

those of the other *cis* compounds, for a given halogenoacetato ligand, the following order is found

$$\nu_{\text{trien}} > \nu_{(\text{en})_2} > \nu_{\text{tren}} > \nu_{(\text{NH}_3)_4}$$

This is believed to indicate that the ligand field strength of the tren ligand is between that of en and NH_3 and less than that of trien. This trend is not surprising since the less flexible branched structure of tren gives rise to a somewhat distorted octahedral complex. Furthermore, tren has a tertiary nitrogen atom, which is a weaker electron donor than either a secondary or a primary nitrogen atom.

Theory²² suggests that the intensity of a d-d transition should be enhanced by increasing the asymmetry of the ligand field, and this proposition has been supported by experiments.²³ It seems reasonable, then, that the rise in the ϵ value accompanying the more rigid tetramine ligands is caused by increased distortion of the octahedral field. On this basis, one would expect that the absorption intensity of the tren complexes should have a higher value than that of the trien complexes, since trien is more flexible than branched tren. Comparing the visible spectra of a series of amine complexes

(22) F. A. Cotton, "Chemical Application of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963, p 231.

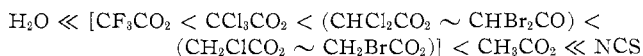
(23) R. L. Belford and W. A. Yeranov, *Mol. Phys.*, **6**, 121 (1963); P. W. Schneider and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1717 (1964).

for a given halogenoacetato ligand, the absorption intensities are in the order

$$\epsilon_{\text{tren}} \sim \epsilon_{\text{trien}} > \epsilon_{(\text{en})_2} > \epsilon_{(\text{NH}_3)_4}$$

Collman and Schneider²⁴ found that the ϵ values of dichlorocobalt(III)-trien and -tren complexes are about the same (130 and 125). However, for the complexes with a larger central atom such as *cis*-dichlororhodium(III)-trien and -tren complexes, the ϵ values differ by a factor of 3 (101 and 300). Therefore, it appears that the increase of the distortion from trien to tren complex is minimal for the relatively smaller Co(III) central atom.

We have also observed that when one compares the electronic absorption spectra of the different halogenoacetato complexes for a given amine ligand, the intensity of the absorption maxima increase in the order



This trend suggests that the intensity of the absorption maxima is related to the inductive effect of the halogenoacetato ligands.

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(24) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).

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The Isomerization of *cis*-Diacetatobis(ethylenediamine)cobalt(III) Perchlorate in Acetic Acid

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The kinetics of the isomerization of *cis*-[Co(en)₂(OAc)₂]ClO₄ were studied as a function of added sodium acetate in acetic acid in the range 68.8–84.5° by observing the absorbance decrease at 20.00 kK. It was found that sodium acetate retarded the rate of isomerization and the first-order rate constant appeared to have an acetate dependence of the form

$$k_{\text{obsd}} = \frac{k_a + k_b K K_1^{1/2} [\text{NaOAc}]^{1/2}}{1 + K K_1^{1/2} [\text{NaOAc}]^{1/2}} \quad (k_a > k_b)$$

where K_1 is the ionization constant for sodium acetate in acetic acid. The decreased rate is attributed to formation of an acetate ion pair that is less reactive than the perchlorate ion pair initially present. It is proposed that the isomerization within the ion pairs involves a solvent-assisted dissociation.

The isomerization, racemization, and substitution reactions of disubstituted bis(ethylenediamine)cobalt(III) complexes in nonaqueous media have been fairly extensively studied and reviewed.^{1,2} Kinetic studies of *cis-trans* isomerization in nonaqueous media have centered on the dichloro compound $\text{Co}(\text{en})_2\text{Cl}_2^+$, which has been studied in methanol^{3,4} and other alcohols,⁵

2-methoxyethanol,⁶ dimethyl sulfoxide,⁷ dimethylformamide and dimethylacetamide,⁸ and sulfolane.⁹ The ions $\text{Co}(\text{en})_2\text{Br}_2^+$ and $\text{Co}(\text{en})_2\text{BrCl}^+$ have also been studied in a variety of aprotic solvents.^{10,11} In addition, the *cis-trans* isomerizations of diaquobis(ethylene-

(1) (a) M. L. Tobe, *Advances in Chemistry Series*, No. 48, American Chemical Society, Washington, D. C., 1965, p 7; (b) *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 79 (1966).

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, pp 207–216 and Chapter 4.

(3) D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953).

(4) B. Bosnich, C. Ingold, and M. L. Tobe, *ibid.*, 4074 (1965).

(5) R. C. Brasted and C. Hirayama, *J. Am. Chem. Soc.*, **80**, 788 (1958).

