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Cobalt-59 Nuclear Magnetic Resonance Study of Isomerization Reactions of *mer-* and *fac*-Co(en)(NH₃)₃OH²⁺ Ions and *trans-, cis,trans-,* and *cis,cis*-Co(en)(NH₃)₂(OH)₂⁺ Ions

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Cobalt-59 nmr has been successfully used to study isomerization reactions of $Co(en)(NH_3)_3OH^{2+}$, $Co(en)(NH_3)_2(OH)_2^+$, $Co(en)_2NH_3OH^{2+}$, and $Co(en)_2(OH)_2^+$ ions. The isomerization rate constants and equilibrium constants for these complexes have been determined by using intensities of ⁵⁹Co nmr signals. Each of the three isomers of the $Co(en)(NH_3)_2(OH)_2^+$ ion shows a characteristic reaction path for isomerization. Namely, *trans*-dihydroxodiammine (trans) ion and *cis*-dihydroxo-*trans*-diammine (cis,trans) ion isomerize to *cis*-dihydroxo-*cis*-diammine (cis,cis) ion, and the cis,cis ion rearranges to give the trans ion. These results are used to discuss possible isomerization mechanisms for $Co(en)(NH_3)_2(OH)_2^+$ ion. No isomerization between *mer-* and *fac*-Co(en)(NH₃)₃OH²⁺ ions is observed in the temperature range from 25.0 to 80.0°. The results for $Co(en)_2NH_3OH^{2+}$ and $Co(en)_2(OH)_2^+$ ions obtained at relatively high concentrations of the complexes are compared with those obtained by several workers spectrophotometrically in dilute solutions.

Introduction

The cis–trans isomerizations of $Co(en)_2NH_3OH^{2+}$ and $Co(en)_2(OH)_2^+$ ions have been widely investigated using spectrophotometry.[1-4] However, no data have been reported for the isomerization of mono(ethylenediamine)–hydroxo complexes such as *mer-* and *fac-* Co(en)(NH₃)₃OH²⁺ ions, and *trans-, cis,cis-,* and *cis,trans*-Co(en)(NH₃)₂(OH)₂⁺ ions. In the present study ⁵⁹Co nmr was measured to obtain concentration equilibrium quotients and isomerization rate constants for the above mono(ethylenediamine)–hydroxo complexes along with bis(ethylenediamine)–hydroxo complexes. The kinetic and equilibrium data are discussed in terms of the inter- and intramolecular mechanisms which have been proposed for the isomerization of bis-(ethylenediamine)–hydroxo complexes on the basis of ¹⁸O-labeled experiments.[3,4]

The rate constants and equilibrium constants obtained from ⁵⁹Co nmr in highly concentrated solutions are compared with those obtained from spectrophotometry and titrimetry in dilute solutions.

Experimental Section

Materials.—*cis-* and *trans*-[Co(en)₂NH₃H₂O] Br₃ were prepared from *cis*-[Co(en)₂NH₃Br] Br₂[5] and purified by recrystallization. The cis isomer was obtained of 100% purity, whereas the trans isomer contained about 5% of the cis isomer.[6] *cis-* and *trans*-[Co(en)₂(H₂O)₂] (NO₃)₃ were prepared by using the methods of Werner[7] and of Bjerrum,[1] respectively. *fac-* and *mer*-[Co(en)-(NH₃)₃H₂O] (NO₃)₃ were prepared from *trans*-[Co(en)(NH₃)₂Br₂] Br as follows. Eight grams of *trans*-[Co(en)(NH₃)₂Br₂] Br was dissolved in 12 ml of 10% aqueous ammonia. The solution was heated in a flask loosely stoppered, at 60 ± 1° for 10 min. After the excess ammonia was eliminated by bubbling air through the solution (until pH of the solution became below 8.5), 10 g of AgNO₃ was added to the solution cooled in an ice bath. The precipitated AgBr was sufficiently ground in the solution and was filtered off. When the filtrate was allowed to stand in a refrigerator, [Co(en)(NH₃)₃OH] [Co(en)(NH₃)₃H₂O] (NO₃)₅ which con-

