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# Kinetics of the Acid-catalyzed Aquation of *cis*- and *trans*-Diacetatobis-(1,2-propanediamine)cobalt(III) Cations*

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## Abstract

The aquation of both *cis*- and *trans*-Co(pn)$_2$(AcO)$_2$$^+$ is catalyzed by H$^+$, in aqueous solutions. The observed pseudo first-order rate constant, $k_{\text{obsd}}$, shows a linear dependence on [H$^+$] and there is kinetic, and in the case of the trans isomer spectrophotometric, evidence for a pre-equilibrium association of the complex cation with the proton. The kinetics obey the rate law $-\text{d}\ln[\text{complex}]/\text{d}t = \alpha Q[\text{H}^+]/1 + Q[\text{H}^+]$ (where $Q$ = the pre-equilibrium constant for protonation and $\alpha$ = the aquation rate constant for the protonated species). The *cis* diacetato cation aquates with complete retention of configuration yielding *cis*-Co(pn)$_2$(AcO)(H$_2$O)$^{2+}$. Aquation of the trans diacetato proceeds with stereochemical change to yield an equilibrium mixture of *cis*- and *trans*-Co(pn)$_2$(AcO)(H$_2$O)$^{2+}$ in the ratio 3:1, respectively. Both *cis*- and *trans*-Co(pn)$_2$(AcO(H$_2$O)$^{2+}$ isomerize to an equilibrium mixture that is 75% *cis* and 25% *trans*.

## Introduction

There are a large number of results which indicate that the aquation of diacidoaminecobalt(III) complexes involves a dissociative mechanism [1–5]. The aquation of *cis*- and *trans*-dicarboxylatobis(ethylenediamine) cations was reported to be acid-catalyzed and the kinetic results conform to a reaction mechanism involving a rapid pre-equilibrium followed by a slow rate determining-step involving the loss of the protonated carboxylate group [6, 7]. In common with Co(III) chemistry, *trans* complexes aquate with steric change, whereas a virtually complete retention of configuration is observed for *cis* isomers [6, 7].

In the present study, the acid-catalyzed aquation of *cis*- and *trans*-diacetatobis(1,2-propanediamine)cobalt(III) complexes and the isomerization of reaction products are reported. These results are discussed and compared with their ethylenediamine analogs in terms of reactivities, effects of C-methylation, protonation constants and steric effects.

## Experimental

### Materials

*Trans*- and *cis*-[Co(pn)$_2$(AcO)$_2$]ClO$_4$·H$_2$O were prepared by literature procedures [8]. *trans*-[Co(pn)$_2$(AcO)(H$_2$O)](AcO)$_2$·H$_2$O was prepared by treating 5 g of [Co(pn)$_2$CO$_3$]ClO$_4$, in 25 ml of water, with glacial acetic acid (7.5 ml). After evaporation on hot plate, acetic acid (5 ml) was added along with 95% ethanol (*ca.* 80 ml) and the solution was evaporated to dryness. The evaporation procedure was repeated five times, but the final evaporation was stopped when the volume reached 5 ml and the concentrated solution kept in the refrigerator for 5–7 days. The dark red crystals were filtered by suction, washed with absolute ethanol, followed by ether and dried under vacuum. *Anal.* Calcd for CoC$_{12}$H$_{33}$N$_4$O$_8$: Co, 14.04; C, 34.29; H, 7.86; N, 13.34. Found: Co, 13.96; C, 34.25; H, 7.27; N, 12.81. *cis*-Co(pn)$_2$(AcO)(H$_2$O)$^{2+}$ was prepared *in situ* by adding the appropriate amount of HClO$_4$ to an aqueous solution of *cis*-[Co(pn)$_2$(AcO)$_2$]ClO$_4$ at room temperature. The spectrum of this species is identical with that of the chromatographically isolated species in the first-stage aquation of *cis*-[Co(pn)$_2$(AcO)$_2$]ClO$_4$.

Electronic spectra, aquation and isomerization rates of complexes used in this study were measured with a Cary-14 recording spectrophotometer. Spectral data are collected in Table I.

### Analytical Methods

Cobalt was determined by the method of Hughes *et al.* [9]. The remaining elements were determined by M–H–W Microanalytical Laboratories, Phoenix, AZ. Chromatographic techniques were used to isolate aquation products and to check the isomeric purity of all complexes (solids and those generated in solution) [10]. Heating of *cis*-[Co(pn)$_2$(AcO)$_2$]ClO$_4$·

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*Abbreviations used: en = ethylenediamine, pn = propylenediamine = 1,2-diaminopropane, AcO = acetate.

