*-$[Co(en)_2(OAc)_2]ClO_4$ 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 $NaHCO_3$ 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 D_2O showed that CH_3 peaks were absent.

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

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

The kinetics of the isomerization of *trans*-$[Co(en)_2(CH_3COO)_2]ClO_4$ 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*-$[Co(en)_2(CH_3COO)_2]ClO_4$ in CD_3COOD showed that the CH_3 peak in the *trans* isomer was shifted 12–13 cps upfield from the *cis*-CH_3 peak and that this effect could be used for measurement of the exchange rate of coordinated CH_3COO^- with CD_3COOD (*vide infra*). The exchange rate was followed by observing the decrease of the *trans* isomer CH_3 peak with time (the *cis* isomer CH_3 peak and the 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*-$[Co(en)_2(CH_3COO)_2]ClO_4$ in CD_3COOD. The runs with added NaO_2CCD_3 were performed on solutions prepared by adding a suitable amount of 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*-CH_3 peak was calculated with reference to the CH_2 (from ethylenediamine) peak intensity, *i.e.*, $R_t = I(trans\text{-}CH_3)/(CH_2)$. 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*-$[Co(en)_2(CH_3COO)_2]ClO_4$ were consistent with previously reported spectra of *cis*- and *trans*-bis(ethylenediamine)cobalt-

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[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.

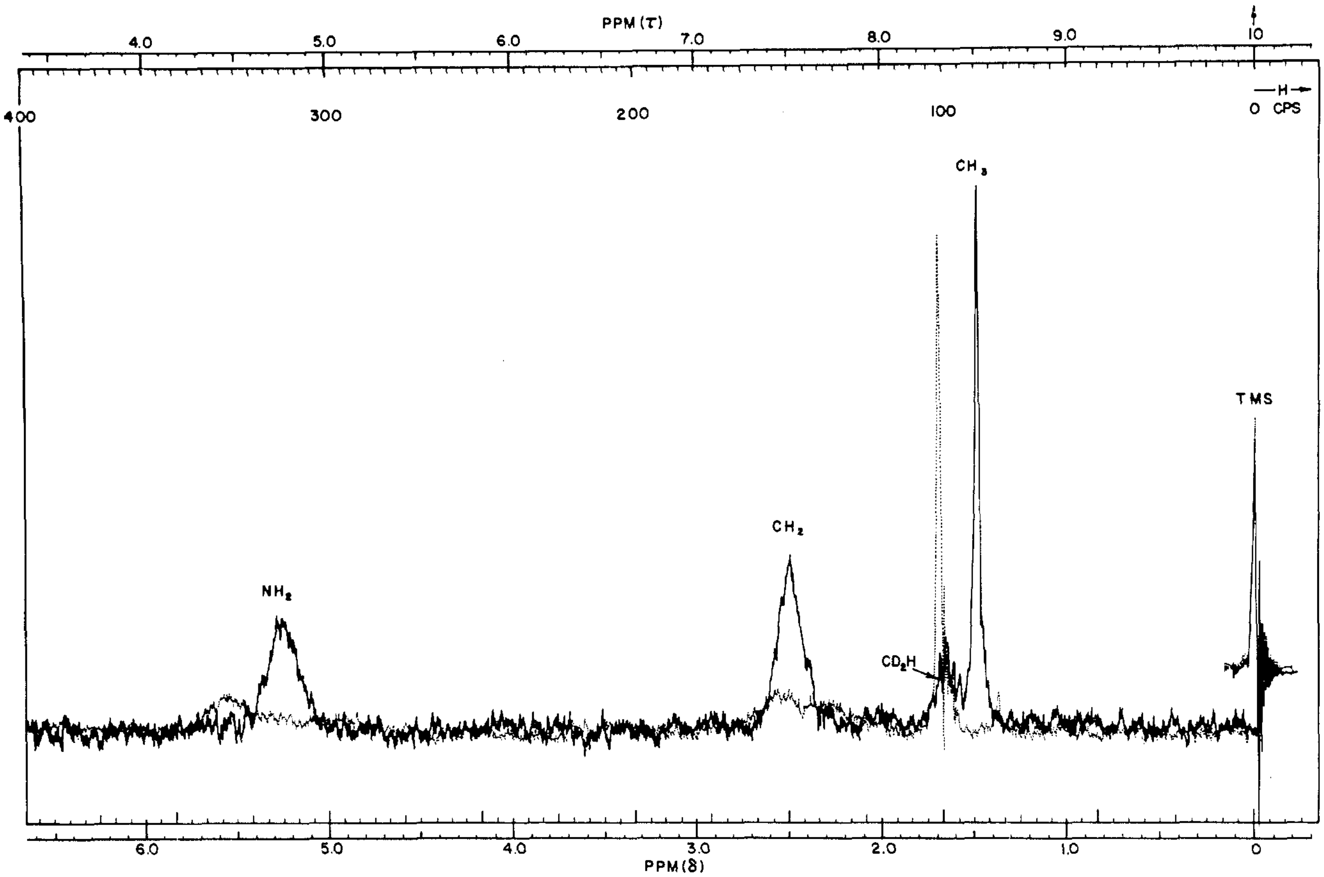

Figure 1.—The pmr spectra of *cis*- (......) and *trans*- (——) $[Co(en)_2(CH_3COO)_2]ClO_4$ in CD_3COOD.