tained 90% of the fac and 10% of the mer isomer was crystallized, yield 1.7 g (25%). This crystalline product was dissolved in a small quantity of water. By adding concentrated HNO₃ in the solution cooled in an ice bath, almost pure *fac*-[Co(en)(NH₃)₃-H₂O] (NO₃)₃ was obtained. The mer isomer was obtained from the washings of the AgBr precipitate. The precipitate was extracted with 5 ml of water three times. When the extracts were allowed to stand in a refrigerator, *mer*-[Co(en)(NH₃)₃OH] [Co-(en)(NH₃)₃H₂O] (NO₃)₅ was obtained, yield 1.6 g (23%). This crystalline product contained 80% of the mer and 20% of the fac isomers. This crystalline product was dissolved in a small quantity of water. By adding concentrated HNO₃ in the solution cooled in an ice bath, *mer*-[Co(en)(NH₃)₃H₂O] (NO₃)₃ was obtained. *trans*-[Co(en)(NH₃)₂Br₂] Br, *trans*-[Co(en)(NH₃)₂Cl₂] Cl· ¹/₂H₂O, and *cis,trans*-[Co(en)(NH₃)₂Cl₂] Cl·H₂O were prepared by using the method of Bailar and Peppard.[8]

Anal. Calcd for *mer*-[Co(en)(NH₃)₃OH] [Co(en)(NH₃)₃H₂O]-(NO₃)₅: Co, 17.20; C, 7.01; H, 5.45; N, 30.66. Found: Co, 17.02; C, 6.97; H, 5.74; N, 30.82. Calcd for *fac*-[Co(en)(NH₃)₃-OH] [Co(en)(NH₃)₃H₂O] (NO₃)₅: Co, 17.20; C, 7.01; H, 5.45; N, 30.66. Found: Co, 17.05; C, 7.05; H, 5.69; N, 30.50. Calcd for *mer*-[Co(en)(NH₃)₃H₂O] (NO₃)₃: Co, 15.75; C, 6.42; H, 5.13; N, 29.95. Found: Co, 15.51; C, 6.56; H, 5.11; N, 29.69. Calcd for *fac*-[Co(en)(NH₃)₃H₂O] (NO₃)₃: Co, 15.75; C, 6.42; H, 5.13; N, 29.95. Found: Co, 15.49; C, 6.50; H, 5.09; N, 29.85.

Nmr Measurements.—Cobalt-59 nmr measurements were made at 25.0° with the use of a JEOL LMN-WB-20 spectrometer operating at 13.5550 MHz. Chemical shifts were measured in aqueous solutions containing a trace amount of $Co(NH_3)_6^{3+}$ ion as an internal standard. Line widths were obtained as the peak-to-peak interval of the first derivative of absorption signals with a small amplitude of modulation at a frequency of 35 Hz. The observed ⁵⁹Co line shape was very well approximated by a Lorentzian, if the amplitude of modulation was kept less than one-third of the line width. When the signals are separated sufficiently from each other, the relative intensity of each spectrum was given simply by (peak-to-peak height) × (peak-to-peak interval)². The relative intensities for *cis-* and *trans*-Co(en)₂-NH₃OH²⁺ ions and for *trans-* and *cis,cis*-Co(en)(NH₃)₂(OH)₂⁺ ions were determined in this way. However, the signals of *cis-* and *trans*-Co(en)₂(OH)₂⁺ ions overlapped significantly with each other. The line widths and relative intensities of these signals were determined by spectrum simulation. The simulation was performed for two Lorentzians with five adjustable parameters, *i.e.*, line widths, chemical shifts, and the ratio of populations for two isomers. Calculations were carried out on a HITAC 5020E computer at the University of Tokyo.[9] The intensity ratios for *cis,trans*-Co(en)(NH₃)₂(OH)₂⁺ ion and *cis,cis*-Co(en)(NH₃)₂-(OH)₂⁺ ion were determined in the same way.

Chemical shift and line width data are summarized in Table I

(1) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(2) J. Y. Tong and P. E. Yankwich, *J. Amer. Chem. Soc.*, **80**, 2664 (1958).