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TABLE I. Spectral Data for Diacetato- and Acetatoaquabis(1,2-propanediamine)cobalt(III) Complexes.

| Compound | λ (nm) | ε ($M^{-1}$ $cm^{-1}$) |
|---|---|---|
| *trans*-$Co(pn)_2(AcO)_2^{+}$ [a] | 535, 460, 356 | 62.8, 35.0, 77.2 |
| *cis*-$Co(pn)_2(AcO)_2^{+}$ [a] | 507, 362 | 114.1, 85.9 |
| *trans*-$Co(pn)_2(AcO)(H_2O)^{2+}$ [b] | 538, 450, 354 | 62.2, 33.8, 78.3 |
| *cis*-$Co(pn)_2(AcO)(H_2O)^{2+}$ [b] | 494, 356 | 106.4, 80.4 |

[a] At 0 °C in water. [b] In 0.1 M $HClO_4$ at 20 °C.

$H_2O$ resulted in dehydration accompanied by isomerization to the *trans* isomer whereas the *trans*-diacetato complex was dehydrated without isomerization.

### *Kinetics*

Reactions were followed in a 5-cm quartz cell in the thermostatted cell compartment of the spectrophotometer. Temperatures below 50 °C were controlled to ±0.1 and above 50 °C to ±0.5 °C. A sample of a thermostatted aqueous solution of the complex (*ca.* $5 \times 10^{-3}$ M) was added to a $NaClO_4$–$HClO_4$ solution in the spectrophotometer cell. For *trans*-$Co(pn)_2(AcO)_2^{+}$, absorbance was measured as a function of time by scanning the 600–350 nm range at the appropriate time. For the *cis* complex, reactions with half-lives longer than 10 seconds were followed by setting the spectrophotometer to the continuous drive mode at a fixed wave length.

Pseudo-first order rate constants were evaluated from plots of log ($A_\infty - A_t$) *vs.* time, where $A_t$ and $A_\infty$ are absorbances at time t and after *ca.* 8–10 half-lives, respectively.

For reactions with half-lives shorter than 10 seconds (cis complex), a stopped-flow apparatus (Dionex-Rapid Kinetics System-Series-100) connected to an oscilloscope (Aminco-Datasar-Data Aquisition Storage and Retrieval System) was employed. Rate constants were obtained by fitting the decay trace to an exponential curve using a home-made curve-fitting device.

### *Protonation Equilibria for trans-Co(pn)$_2$(AcO)$_2$$^+$*

A thermostatted known volume of $HClO_4$-$NaClO_4$ solution was added to a concentrated aqueous solution of the *trans* complex. Absorbance at 323 nm was measured as quickly as possible.

## Results and Discussion

### *Protonation Equilibria*

When an aqueous solution of *trans*-$Co(pn)_2(AcO)_2^{+}$ was acidified, a marked increase in the absorbance, at 323 nm, was observed. The extent of this increase showed a linear dependence on $[H^+]$. Addition of $NaClO_4$ had no effect on the spectrum in the UV region. The change in absorbance is attributed to a pre-equilibrium association of the proton with the complex, as shown in eqn. 1,

$$trans\text{-}Co(pn)_2(AcO)_2^{+} + H_3O^{+} \overset{Q}{\rightleftarrows} trans\text{-}Co(pn)_2(AcO)(AcOH)^{2+} + H_2O \qquad (1)$$

where $Q$ is the protonation equilibrium constant.

Changes in absorbance were measured at three different temperatures and over a range of 0.10–2.0 M $[H^+]$, and follow the relationship

$$A - A_o/cl = \beta[H^+]/1 + Q[H^+] \qquad (2)$$

where $A$ and $A_o$ are absorbances of protonated and unprotonated complex, respectively, $c$ is total [complex], $l$ is the length of light path, $\beta$ is a constant and $Q$ is the protonation constant in eqn. 1. A plot of $cl/A - A_o$ against $1/[H^+]$ produced a straight line whose slope is $1/\beta$ and intercept is $Q/\beta$. Table V shows a collection of $Q$ values at different temperatures.