(6) R. F. Trimble, *ibid.*, **76**, 6321 (1954).

(7) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1964).

(8) M. L. Tobe and D. W. Watts, *ibid.*, 4614 (1962).

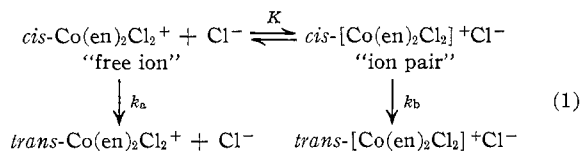
(9) W. R. Fitzgerald and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 821 (1967).

(10) W. R. Fitzgerald and D. W. Watts, *Australian J. Chem.*, **19**, 1411 (1966).

(11) W. R. Fitzgerald and D. W. Watts, *ibid.*, **21**, 595 (1968).

diamine)cobalt(III) complexes (the dihydroxo, diaquo, and aquohydroxo species),¹²⁻¹⁴ dichloro- and chloro-aquobis(ethylenediamine)cobalt(III),¹³ and aquoaminebis(ethylenediamine)cobalt(III)¹⁵ have been studied in aqueous media.

The dominant feature of isomerization and other reactions of these species in nonaqueous media is the influence of ion-pair formation.^{1,2} Bosnich, Ingold, and Tobe⁴ studied the isomerization of $\text{Co}(\text{en})_2\text{Cl}_2^+$ (as the tetraphenylborate) in methanol at 35° as a function of chloride concentration (as added LiCl). They proposed the following mechanism, where K is the ion-pairing constant and k_a and k_b are the rate con-



stants for isomerization of the free ion and ion pair, respectively. Such a mechanism leads to the rate law

$$k_{\text{obsd}} = \frac{k_a + k_b K [\text{LiCl}]}{1 + K [\text{LiCl}]} \quad (2)$$

The results showed that the ion pair isomerized at more than twice the rate of the free ion and the value of K (250 M^{-1}) derived from (2) was in reasonable agreement with that obtained spectrophotometrically by Pearson, Henry, and Basolo.¹⁶ Rate laws such as (2) have been observed in many reactions in nonaqueous media and are attributed to ion-pairing mechanisms similar to (1).¹ The rate enhancement of the ion pair with respect to the free ion has been interpreted as being due to increased charge separation in the transition state due to the presence of anions in the solvation sphere.¹⁶

In the present investigation, the isomerization of diacetatobis(ethylenediamine)cobalt(III) perchlorate, $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$, was studied in acetic acid as a function of added acetate ion in order to investigate the role of the acetic acid solvent in reactions of transition metal complexes. It is worth noting that the diacetato complex in acetic acid is formally analogous to $\text{Co}(\text{en})_2(\text{OH})_2^+$ in aqueous solution; *i.e.*, these are complexes of the *lyate* ion (the anion of the solvent).

Experimental Section

All chemicals were reagent grade. Sodium acetate was dried at 120° before use. Acetic acid containing 0.1-0.2% water was used unchanged, except where noted. Acetic acid- d_1 and - d_4 were obtained from Merck Sharp and Dohme of Canada Ltd.

cis- and *trans*- $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$ were prepared by the method of Linhard and Stirn.¹⁷ The procedure for the preparation of the *cis* isomer involves treatment of *cis*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ with KOAc at 50° followed by removal of insoluble KClO_4 , evaporation of the solvent, and recrystallization from ethanol and ether. Analysis of the samples used in this investigation showed that 0.3-1.2% potassium was present. Further re-

crystallization of a sample gave no improvement. It is assumed that the potassium is present as KOAc, since any remaining KClO_4 would be removed in the recrystallization procedure. In the kinetic runs without added acetate, acetate concentrations were estimated from the potassium content. A typical analysis is given for the *cis* isomer. *Anal.* Calcd for *cis*- $\text{CoC}_8\text{H}_{18}\text{N}_2\text{O}_5\text{Cl}$: C, 24.2; H, 5.6; N, 14.1; K, 0.0. Found: C, 23.1; H, 5.4; N, 13.6; K, 0.3.

The visible spectra were in good agreement with the data of Carunchio, *et al.*¹⁸

Kinetics.—The kinetics of the isomerization of the *cis* compound (see text) were studied spectrophotometrically by following the decrease of the absorbance at 20.00 kK (1 kK = 1000 cm^{-1}) on a Unicam SP800D spectrophotometer. The spectrophotometer was equipped with a constant-temperature cell block in which as many as four cells could be examined simultaneously and automatically. The cell block was connected to an external constant-temperature bath accurate to $\pm 0.05^\circ$. The reaction temperatures (temperatures in the cells) were measured in preliminary experiments with a thermocouple at several temperatures. In this way a relationship between bath temperature and cell temperature was established. It was also found that 10 min was required to attain thermal equilibrium between solution and cell block.