(3) W. Kruse and H. Taube, *ibid.*, **83**, 1280 (1961).

(4) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

(5) H. F. Holtzclaw, Jr., *Inorg. Syn.*, **8**, 200 (1966).

(6) Throughout the present work, identification and determination of the ratio of complex ions in solutions were made with the use of ⁵⁹Co nmr.

(7) A. Werner and G. Jantsch, *Ber.*, **40**, 268 (1907); A. Werner, *ibid.*, **40**, 2119 (1907).

(8) J. C. Bailar and D. F. Peppard, *J. Amer. Chem. Soc.*, **62**, 105 (1940).

(9) The simulation program was coded by H. Ozawa.

TABLE I

CHEMICAL SHIFTS AND LINE WIDTHS FOR MONO- AND
BIS(ETHYLENEDIAMINE)–HYDROXO–COBALT COMPLEXES

Complex	Chemical shift,[a] ppm	Line width, G
cis-Co(en)$_2$NH$_3$OH^{2+}	−220	0.29
trans-Co(en)$_2$NH$_3$OH^{2+}	−110	0.18
cis-Co(en)$_2$(OH)$_2$$^+$	−1150	0.23
trans-Co(en)$_2$(OH)$_2$$^+$	−1130	0.15
fac-Co(en)(NH$_3$)$_3$OH^{2+}	−560	0.18
mer-Co(en)(NH$_3$)$_3$OH^{2+}	−635	0.43
trans-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$	−1580	0.23
cis,trans-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$	−1660	0.59
cis,cis-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$	−1670	0.23

[a] Co(NH$_3$)$_6$$^{3+}$ ion is taken as a standard for the chemical shift.

and are used to identify complex ions that exist in solutions studied.

Preparation of the Solutions for the Kinetic Study.—All solutions for the kinetic study were prepared at 25.0° and were sealed in glass tubes for nmr measurements. Solutions of cis- and trans-Co(en)$_2$(OH)$_2$$^+$ ions were prepared by dissolving a weighed amount of [Co(en)$_2$(H$_2$O)$_2$](NO$_3$)$_3$ in 2 M NaOH stock solution (concentration of the complex is 0.50 M).[10] Solutions of cis- and trans-Co(en)$_2$NH$_3$OH^{2+} and of mer- and fac-Co(en)(NH$_3$)$_3$OH^{2+} ions were prepared by dissolving the corresponding aquo complexes in NaOH solution. The pH's of the solutions were adjusted at about 11 with HNO$_3$ or HBr, because Co(en)$_2$NH$_3$OH^{2+} and Co(en)(NH$_3$)$_3$OH^{2+} ions were hydrolyzed to yield dihydroxo ions in the presence of a large excess of OH$^-$ ion. At this pH, no dihydroxo ions were detected after equilibrium was reached. Solutions of Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ion were prepared by dissolving corresponding dichloro or dibromo complexes in NaOH solutions, because the isolation of [Co(en)(NH$_3$)$_2$(H$_2$O)$_2$]X$_3$ was unsuccessful. The pH's of the solutions were adjusted at 10.30 with HCl in order to suppress the decomposition of the dihydroxo ion.

Analysis of Data.—The relative intensity of an isomer, x_t, was measured at given time intervals. The intensity at equilibrium, x_e, was measured at a time equivalent to about 10 half-lives. That the plot of ln $|x_e − x_t|$ vs. time is linear indicates that the isomerization is first order with respect to the isomer concentration even at high concentrations of complex ions. The first-order rate constant, k_1, is given by

$$\ln |x_e − x_t| − \ln |x_e − x_0| = k_1 t/(x_e − 1) \quad (1)$$

In the case of Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ion, three isomers take part in the isomerization. The rate equations for this system are given by

$$\mathrm{d}a/\mathrm{d}t = k_1 b + k_3 c − k_{−1} a$$
$$\mathrm{d}b/\mathrm{d}t = k_{−1} a + k_2 c − k_1 b \quad (2)$$
$$\mathrm{d}c/\mathrm{d}t = − (k_2 + k_3)c$$