### *Aquation of trans-Co(pn)$_2$(AcO)$_2$$^+$*

Preliminary chromatographic experiments showed that this cation aquates, in acidic solutions, to yield both *cis*- and *trans*-$Co(pn)_2(AcO)(H_2O)^{2+}$. The final spectrum of the first-stage aquation, was identical to that of a mixture of *cis* and *trans* acetatoaqua cations in the ratio of 3:1, respectively. The spectrophotometric studies of the reaction showed that the loss of the second acetate is quite slow compared with either isomerization of products or the loss of the first acetate and, therefore, should not interfere with the spectra during the first-stage aquation reaction.

Acidification of a solution of the *trans* complex produces a rapid spectral change in the UV region, whose magnitude is dependent on $[H^+]$, followed by a slow change with sharp isosbestic points at 536, 438 and 411 nm. The kinetic measurements were performed in aqueous solutions over a wide range of $[H^+]$ at ionic strength, I = 2.00 M maintained with $NaClO_4$.

TABLE II. Kinetics of Aquation of *trans*-$Co(pn)_2(AcO)_2^+$.[a]

| $[H^+]$, M | $10^4\ k_{obsd}$ $(s^{-1})$[b] | | |
|---|---|---|---|
| | 40 °C | 50 °C | 59.5 °C |
| 0.100 | 1.19 ± 0.097 | 6.43 ± 0.14 | 16.4 ± 0.1 |
| 0.15 | 1.83 ± 0.20 | 8.99 ± 0.93 | 25.5 ± 0.1 |
| 0.18 | 2.12 ± 0.09 | 11.3 ± 0.1 | 30.2 ± 0.5 |
| 0.20 | 2.53 ± 0.22 | 12.7 ± 0.1 | 33.0 ± 0.1 |
| 0.40 | 3.66 ± 0.42 | 20.7 ± 0.3 | 61.8 ± 0.3 |
| 0.50 | 4.58 ± 0.01 | 21.7 ± 0.1 | 73.7 ± 0.5 |
| 0.80 | 5.55 ± 0.04 | 35.9 ± 0.1 | 73.5 ± 0.5 |
| 1.00 | 7.87 ± 0.01 | | |

[a] [complex] = $5.5 \times 10^{-3}$ M: I = 2.0 M maintained with $NaClO_4$. [b] Each entry is the average of three measurements.

A summary of the kinetic results for aquation of *trans*-$Co(pn)_2(AcO)_2^+$ is shown in Table II. It can be seen that the reaction is catalyzed by acid and the observed rate constant, $k_{obsd}$, has a first-order dependence on $[H^+]$, over the concentration range covered. Less than first-order dependence was observed at all higher acid concentrations. The acid dependence is described by the relationship

$$k_{obsd} = \frac{\alpha Q[H^+]}{1 + Q[H^+]} \qquad (3)$$

and the values of $\alpha$ and $Q$, shown in Table V, were obtained by a weighted-least squares fitting of data in Table II to eqn. 3.

The ratio of *cis*- to *trans*-$Co(pn)_2(AcO)(H_2O)^{2+}$ produced in the aquation reaction was determined by examining the spectral scans in the 550–400 nm range for *ca.* one half-life. This ratio was calculated from the experimental spectra using the known values of the absorption coefficients of the starting material and the two acetatoaqua isomers*.

### *Aquation of cis-$Co(pn)_2(AcO)_2^+$*

The chromatographic and spectrophotometric studies showed that this cation aquates with complete retention of configuration yielding only *cis*-$Co(pn)_2(AcO)(H_2O)^{2+}$. Rate constants are collected in Table III and it can be seen that the first-order dependence of $k_{obsd}$ on $[H^+]$ obeys eqn. 3 for $[H^+]$ up to 1.00 M. At all higher acid concentrations however, a less than first-order dependence was observed. Values of $\alpha$ and $Q$ are collected in Table V.

TABLE III. Kinetics of Aquation of *cis*-$Co(pn)_2(AcO)_2^+$.[a]