Reaction solutions were made up from fresh stock solutions of the *cis* isomer (0.05 M) in acetic acid and stock solutions (0.1 and 1.0 M) of NaOAc in acetic acid by dilution in a volumetric flask at room temperature. The concentration of the complex was 0.01 M except where otherwise noted. A 3-ml sample of the reaction solution was placed in a 1-cm silica cell sealed with a rubber septum. The solution was then allowed to attain thermal equilibrium in the cell block for 10 min before beginning absorbance readings. The reactions were run for 2-4 half-lives depending on rate and temperature.

Infinite-time samples (equilibrium solutions) were obtained by sealing another 3-ml sample of the original solution in an ampoule and placing the ampoule in a separate constant-temperature bath at the reaction temperature for 12-30 hr. The ampoule was then cracked and the absorbance read at reaction temperature in the spectrophotometer.

All calculations reported below which involved fitting points to a straight line were performed by least-squares analysis on an IBM 7040 computer. When necessary, standard deviations of the slope and intercept were calculated with the formulas given by Youden.¹⁹ For individual kinetic runs, the standard deviation of the slope was $\leq 2\%$. Rate constants were reproducible to $\pm 5\%$.

Results and Discussion

The spectral changes during the isomerization of *cis*- to *trans*- $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$ in acetic acid are illustrated in Figure 1 for the reaction at 76.6°. The upper curve represents the starting material (pure *cis*) and the lower curve represents the equilibrium mixture ($\sim 80\%$ *trans*, $\sim 20\%$ *cis*). The spectral differences between pure *trans* and the equilibrium mixture are quite small and the determination of accurate rate constants starting with pure *trans* is precluded. The isomerization was followed by starting with solutions of the pure *cis* compound and observing the absorbance decrease at 20.00 kK, where there is the greatest absorbance difference between *cis* and equilibrium solutions. Rate constants were determined as the slope of the plot of $\ln(A - A_\infty)$ vs. time. Equilibrium concentrations were determined for each run from A_∞ and a knowledge

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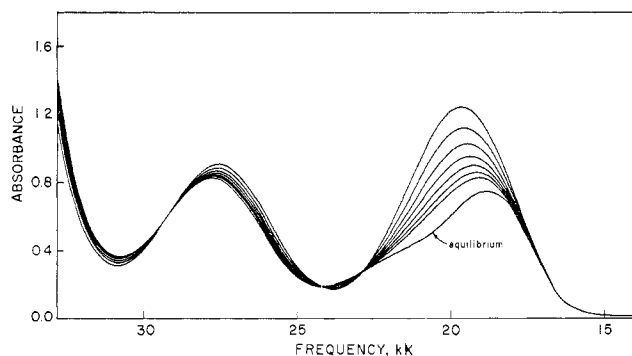


Figure 1.—Visible spectra during the isomerization of *cis*-[Co(en)₂(OAc)₂]ClO₄ in acetic acid at 76.6°. The spectra were run at 6.4-min intervals. The bottom curve is the infinite-time spectrum.

of the molar absorbances of pure *cis*- and *trans*-[Co(en)₂(OAc)₂]ClO₄ at 20.00 kK (150 and 37 M⁻¹ cm⁻¹, respectively).

There are three isosbestic points at 22.9, 24.3, and 29.1 kK. These points are invariant when acetate is added and are shifted only very slightly by temperature. Addition of excess sodium acetate to solutions of the pure *cis* and *trans* compounds at room temperature showed that acetate has no effect on any portion of the spectrum.

Effect of Acetate.—The values of the rate constants at different sodium acetate concentrations were determined at three temperatures (68.8, 76.6, and 84.5°). Some typical data are given in Table I; Figure 2 shows a plot of k_{obsd} vs. [NaOAc] at 68.8°. The concentration of the complex in all experiments was 0.01 M. The listed values of sodium acetate concentration have been corrected for the thermal expansion of acetic acid according to data from the "International Critical Tables."²⁰ The equilibrium concentrations were found to be invariant with both acetate concentration and temperature at about 80% *trans*–20% *cis*.