where k_1, $k_{−1}$, k_2, and k_3 were the isomerization rate constants (see Figure 1), and a, b, and c were the mole fractions of trans, cis,cis, and cis,trans isomers, respectively. The rate constants, k_1 and $k_{−1}$, were determined from the isomerization between trans- and cis,cis-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ions. By giving a trial set of values of k_2 and k_3, with initial conditions a_0, b_0, and c_0, and the rate constants k_1 and $k_{−1}$, simultaneous differential equations (2) were numerically integrated. The initial values for k_2 and k_3 were adjusted iteratively to reach an optimum agreement between the observed and the calculated populations of each isomer. The iterative calculations were carried out on a HITAC 5020E computer at the University of Tokyo. A modified version of library program D2/HC/DMLN was used for the numerical integration of differential equations by the Milne method.

Equilibrium Quotient.—Concentration equilibrium quotients for isomerization were obtained by using relative intensities of ^{59}Co nmr signals. The concentration dependence of equilibrium
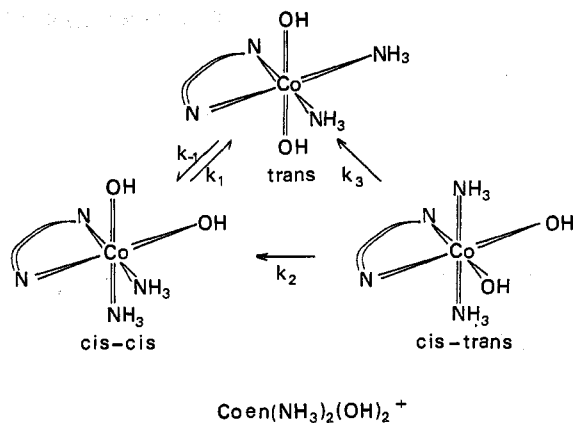

Co en(NH$_3$)$_2$(OH)$_2$$^+$

Figure 1.—The isomerization scheme for three isomers of the Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ion.

B   **A**
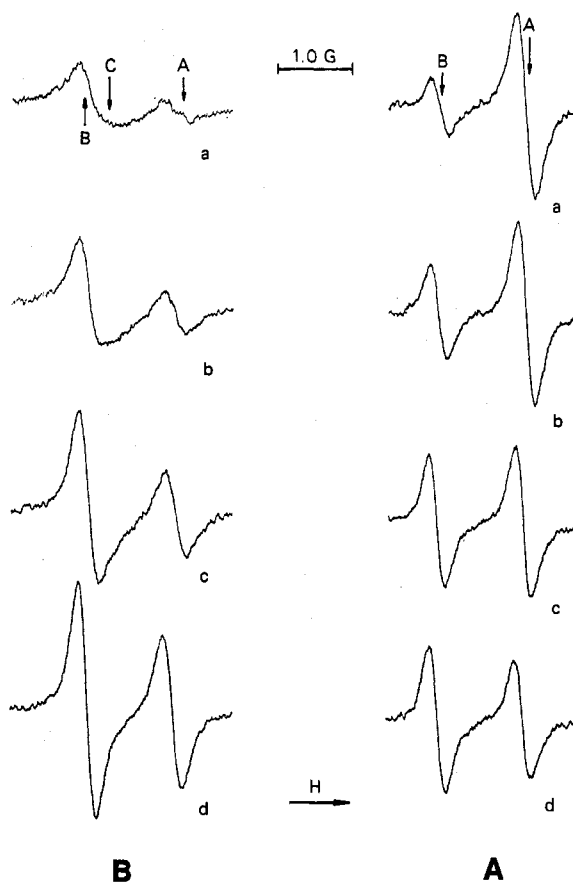
Figure 2.—Time variation of ^{59}Co nmr spectra of (A) trans- and cis,cis-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ions (a) after 1 hr, (b) after 3 hr, (c) after 7 hr, and (d) after 48 hr; (B) cis,trans-, cis,cis-, and trans-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ions (a) after 2 hr, (b) after 7 hr, (c) after 20 hr, and (d) after 48 hr. A, trans isomer; B, cis,cis isomer; C, cis,trans isomer.

quotients was examined for Co(en)$_2$(OH)$_2$$^+$ ion in the concentration range 0.1–0.8 M.