| $[H^+]$, M | $10^2\ k_{obsd}$ $(s^{-1})$[b] | | |
|---|---|---|---|
| | 15 °C | 20 °C | 25 °C |
| 0.010 | 2.30 ± 0.10 | 3.10 ± 0.10 | 3.90 ± 0.10 |
| 0.020 | 3.70 ± 0.10 | 5.10 ± 0.01 | 6.70 ± 0.50 |
| 0.030 | 4.50 ± 0.20 | 6.30 ± 0.10 | 8.10 ± 0.01 |
| 0.040 | 5.20 ± 0.22 | 7.10 ± 0.40 | 9.40 ± 0.80 |
| 0.050 | 6.30 ± 0.04 | 8.50 ± 0.05 | 11.4 ± 0.1 |
| 0.080 | 6.80 ± 0.30 | 9.80 ± 0.11 | 12.3 ± 0.1 |
| 0.100 | 7.04[c] | 10.4[c] | 13.4 ± 0.5 |
| 0.200 | | | 14.5[c] |
| 0.400 | | | 15.5[c] |
| 0.600 | | | 15.85[c] |
| 0.800 | | | 16.0[c] |
| 1.00 | | | 17.8 ± 1.7 |
| 1.50 | | | 17.7 ± 0.8 |
| 2.00 | | | 17.6 ± 0.4 |

[a] [complex] = $5.63 \times 10^{-3}$ M. I = 2.00 M adjusted with $NaClO_4$. [b] Each entry is the average of three measurements. [c] Single Measurement.

### *The Isomerization of cis- and trans-$Co(pn)_2(AcO)(H_2O)^{2+}$ Cation*

The spectrum of acidified solutions of *trans*-$Co(pn)_2(AcO)(H_2O)^{2+}$ changed with time with isosbestic points at 539, 440 and 407 nm. The equilibrium constant was found to be independent of temperature in the range 30–50°C. A solution of known concentration of the desired acetatoaqua complex that had been brought to the desired temperature was added to a thermostatted solution of $HClO_4$–$NaClO_4$ in the spectrophotometric cell and absorbance at 494 nm was measured as a function of time. The composition of the equilibrium mixture (74.6% *cis* and 25.4% *trans*) was constant at all temperatures and independent of whether the starting complex was *cis* or *trans*. The approach to equilibrium ($k_1 + k_{-1}$) is first order in [complex] and is also independent of the starting acetatoaqua complex. Table IV shows the kinetic parameters for the isomerization process.

The two previous studies [6, 7] on the acid catalyzed aquation *cis*- and *trans*-$Co(en)_2(AcO)_2^+$ cations showed that these reactions proceed by a rapid pre-equilibrium followed by a slow aquation of the protonated species. Dasgupta and Tobe [6] found that the *cis* aquated with retention of configuration whereas the trans isomer gave 75% *cis*- and 25% *trans* acetatoaqua products. These authors assigned a dissociative mechanism involving Co–O bond breaking to both isomers. The assignment was considered tentative in the *cis* case because the stereochemical result did not distinguish between Co–O and C–O bond fission. More recently, Haim *et al.* [7] carried out oxygen-18 tracer studies

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*Computation was performed using a FORTRAN IV program written by L. C. Cusachs, Tulane University, 1965.

TABLE IV. Rate Constants for the Isomerization Reaction[a] *trans*-$Co(pn)_2(AcO)(H_2O)^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ *cis*-$Co(pn)_2(AcO)(H_2O)^{2+}$.

| $[H^+]$, M | °C | $10^3\ (k_1 + k_{-1})\ (s^{-1})$ | % *cis* | $10^3 k_1{}^b$, $s^{-1}$ | $10^3 k_{-1}{}^b$, $s^{-1}$ |
|---|---|---|---|---|---|
| starting with *trans*-$Co(pn)_2(AcO)(H_2O)^{2+}$ | | | | | |
| 1.00 | 30.0 | 0.09 ± 0.01 | 74.3 ± 2.1 | 0.03 | 0.01 |
| 1.00 | 40.0 | 0.32 ± 0.01 | 74.1 ± 1.1 | 0.24 | 0.08 |
| 1.00 | 50.0 | 1.06 ± 0.02 | 74.1 ± 2.9 | 0.79 | 0.27 |
| starting with *cis*-$Co(pn)_2(AcO)(H_2O)^{2+}$ | | | | | |
| 1.00 | 30.0 | 0.09 ± 0.01 | 75.1 ± 3.4 | 0.07 | 0.02 |
| 1.00 | 40.0 | 0.31 ± 0.01 | 74.8 ± 2.5 | 0.23 | 0.08 |
| 1.00 | 50.0 | 0.97 ± 0.02 | 75.1 ± 3.0 | 0.72 | 0.25 |

[a] Measurements made at 494 nm; I = 2.00 M adjusted with $NaClO_4$. [b] Calculated using an average value of $K_{isom}$ = 2.94. $\Delta H^\ddagger$ = 105 ± 3 kJ $mol^{-1}$; $\Delta S^\ddagger$ = 14.0 ± 1.8 $JK^{-1}$ $mol^{-1}$.