In order to treat the data according to (2), one refinement must be added. The ionization constant of sodium acetate has been found²¹ to be $K_i = 2.6 \times 10^{-7}$ at 25° for



in acetic acid. The free acetate ion concentration can therefore be approximated by

$$[\text{OAc}^-] = K_i^{1/2}[\text{NaOAc}]^{1/2} \quad (4)$$

Replacing Cl⁻ by OAc⁻ in (1) and incorporating (4) results in

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

Equation 5 may be rearranged⁴ to give

$$\frac{1}{k_{\text{obsd}} - k_a} = \frac{1}{(k_b - k_a) K' K_i^{1/2} [\text{NaOAc}]^{1/2}} + \frac{1}{k_b - k_a} \quad (6)$$

A plot of $(k_{\text{obsd}} - k_a)^{-1}$ vs. $[\text{NaOAc}]^{-1/2}$ should be linear with a slope of $[(k_b - k_a) K' K_i^{1/2}]^{-1}$ and an

(20) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 28.

(21) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

TABLE I
THE EFFECT OF SODIUM ACETATE CONCENTRATION ON THE RATE OF ISOMERIZATION OF 0.01 M *cis*-[Co(en)₂(OAc)₂]ClO₄ IN ACETIC ACID

| [NaOAc], M | 10 ⁴ k _{obsd} , sec ⁻¹ | [NaOAc], M | 10 ⁴ k _{obsd} , sec ⁻¹ |
|-----------------------|---|-----------------------|---|
| 68.8° | | | |
| (0.0003) ^a | 9.3 | 0.008 | 4.6 |
| (0.001) ^a | 2.6 | 0.010 | 4.2 |
| 0.002 | 2.3 | 0.023 | 3.8 |
| 0.003 | 2.0 | 0.047 | 3.6 |
| 0.006 | 1.8 | 0.094 | 3.3 |
| 0.008 | 1.7 | 0.236 | 3.3 |
| 0.010 | 1.7 | 0.472 | 3.2 |
| 0.024 | 1.5 | | |
| 0.048 | 1.4 | 84.5° | |
| 0.071 | 1.3 | (0.0003) ^a | 50–100 ^b |
| 0.095 | 1.3 | (0.001) ^a | 15.0 |
| 0.190 | 1.2 | 0.003 | 13.9 |
| 0.381 | 1.2 | 0.005 | 12.5 |
| 0.571 | 1.1 | 0.007 | 10.6 |
| | | 0.010 | 10.2 |
| 76.6° | | | |
| (0.0003) ^a | 24.0 | 0.023 | 9.1 |
| (0.001) ^a | 6.1 | 0.047 | 8.6 |
| 0.003 | 5.2 | 0.094 | 8.4 |
| 0.006 | 4.7 | 0.233 | 7.8 |
| | | 0.467 | 7.6 |

^a Estimated from K content of sample used (see Experimental Section); no NaOAc added. ^b Too rapid for accurate measurement.

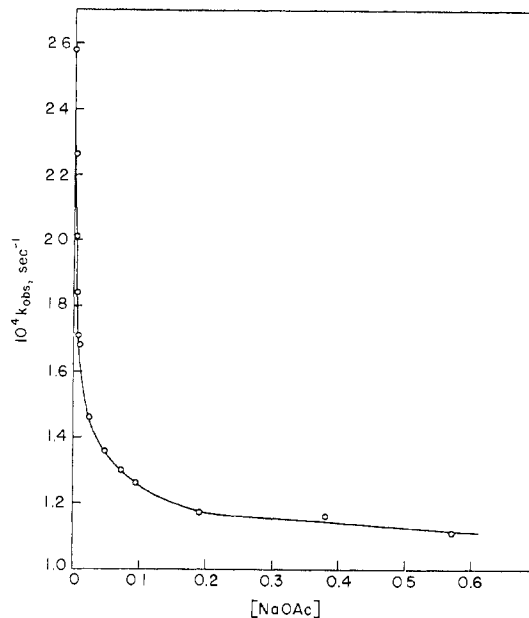


Figure 2.—The variation of the rate constant for the isomerization of *cis*-[Co(en)₂(OAc)₂]ClO₄ with sodium acetate concentration at 68.8°.

intercept of $(k_b - k_a)^{-1}$. The value of k_a cannot be obtained directly from the data due to the KOAc impurity in the compound. The acetate concentrations in parentheses in Table I are estimated from the potassium composition of the samples used. Estimates of $K' K_i^{1/2}$ and k_b can be obtained by assuming reasonable values of k_a based on extrapolation of the data. These estimates are shown in Table II for a reasonable range of k_a . The limiting rate k_b obtained is insensitive

TABLE II

| Temp, °C | ESTIMATED CONSTANTS FOR EQ 5 | | |
|-------------|--|-----------------------------------|-------------------------|
| | Range of $10^4 k_a$, sec ⁻¹ | $10^4 k_b$, sec ⁻¹ | $K'K_1^{1/2}, M^{-1/2}$ |
| 68.8 | 10-20 | 1.1 | 100-400 |
| 76.6 | 25-50 | 2.9 | 100-400 |
| 84.5 | 100-200 | 7.6 | 200-800 |

to variation of k_a . Only data for $[\text{NaOAc}] \geq 0.01 M$ were used in calculating these values.