Results and Discussion

Co(en)(NH$_3$)$_3$OH^{2+} Ion.—The ^{59}Co nmr spectra of mer- and fac-Co(en)(NH$_3$)$_3$OH^{2+} ions in solution do not change when the solutions are allowed to stand for 90 days at 25.0° or are heated at 80.0° for 30 min. When the solution is heated above 80.0°, decomposition of the ions occurs to give a precipitate. These results clearly show that isomerization does not occur between

(10) In the present experiments where the concentration of complexes was quite high, it was impossible to adjust the ionic strength by merely adding an inert electrolyte. Since the isomerization does not affect the charge and concentration of complex ions in solution, the ionic strength may not change a great deal during the cis–trans isomerization.

mer- and *fac*-Co(en)(NH$_3$)$_3$OH^{2+} ions. It should be noted that a similar type of complexes, *cis-* and *trans*-Co(en)$_2$NH$_3$OH^{2+} ions, isomerizes at 25.0° to yield an equilibrium mixture after 1 week.

Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ Ion.—Nmr spectra of Co(en)-(NH$_3$)$_2$(OH)$_2$$^+$ ion are shown in Figures 2a and 2b. Figure 2a shows that *trans*-[Co(en)(NH$_3$)$_2$Cl$_2$]Cl· $^1/_2$H$_2$O in 2 *M* NaOH solution gives a mixture of 80% of *trans-* and 20% of *cis,cis*-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ions (concentration of the complex ion is 0.5 *M*). In contrast to this, a large amount of *cis,trans*-Co(en)(NH$_3$)$_2$-(OH)$_2$$^+$ ion forms on dissolving *cis,trans*-[Co(en)-(NH$_3$)$_2$Cl$_2$]Cl in 2 *M* NaOH solution (Figure 2b).[11,12] The isomerization rate constants between the trans and cis,cis isomers and the equilibrium quotient are obtained from the data shown in Figure 2a. Figure 2a indicates that neither the trans nor the cis,cis isomer rearranges to the cis,trans isomer and that the equilibrium mixture consists of the trans and cis,cis isomers. No signal of the cis,trans isomer is detected after equilibrium is reached. The rate constants k_1 and k_{-1} and the concentration equilibrium quotient are listed in Table II. The rate constants for isomerization from

TABLE II
ISOMERIZATION RATE CONSTANTS AND
EQUILIBRIUM QUOTIENTS (25.0°)

Reaction	$10^6 k$, sec^{-1}	K
trans-Co(en)$_2$NH$_3$OH^{2+} → *cis*-	4.3	
cis,cis-Co(en)$_2$NH$_3$OH^{2+} → *trans*-	1.7	2.5^a
trans-Co(en)$_2$(OH)$_2$$^+$ → *cis*-	1.8	
cis-Co(en)$_2$(OH)$_2$$^+$ → *trans*-	3.6	0.52^a
mer-Co(en)(NH$_3$)$_3$OH^{2+} → *fac*-		
fac-Co(en)(NH$_3$)$_3$OH^{2+} → *mer*-		No isomerizn
trans-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ → *cis,cis*-	35	
cis,cis-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ → *trans*-	43	1.21^b
cis,trans-Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ → *cis,cis*-	10	

^{a} K = (cis)/(trans). ^{b} K = (cis,cis)/(trans).

the cis,trans to the other two isomers can be obtained from the data shown in Figure 2b. The calculated and experimental populations for the three isomers are shown in Figure 3. The rate constants for isomerization from the cis,trans to cis,cis, k_2, and from cis,trans to trans, k_3, are estimated at $(1.0 \pm 0.05) \times 10^{-5}$ sec^{-1} and 0.0 sec^{-1}, respectively. These rate constants indicate that the cis,trans isomer isomerizes to yield the cis,cis isomer and does not directly produce the trans isomer. The above results may be used to obtain information about the isomerization mechanism of Co-(en)(NH$_3$)$_2$(OH)$_2$$^+$ ion. Two mechanisms have been proposed[3,4] for the isomerization of bis(ethylenediamine)-hydroxo complexes, Co(en)$_2$(OH)$_2$$^+$ and Co-(en)$_2$NH$_3$OH^{2+} ions; one is based on ligand exchange between the coordinated OH$^-$ group and solvent water with rearrangement of a trigonal-bipyramidal intermediate,[3] and the other is the intramolecular rearrange-