TABLE V. Equilibrium and Kinetic Parameters for Protonation and Aquation of *cis*- and *trans*-$Co(AA)_2(AcO)_2{}^+$ Complexes.[a]

| °C | AA | $Q\ (M^{-1})^b$ | $10^3\ \alpha\ (s^{-1})^b$ |
|---|---|---|---|
| *cis*-$Co(pn)_2(AcO)_2{}^+$ | | | |
| 15.0 | pn | 31.5 ± 0.5 | 95.8 ± 4 |
| 20.0 | pn | 32.2 ± 0.9 | 129 ± 2 |
| 25.0 | pn | 43.7 ± 0.4 | 166 ± 4 |
| 25.0 | en | 5.2[c] | 79[c] |
| $\Delta H^\circ$ = 5.69 ± 0.05 kJ $mol^{-1}$; $\Delta S^\circ$ = –10.4 ± 0.2 $JK^{-1}$ $mol^{-1}$ | | | |
| $\Delta H^\ddagger$ = 37.6 ± 0.5 kJ $mol^{-1}$; $\Delta S^\ddagger$ = –161 ± 2 $JK^{-1}$ $mol^{-1}$ | | | |
| *trans*-$Co(pn)_2(AcO)^{2+}$ | | | |
| 30.0 | pn | (0.95)[d] | |
| 40.0 | pn | 1.09 ± 0.07 (1.06) | 1.29 ± 0.11 |
| 39.0 | en | 1.05[e] | 1.03[e] |
| 50.0 | pn | 1.21 ± 0.05 (1.20) | 6.06 ± 0.59 |
| 59.5 | pn | 1.53 ± 0.03 | 15.6 ± 1.9 |
| $\Delta H^\circ$ = 9.12 ± 0.06 (8.74 ± 0.84) kJ $mol^{-1}$; | | | |
| $\Delta S^\circ$ = 29.8 ± 0.8 (28.7 ± 2.68) $JK^{-1}$ $mol^{-1}$; | | | |
| $\Delta H^\ddagger$ = 94.8 ± 1.1 kJ $mol^{-1}$; $\Delta S^\ddagger$ = –6.07 ± 3.31 $JK^{-1}$ $mol^{-1}$ | | | |

[a] Ionic strength 2.00 M maintained with $NaClO_4$. [b] Defined by eqn. 3. [c] Table VII in ref. 7. [d] Values in parentheses are from spectrophotometric measurements. [e] Ref. 6.

on the *cis* complex which showed conclusively that it also proceeds by Co–O bond breaking. In addition, the calculations made by the latter authors for the rate of formation of $Co(NH_3)_5(AcO)_2{}^{2+}$ suggests that the Co–O rather than C–O bond breaking [11, 12] should also be the preferred bond rupture mode in this case.

Even though the two above aquation studies were carried out at different ionic strengths two common features of *cis* isomers emerged. *Cis* isomers have: (1) larger protonation equilibrium constants and (2) much faster aquation rates than the *trans* isomers. Our results in the present study are consistent with those in the two previous studies and are described by the rate law in eqn. 3. These acid catalyzed aquations of both pn isomers involve a rapid pre-equilibrium followed by the rate determining step.

$$Co(pn)_2(AcO)_2{}^+ + H_3O^+ \overset{K}{\rightleftharpoons} Co(pn)_2(AcO)(AcOH)^{2+} + H_2O$$

$$Co(pn)_2(AcO)(AcOH)^{2+} + H_2O \xrightarrow{k} Co(pn)_2(AcO)(H_2O)^{2+} + AcOH$$

Accordingly, the observed pseudo first-order rate constant, $k_{obsd}$, given in eqn. 3 with $k = Q$ and $k = \alpha$, reflects the observed dependence on $[H^+]$.