Effect of Water.—Added water accelerated the isomerization. For 2, 4, 6 and 8 vol % of added H_2O , the rate constants at 76.6° were 6.1, 6.8, 7.7, and $8.8 \times 10^{-4} \text{ sec}^{-1}$, respectively. The increase is in part related to the increase in dielectric constant of the solvent, although at the higher amounts (4-8%) the value of A_∞ was considerably reduced (possibly a small amount of hydrolysis occurs in addition to the dielectric effect).

Sodium acetate had the same retarding effect in the presence of water. For 0.10 M NaOAc and 2, 4, 6, and 8 vol % of H_2O , the rate constants were 3.6, 3.9, 4.1, and $4.2 \times 10^{-4} \text{ sec}^{-1}$. Proll, Sutcliffe, and Walkely²² have studied the effect of water and sodium acetate on cobaltous acetate in acetic acid and found that the addition of water up to 25 vol % affected only the values of the equilibrium constants for formation of $\text{Co}(\text{OAc})_4^{2-}$. The changes were attributed solely to a dielectric effect. The presence of small amounts of water (0.1-0.2%) in the acetic acid used in the present study can therefore be expected to alter the values of the constants slightly (rate and equilibrium) relative to pure acetic acid, but not the observed phenomena. As the rate constants given above indicate, the same phenomenon of rate retardation is present when >8 vol % of H_2O is present.

Effect of Concentration.—Like acetates, perchlorates are also largely un-ionized in acetic acid. At 25° , the ionization constants of sodium and diethylanilinium perchlorates are²¹ 3.3×10^{-4} and 1.5×10^{-6} , respectively. It seems unlikely that the free ions of the *cis* and *trans* complexes are involved as in (1) but that the equilibrium is actually between perchlorate and acetate ion pairs. To determine whether a free ion is in fact involved, the rate of isomerization was studied over a 20-fold concentration range in the absence of added acetate. The results are given in Table III for 68.8° .

TABLE III
EFFECT OF CONCENTRATION ON THE RATE OF
ISOMERIZATION OF *cis*- $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$
IN ACETIC ACID AT 68.8°

| Concn, M | $10^4 k_{\text{obsd}}$, sec ⁻¹ | Concn, M | $10^4 k_{\text{obsd}}$, sec ⁻¹ |
|----------------------|---|----------------------|---|
| 1.0×10^{-2} | 2.6 | 1.0×10^{-3} | 2.8 |
| 5.0×10^{-3} | 2.5 | 5.0×10^{-4} | 2.5 |
| 2.5×10^{-3} | 2.7 | | |

Av 2.6 ± 0.1

The rate constant is unchanged by dilution. If a free ion-perchlorate ion pair equilibrium were significant, the rate constant should vary smoothly according to a rate law similar to (5). The lack of change indi-

(22) P. J. Proll, L. H. Sutcliffe, and J. Walkely, *J. Phys. Chem.*, **65**, 451 (1961).

cates that only the perchlorate ion pair, $\text{Co}(\text{en})_2(\text{OAc})_2^+ \text{ClO}_4^-$, need be considered in the absence of acetate.

Isotope Effect.—The isomerization rate was investigated in acetic acid- d_1 and $-d_4$. The results are presented in Table IV. Both the mono- and tetradeuterated solvent reduce the rate equally at 76.6° , indicating that isomerization is at least partially dependent on the ionization of the solvent.

TABLE IV

THE EFFECT OF DEUTERATION OF ACETIC ACID ON THE RATE
CONSTANT FOR ISOMERIZATION OF 0.01 M
cis- $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$

| | Temp, °C | | |
|--------------------|-------------------|------|------|
| | 68.8 | 76.6 | 84.5 |
| Acetic acid | 2.58 ^a | 6.12 | 15.0 |
| Acetic acid- d_1 | ... | 4.83 | ... |
| Acetic acid- d_4 | 1.94 | 4.63 | 9.5 |

^a Rate constants in 10^4 sec^{-1} .

Mechanism.—The above results indicate that any mechanism must involve an ion pair-ion pair equilibrium, not a free ion-ion pair equilibrium, and result in a dependence of k_{obsd} of the form of (5). The proposed mechanism is shown in Figure 3, in which the two reactive species are perchlorate and acetate ion pairs.