(11) In CoA$_4$B$_2$ and CoA$_2$A'$_2$B$_2$ types of complexes which have been examined, the chemical shift of any trans isomer is always higher than that of the corresponding cis isomer.[12] Therefore, the high-field signal in Figure 2b was assigned to the *trans*-dihydroxo isomer, and two overlapping signals at low field were assigned to the two *cis*-dihydroxo isomers. These two signals with quite similar chemical shifts possess quite different line widths. A simple point charge calculation predicts that the line width of the cis,trans isomer should be about twice as large as that of the cis,cis isomer. Therefore, the broad and the sharp spectra were assigned to the cis,trans and cis,cis isomers, respectively: A. Yamasaki, F. Yajima, and S. Fujiwara, *Inorg. Chim. Acta*, **2**, 39 (1968).

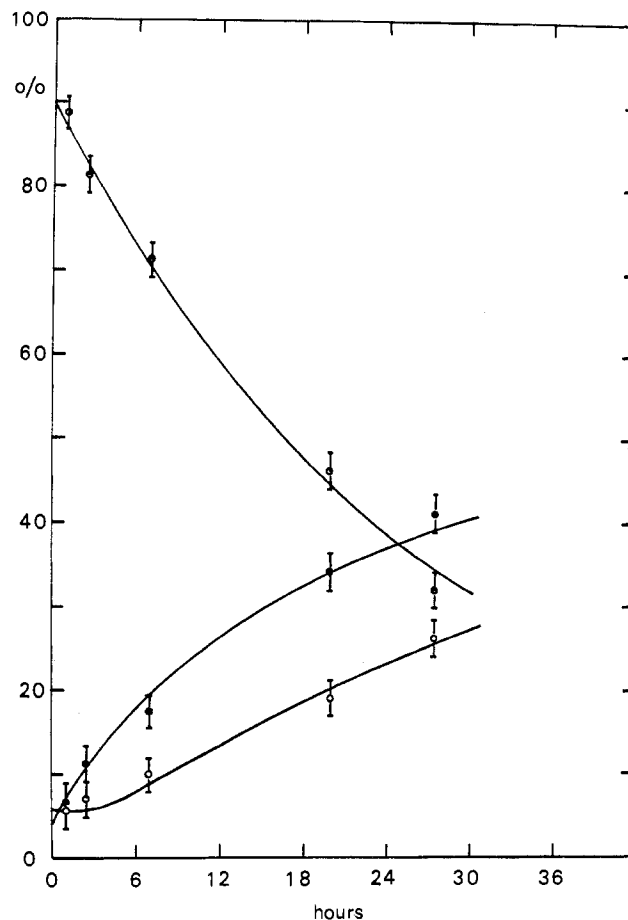(12) F. Yajima and S. Fujiwara, in preparation.

Figure 3.—Relative intensities *vs.* time for three isomers of the Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ion. Calculated curves are shown as solid lines and the experimental data are shown using ⊘ for trans, ● for cis,cis, and ⊖ for cis,trans ions.

ment involving the dissociation of one end of the ethylenediamine group.[4]

In the second column in Table III, isomerization

TABLE III
OBSERVED AND EXPECTED ISOMERIZATION PATHS FOR THREE
ISOMERS OF THE Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ION

Obsd results	Predicted from oxygen-exchange mechanism	Predicted from chelate-dissocn mechanism
trans → cis,cis	trans → cis,cis	trans → cis,cis
cis,trans → cis,cis	cis,trans → cis,cis	cis,trans → cis,cis
cis,cis → trans	cis,cis → trans and cis,trans	cis,cis → cis,trans^a cis,cis → trans^b

^{a} Corresponds to dissociation of a nitrogen atom of ethylenediamine which is trans with respect to the NH$_3$ group. ^{b} Corresponds to dissociation of a nitrogen atom of ethylenediamine which is trans with respect to the OH$^-$ group.

paths are presented for Co(en)(NH$_3$)$_2$(OH)$_2$$^+$ ion which are expected from the oxygen-exchange mechanism which involves the rearrangement through a trigonal-bipyramidal intermediate. The fact that the cis,trans and trans isomers rearrange to the cis,cis isomer is consistent with these isomerization paths. However, this model would not account for the experimental observation that the cis,cis isomer rearranges to give only the trans isomer.