(III) isomers in the CH_2 and NH_2 regions;[5-9] the spectra are shown in Figure 1 in CD_3COOD. The CH_3 (from acetate) resonances in the two isomers did not occur at the same chemical shift: the *trans*-CH_3 resonance occurred 12–13 cps upfield from the *cis*-CH_3 resonance (the quintet observed in the *trans* spectrum in Figure 1 is due to CD_2H present as an impurity in CD_3COOD; it is obscured in the *cis* spectrum by the CH_3 resonance, which occurs at the same position). For both isomers, the $CH_3:CH_2$ intensity ratio was close to the theoretical value of 0.75. The relative and absolute positions of the CH_3 resonances were found to be independent of concentration; mixtures of the two isomers in any proportion resulted in the two resonances being observed in the appropriate intensity ratio. Free acetate ion had the same shift as the *cis* isomer. Upon heating solutions of *trans*-$[Co(en)_2(CH_3COO)]ClO_4$ in CD_3COOD, the *trans*-CH_3 resonance decreased in intensity while the combination *cis*-CH_3 and free acetate resonance increased; the ratio (total CH_3):CH_2 remained at 0.75. It was therefore possible to follow the kinetics of acetate exchange in the *trans* isomer by observing the decrease of the (*trans*-CH_3):CH_2 intensity ratio with time. This isomer shift appears to be general and occurs with other isomer pairs and in other solvents; it will be discussed in a separate publication.

Upon heating a solution of *trans*-$[Co(en)_2(CH_3COO)_2]ClO_4$ in CD_3COOD, the intensity of the CH_2 resonance remained constant with time, although broadening was observed due to *cis* formation (see Figure 1). The loss of protonated *trans*-diacetate was followed by determining the ratio $R_t = I(trans\text{-}CH_3)/I(CH_2)$ as a function of time. Since the solvent was in large excess, $R_\infty \approx 0$; also, $R_0 = 0.75$. The exchange rate was obtained as a first-order rate constant from a plot of ln (R_t) *vs.* time. The rate constants were determined as a function of added NaO_2CCD_3.

The data were not of high quality, much scatter being observed in the plots. Typical plots, for 0.0 and 0.301 *M* NaO_2CCD_3, are shown in Figure 2. The scatter is a result of the low complex concentrations necessary (due to poor solubility) and the consequent poor response of the spectrometer. The exchange rate constants are given in Table I. Also given in Table I are the rates of isomerization of *trans*-$[Co(en)_2(CH_3COO)_2]ClO_4$ in CD_3COOD as a function of added NaO_2CCD_3.

The proposed mechanism for the isomerization is the ion pair–ion pair equilibrium

$$\begin{tikzcd}
\textit{cis}\text{-Co(en)}_2(\text{OAc})_2{}^+\text{ClO}_4{}^- + \text{OAc}^- \arrow[r, shift left, "K"] \arrow[d, shift right, "k_1"'] & \textit{cis}\text{-Co(en)}_2(\text{OAc})_2{}^+\text{OAc}^- + \text{ClO}_4{}^- \arrow[l, shift left] \arrow[d, shift right, "k_2"'] \\
\textit{trans}\text{-Co(en)}_2(\text{OAc})_2{}^+\text{ClO}_4{}^- + \text{OAc}^- \arrow[u, shift right, "k_{-1}"'] \arrow[r, shift left, "K"] & \textit{trans}\text{-Co(en)}_2(\text{OAc})_2{}^+\text{OAc}^- + \text{ClO}_4{}^- \arrow[l, shift left] \arrow[u, shift right, "k_{-2}"']
\end{tikzcd} \quad (1)$$

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(5) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

(6) S. T. Spees, L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

(7) B. M. Fung, *J. Amer. Chem. Soc.*, **89**, 5788 (1967).

(8) I. R. Lantzke and D. W. Watts, *Australian J. Chem.*, **20**, 35 (1967).

(9) A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966).

which leads to the following expression for the first-order rate constant as a function of acetate[1]

$$k_{\text{obsd}} = \frac{k_a + k_b KK_i^{1/2}[\text{NaOAc}]^{1/2}}{1 + KK_i^{1/2}[\text{NaOAc}]^{1/2}} \qquad (2)$$

where $k_a = k_1 + k_{-1}$, $k_b = k_2 + k_{-2}$, and K_i is the ionization constant of NaOAc in acetic acid. It was previously found[1] that $k_a \approx 10k_b$; *i.e.*, addition of acetate retarded the reaction. In CD_3COOD the rates are slower than in the protonated solvent; k_a and k_b may be estimated on the basis of the isomerization rate data in Table I to be $k_a \approx 35 \times 10^{-4}$ sec^{-1} and $k_b \approx 5 \times 10^{-4}$ sec^{-1}.