Earlier studies [13–15] on the first-stage aquation of *cis*- and *trans*-$Co(AA)_2Cl_2{}^+$ (where AA = en or pn) showed that C-methylation increases the rate. The ratios of rate constants for a given isomer in the two systems, $k_{pn}/k_{en}$, are 1.7 and 1.8 for *cis* and *trans* isomers, respectively. The ratios of rate constants for the two isomers of a given system, $k_c/k_t$, are 6.8 for en and 6.6 for pn. Our results in the present system and those in the two prior aquation studies on *cis*- and *trans*-$Co(en)_2(AcO)_2{}^+$ show that $k_c/k_t$ is approximately 300. This large difference in aquation reactivity, which is atypical of Co(III) diacidodiamine isomers, was attributed to an increase in basicity caused by a 'special effect' in the case of the *cis* isomers [7]. Protonation of $Co(NH_3)_5(AcO)^{2+}$

TABLE VI. Activation Parameters for Aquation of $Co(AA)_2(AcO)(AcOH)^{2+}$ Complexes (AA = en, pn).[a]

| Complex | $\Delta H^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta S^{\ddagger}$ (JK$^{-1}$ mol$^{-1}$) | $\Delta H^{\circ}$ (kJ mol$^{-1}$) | $\Delta S^{\circ}$ (JK$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|
| *cis*-pn[b] | 37.6 | −161 | 5.69 | −10.4 |
| *cis*-en[c] | 64.4 | −54.4 | 7.11 | 37.7 |
| *trans*-pn[b] | 94.8 | −6.07 | 9.12 | 29.8 |
| *trans*-en[c] | 96.2 | 4.18 | 15.1 | 48.1 |

[a] Ionic strength 2.00 M maintained with $NaClO_4$. [b] This work. [c] Calculated for 40 °C from data in ref. 6.

and *trans*-$Co(en)_2(AcO)_2^+$ occurs at a single oxygen atom bound to the metal atom. In contrast, the geometry of the *cis* isomer permits the proton to be bound to two different oxygen atoms (one in each of the acetate ligands). The resulting protonated species is a hydrogen bonded ring structure which accounts for the higher basicity in the *cis* case.

A dissociative mechanism predicts that steric crowding resulting from C-methylation would cause aquation rates to be greater in our pn system than the en analog. Furthermore, in the *cis* pn case the electron donating power of the methyl group should lead to an increase in basicity and therefore, enhance the special effects. Table V includes data for the en system from the two previous studies [6, 7] where temperature and ionic strength give the closest match to the experimental conditions employed in the present study. It is seen that both equilibrium and aquation rate data are very similar for the *trans* en and pn isomers [17]. A comparison of $Q$ and $\alpha$ for the *cis* isomers shows that both constants are significantly larger for the pn diacetato complex. This difference, which occurs at the same ionic strength, is far too large to attribute to medium effects ($LiClO_4$ *vs.* $NaClO_4$). These results for the acid catalyzed aquation of *cis* pn is supportive of a protonated species stabilized by hydrogen bonding, *i.e.* the 'special effect'. Table VI shows that both activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, are more positive for *trans*-$Co(AA)_2(AcO)_2^+$ than the *cis* isomers. This behavior is diagnostic of a dissociative type mechanism, where high values are associated with stereochemical change and low values are indicative of retention of configuration [16]. Furthermore, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are both more positive for a given en isomer than its pn analog. The small differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ between *trans* en and pn (1.4 kJ mol$^{-1}$ and 10.3 JK$^{-1}$) are in accord with their similar rate behavior. On the other hand, differences for *cis* complexes are considerably larger, ($\Delta\Delta H^{\ddagger} = 26.8$ kJ mol$^{-1}$ and $\Delta\Delta S = 107$ JK$^{-1}$ mol$^{-1}$) and reflect the increased reactivity of the *cis* pn complex. Similarly, differences in $\Delta H^{\circ}$ and $\Delta S^{\circ}$ (*ca.* 6.0 and 18 for *trans* and 1.4 and 48 again respectively, for *cis*) follow the same pattern.

The isomerization rate for an aqua complex of the type $Co(en)_2A(H_2O)^{n+}$ is often similar to the rate of aquation of the parent chloro complex $Co(en)_2ACl^{(n-1)+}$ suggesting that the two reactions are mechanistically similar [17]. In this study, *cis* ⇌ *trans* isomerization of $Co(pn)_2(AcO)(H_2O)^{2+}$ produced an equilibrium mixture containing 74.6% *cis* and 25.4% *trans*. The rates, shown in Table IV, are quite similar to those for the aquation of the *trans*-$Co(pn)_2(AcO)_2^+$ cation. The observed aquation rate constant at 40 °C for *trans* diacetato = $7.87 \times 10^{-4}$ s$^{-1}$ and $k_{isom} = 3.1 \times 10^{-4}$ s$^{-1}$.

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