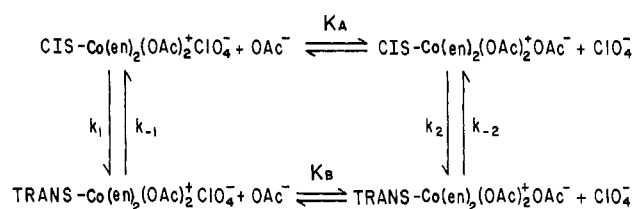


Figure 3.—Proposed mechanism for the isomerization of *cis*- $[\text{Co}(\text{en})_2(\text{OAc})_2]\text{ClO}_4$ in acetic acid.

In the derivation, it is also assumed that the constants K_A and K_B are sufficiently large that they may be approximated by

$$K_A' = \frac{K_A}{[\text{ClO}_4^-]} = \frac{[\text{cis-Co}(\text{en})_2(\text{OAc})_2^+\text{OAc}^-]}{[\text{cis-Co}(\text{en})_2(\text{OAc})_2^+\text{ClO}_4^-][\text{OAc}^-]} \quad (7a)$$

$$K_B' = \frac{K_B}{[\text{ClO}_4^-]} = \frac{[\text{trans-Co}(\text{en})_2(\text{OAc})_2^+\text{OAc}^-]}{[\text{trans-Co}(\text{en})_2(\text{OAc})_2^+\text{ClO}_4^-][\text{OAc}^-]} \quad (7b)$$

By use of eq 4, 7a, and 7b and a treatment similar to that used by Bosnich, *et al.*,⁴ for the mechanism given by (1), the derived rate law is

$$\frac{d[\text{cis}]}{dt} = \left(\frac{k_1 + k_2 K_A' K_1^{1/2} [\text{NaOAc}]^{1/2}}{1 + K_A' K_1^{1/2} [\text{NaOAc}]^{1/2}} \right) [\text{cis}] - \left(\frac{k_{-1} + k_{-2} K_B' K_1^{1/2} [\text{NaOAc}]^{1/2}}{1 + K_B' K_1^{1/2} [\text{NaOAc}]^{1/2}} \right) [\text{trans}] \quad (8)$$

where $[\text{cis}]$ and $[\text{trans}]$ are the total concentrations (the sum of the ion-pair concentrations). For a first-order equilibrium $A \rightleftharpoons B$, the observed first-order rate constant is²³ $k_{\text{obsd}} = k_f + k_r$. The first-order constant for (8) is given by

$$k_{\text{obsd}} = \frac{k_1 + k_2 K_A' K_1^{1/2} [\text{NaOAc}]^{1/2}}{1 + K_A' K_1^{1/2} [\text{NaOAc}]^{1/2}} + \frac{k_{-1} + k_{-2} K_B' K_1^{1/2} [\text{NaOAc}]^{1/2}}{1 + K_B' K_1^{1/2} [\text{NaOAc}]^{1/2}} \quad (9)$$

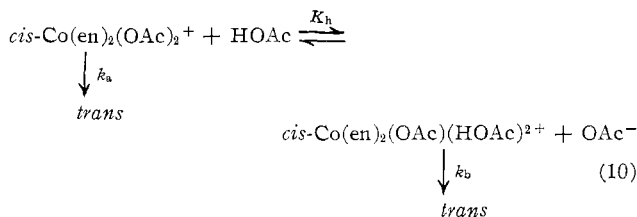
(23) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 186.

If $K_A' = K_B' = K'$, then (9) is reduced to (5) with $k_a = k_1 + k_{-1}$ and $k_b = k_2 + k_{-2}$. It has generally been found that free ion-ion pair equilibrium constants are larger for *cis* than for *trans* cations.^{2,4,7-11} However, since the equilibria involved in the mechanism of Figure 3 are of the ion pair-ion pair type, it is reasonable to assume that the constants are equal. Confirmation of this view may be derived from the lack of variation of the *cis-trans* equilibrium constant and the lack of any observable spectral change with added acetate. The exchange of acetate for perchlorate in the outer sphere does not affect the electronic structure or energetics of the inner sphere, in spite of the rather drastic rate reduction observed.

It is possible to estimate K' from the data in Table II. Under the conditions used in this study (0.1–0.2% H₂O, 68.8–84.5°), a reasonable value for $K_1^{1/2}$ would be 10^{-3} giving a range of K' over the temperature range investigated of $(1-8) \times 10^5$. Such a range of values satisfies the approximation of eq 7 (*i.e.*, for $[\text{NaOAc}] > [\text{complex}]$), then $[\text{ClO}_4^-] = [\text{complex}]$). Since the complex was kept at 0.01 *M*, then $K = K_A \simeq K_B$ is in the range 1000–8000 for the interchange of acetate for perchlorate ions.