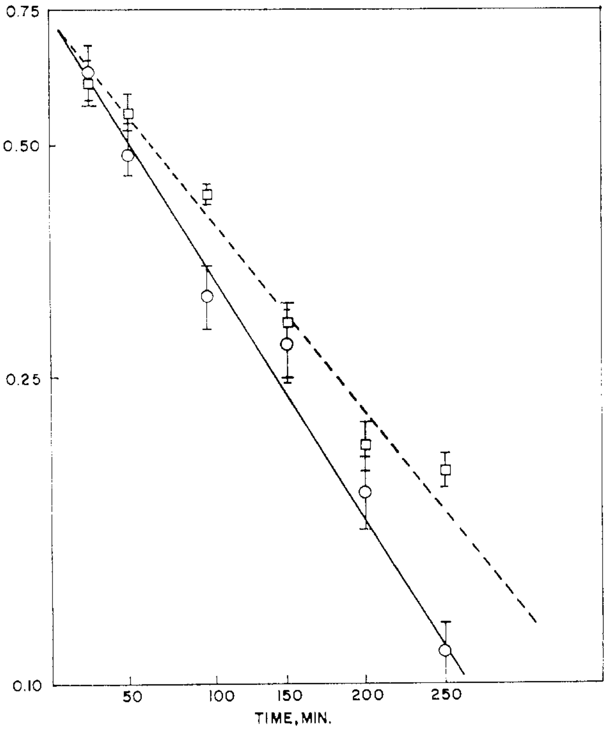

Figure 2.—Kinetic plots for the acetate exchange of *trans*-$[Co(en)_2(CH_3COO)_2]ClO_4$ in CD_3COOD for 0.0 *M* (——) and 0.301 *M* (-----) NaO_2CCD_3.

TABLE I

OBSERVED EXCHANGE AND ISOMERIZATION RATE CONSTANTS[a] FOR *trans*-$[Co(en)_2(CH_3COO)_2]ClO_4$ IN CD_3COOD AT 84.5°

Exchange[b]		Isomerization[c]	
$[NaO_2CCD_3]$, *M*	10^4k_e, sec^{-1}	$[NaO_2CCD_3]$, *M*	10^4k_i, sec^{-1}
0.00	1.2 ± 0.08	0.00	34 ± 1
0.047	1.1 ± 0.16	0.047	7.3 ± 0.2
0.099	1.0 ± 0.1	0.098	7.2 ± 0.1
0.199	0.9 ± 0.05	0.199	5.6 ± 0.2
0.300	0.9 ± 0.05	0.299	5.7 ± 0.2
0.500	0.8 ± 0.06		

[a] Errors are given as $\pm\sigma$, where σ is the standard deviation of the slope. [b] Concentration 0.05 *M*. [c] Concentration 0.01 *M*.

The exchange rates of *trans*-$[Co(en)_2(CH_3COO)_2]ClO_4$ in Table I should be compared with the isomerization rate constants k_{-1} and k_{-2} in (1). The *cis–trans* equilibrium constant was found[1] to be independent of added acetate and had a value of $[trans]_{eq}/[cis]_{eq} = 4$. Therefore, k_{-1} and k_{-2} are approximately 7×10^{-4} and 1×10^{-4} sec^{-1}, respectively. The exchange rates show only a small variation with acetate; apparently the perchlorate and acetate ion pairs of the *trans* isomer in (1) undergo acetate exchange at essentially the same rate, $k_e \approx 1 \times 10^{-4}$ sec^{-1}, which is the same as the isomerization rate constant k_{-2} (within the limits of experimental error).

When *cis*-$[Co(en)_2(CH_3COO)_2]ClO_4$ is heated in CD_3COOD, in the presence and absence of NaO_2CCD_3, there is no change in the pmr spectrum, indicating that the *trans* isomer is formed fully deuterated, *i.e.*, as *trans*-$[Co(en)_2(CD_3COO)_2]ClO_4$. Thus, the *cis* ion pairs exchange more rapidly than they isomerize, which implies that the *trans* ion pairs exchange predominantly by prior isomerization to the *cis* form.

A reasonable model involves isomerization of both isomers through a single transition state. Such a model implies an intramolecular mechanism in both directions, with no involvement of solvent exchange in the isomerization.

The previously proposed mechanism of solvent-assisted dissociation within the inner sphere[1-3] is consistent, at least in part, with this model. The lack of acetate dependence in the exchange rate (k_{-2}) implies that only the *cis*-acetate ion pair is exchanging with solvent at a significant rate. Since the three other pairs are isomerizing without exchange, this model, in which isomerization occurs *via* a solvent-assisted, intramolecular mechanism, is in accord with the observations. The acetate ligand labilized by hydrogen bonding with the solvent does not leave the inner sphere. According to this model, ligand exchange is not involved in the isomerization.

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