The proposed mechanism (Figure 3) indicates that the acetate salt *cis*-[Co(en)₂(OAc)₂]OAc should isomerize with the rate constant k_b . Attempts to prepare the solid compound met with failure. However, it was possible to prepare a solution of the acetate salt by mixing equimolar quantities of KOAc and *cis*-[Co(en)₂(OAc)₂]ClO₄ in acetic acid. Insoluble KClO₄ precipitated and was removed by filtration. At 84.5°, $k_{\text{obsd}} = (7.5 \pm 0.1) \times 10^{-4} \text{ sec}^{-1}$, identical with k_b at this temperature (Table III). Further addition of NaOAc had no effect on the rate, confirming that the rate constant k_b may be identified with the acetate ion pair.

An alternate mechanism based on acid catalysis (eq 10) also results in the rate law of eq 5, the observed retardation now being explained as the suppression of solvent ionization. Mechanism 10 is consistent with



the greater reactivity observed for the protonated forms of Co(en)₂(OH)₂⁺ in water¹⁴ but inconsistent with the lower reactivity observed for solvated intermediates in nonaqueous solvents.^{7,24} The protonation of the acetate ligand might also be promoted by perchlorate by formation of more of the dissociable HClO₄ (from equilibria such as $\text{MClO}_4 + \text{HOAc} \rightleftharpoons \text{MOAc} + \text{HClO}_4$). However, no valid test was possible, since addition of

even small amounts of LiClO₄ led to precipitation of the complex. The acid-catalyzed mechanism is untenable from other observations. It is unlikely that the acetic acid complex *cis*-Co(en)₂(OAc)(HOAc)²⁺ would have exactly the same spectrum or *cis-trans* equilibrium constant as the diacetate, yet such a formulation would be necessary in view of the existence of three isosbestic points during the isomerization and the lack of variation of the equilibrium constant with acetate concentration. The ion pair-ion pair mechanism (Figure 3) is more consistent with the above observations.

The formation of a relatively unreactive acetate ion pair from the perchlorate ion pair initially present is sufficient to explain the observed retardation by acetate. The kinetic effect appears to be related to outer-sphere structure, since inner-sphere properties are the same for both ion pairs. The enthalpies of activation, $\Delta H_a^\ddagger = 26.4 \pm 0.7 \text{ kcal/mol}$ (estimated from k_{obsd} at 0.001 *M* acetate, Table I) and $\Delta H_b^\ddagger = 29.2 \pm 0.2 \text{ kcal/mol}$ (from k_b , Table II), indicate an enthalpy effect. The retardation observed when the acidic proton of acetic acid is replaced by deuterium indicates some involvement of solvent ionization (the $\text{p}K_a$ of acetic acid-*d*₄ is 5.25, while for acetic acid it is 4.75²⁵). The outer-sphere structures of the two ion pairs might differ considerably: the perchlorate ion pair contains the anion as a localized outer-sphere ligand replacing one or more solvent molecules; the acetate ion pair consists of a shell of solvent molecules minus one proton, the negative charge being delocalized over the solvent shell (outer sphere).

A consistent mechanism is that termed SN2FS, or "solvent-assisted dissociation" (SAD),²⁶ in which solvent from the solvation sphere partially enters the coordination sphere and is stabilized by hydrogen bonding. Proton transfer to the acetate ligand, which would be dependent on the ionization constant of the entering acetic acid molecule, would then leave labile acetic acid coordinated with an adjacent associated acetate ion. The dissociation of the coordinated acetic acid allows the adjacent acetate to move into the coordination sphere. The ionization properties of the entering molecule would reflect the solvent properties in the solvent sphere (containing the anion) rather than the bulk solvent. In the acetate ion pair, the delocalized negative charge would substantially reduce ionization of acetic acid in the solvent sphere by imparting a partial negative charge to an entering acetic acid causing the acetate ion pair to be less reactive, unlike the perchlorate ion pair, in which solvent molecules would be much like bulk solvent. The higher activation energy for the acetate ion pair (about 3 kcal) reflects the higher heat of ionization of negatively charged acetic acid, which would not hydrogen bond as effectively to a (partially) negatively charged carboxylato group and

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

(26) See ref 2, pp 134–135.

therefore not penetrate the coordination sphere as effectively. The delocalized nature of the acetate ion pair outer sphere may also account for the marked preference shown by the cation for acetate.

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Mechanism and Steric Course of Octahedral Aquation. XII. The Kinetics and Steric Course of Aquation of Some Isomers of the Dichloro(1,4,8,11-tetraazaundecane)cobalt(III) Cation

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The kinetics and steric course of the aquations of the isomeric *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl₂⁺ and *trans*-(*RS*)-Co(2,3,2-tet)Cl₂⁺ (2,3,2-tet = 1,4,8,11-tetraazaundecane; *R* and *S* refer to the chirality of the coordinated secondary nitrogens) in dilute acid are reported. The more labile (*RR,SS*) isomer ($k_{25} = 2.9 \times 10^{-4} \text{ sec}^{-1}$, $\Delta H^\ddagger = 25.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 12 \text{ cal deg}^{-1} \text{ mol}^{-1}$) initially forms a mixture of *trans*- and β -*cis*-(*RR,SS*)-Co(2,3,2-tet)H₂OCl₂⁺ containing $50 \pm 20\%$ of the unstable *trans* isomer which then rapidly changes to the β -*cis* form. The *trans*-(*RS*)-Co(2,3,2-tet)Cl₂⁺ cation ($k_{25} = 1.5 \times 10^{-5} \text{ sec}^{-1}$, $\Delta H^\ddagger = 24.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 1 \text{ cal deg}^{-1} \text{ mol}^{-1}$) aquates with complete retention of configuration. The mercuric ion catalyzed aquation of the *trans*-(*RR,SS*)-dichloro isomer yields initially $30 \pm 5\%$ *trans*- and $70 \pm 5\%$ β -*cis*-chloroaquo complex, whereas the analogous reaction of the *trans*-(*RS*) isomer yields 100% *trans* product. A *cis*-dichloro isomer (presumed to be β -*cis*-(*RR,SS*)-dichloro) aquates with complete retention of configuration ($k_{25} = 1.1 \times 10^{-3} \text{ sec}^{-1}$, $\Delta H^\ddagger = 22.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$). The β -*cis*-(*RR,SS*)-chloroaquo complex undergoes chloride anation in hydrochloric acid to give only the *trans*-(*RR,SS*)-dichloro complex, but in less acid solution it isomerizes at a rate inversely proportional to [H⁺], to the more stable *trans*-(*RS*) form. These reactions are discussed in connection with those of analogous complexes of the cyclic 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,7,10-tetraazadecane (trien). A dissociative mechanism is assigned in all cases and some conclusions are drawn concerning the nature of the five-coordinate intermediate.

Introduction

In the last three parts of this series²⁻⁴ the kinetics of the substitution and isomerization reactions of *trans*- and *cis*-Co(cyclam)Cl₂⁺ have been reported. In spite of the many possibilities of isomerism arising from the various combinations of the secondary nitrogens, we were only able to isolate one *trans* form and one *cis* form. In an attempt to differentiate effects arising from the use of a macrocyclic ligand from those due to the presence of secondary nitrogen atoms, we have examined the behavior of complexes of an open-chain fragment of the macrocycle 2,3,2-tet. This ligand is closely related to triethylenetetramine whose complexes of the type Co(trien)Cl₂⁺ and their aquoderivatives have been elegantly characterized and studied by Sargeson, *et al.* This work, therefore, serves as a link between the substitution reactions of the macrocyclic complex and those of the stereorestrictive trien ligands. Sargeson⁵ has pointed out the need to take account of the configurations of the secondary nitrogens and has isolated and characterized certain of the isomers and reported the kinetics and steric courses of their spontaneous and induced aquation reactions.⁶

The somewhat more flexible ligand 2,3,2-tet should allow more of the possible isomers to be isolated, and, in the case of the *trans*-Co(2,3,2-tet)Cl₂⁺ complex, Hamilton and Alexander⁷ were able to isolate and characterize both the (*RS*) (*meso*) and (*RR,SS*) (racemate) complexes. They showed that, on aquation, the *trans*-(*RS*) complex gave only *trans*-chloroaquo product, whereas the *trans*-(*RR,SS*) isomer gave the β -*cis*-chloroaquo species. They were also able to separate the *trans*-(*RS*)-chloroaquo complex, produced by the mercury(II)-catalyzed aquation of the dichloro complex, into two isomeric forms, thereby demonstrating the (*RS*) configuration. The (*RS*) form of the analogous trien complex is unknown. It is thus possible to examine the effect that the configuration of the secondary nitrogen exerts upon the kinetics and steric course of aquation of the dichloro complexes.

Experimental Section

trans-Dichloro-(*RS*)-(1,4,8,11-tetraazaundecane)cobalt(III) chloride-2.5-water was prepared by the method of Bosnich, *et al.*⁸ *Anal.* Calcd for C₁₄H₃₀Cl₂Co₂N₈O₅: C, 22.7; H, 6.8; Cl, 28.7; N, 15.1. Found: C, 23.0; H, 6.7; Cl, 28.9; N, 15.6.

cis-Dichloro-(*RR,SS*)-(1,4,8,11-tetraazaundecane)cobalt(III)

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