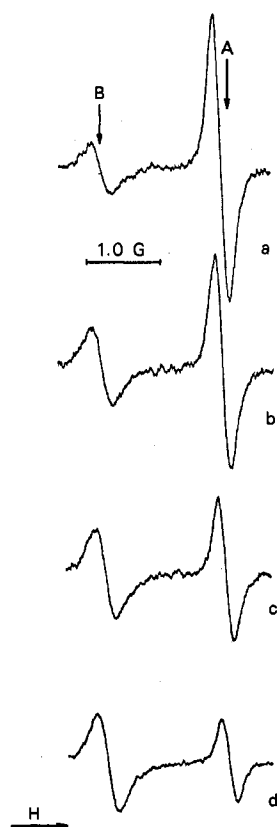The dissociation of the ethylenediamine would lead to isomerization paths which are given in the third col-

Figure 4.—Time variation of ^{59}Co nmr spectra of *cis*- and *trans*-Co(en)$_2$NH$_3$OH^{2+} ions (a) after 3 hr, (b) after 24 hr, (c) after 72 hr, and (d) after 480 hr. A, trans isomer; B, cis isomer.

umn in Table III. This mechanism is consistent with the observed paths for isomerization from the trans and cis,trans isomers to the cis,cis isomer. However, there would be two possible isomerization paths for the cis,cis isomer. Since the OH$^-$ group has stronger labilizing power than the NH$_3$ group,[4] dissociation of one end of the ethylenediamine which occupies the opposite site of the OH$^-$ group should be much easier than that of the other end of the ethylenediamine which occupies the opposite site of the NH$_3$ group. In this case, the chelate dissociation mechanism gives the isomerization path which is consistent with the observed results. However, the present experiment is not enough to decide which mechanisms are dominant in the present system. Oxygen-18-labeled experiments would be useful for this purpose.

Co(en)$_2$(OH)$_2^+$ Ion.—The isomerization rate constants and equilibrium constant in eq 3 have been mea-

$$trans\text{-}Co(en)_2(OH)_2{}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}Co(en)_2(OH)_2{}^+ \qquad (3)$$
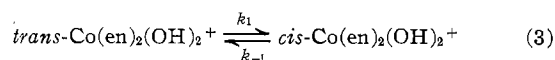
sured spectrophotometrically by several workers.[1–3]

In the spectrophotometric method the molar extinction coefficients of individual isomers have to be determined. In contrast to this, ^{59}Co nmr gives the equilibrium constants by merely using the intensity ratio of nmr signals at equilibrium. Using the spectrophotometric method, Bjerrum and Rasmussen[1] and Kruse and Taube[3] obtained the value of the equilibrium constant in eq 3 as 0.80 and 0.85, respectively. These values are larger than the value of 0.52 ± 0.02 which was obtained at a concentration of 0.5 M with the use of ^{59}Co nmr in the present experiments. This discrepancy suggests that the equilibrium constant for the Co(en)$_2$(OH)$_2^+$ ion is strongly dependent on the concentration of the complex ion. In the spectrophotometric measurements the concentration of the complex is about one-tenth of the concentrations used in ^{59}Co nmr measurements. From ^{59}Co nmr measurements, the concentration equilibrium constants are obtained as 0.41, 0.52, 0.64, 0.70, and 0.75 for 0.73, 0.50, 0.30, 0.20, and 0.10 M, respectively. The value extrapolated to the infinite dilution is in good agreement with the values obtained spectrophotometrically. The rate constants k_1 and k_{-1} determined at 25.0° using the ^{59}Co nmr data are $(1.8 \pm 0.1) \times 10^{-6}$ sec^{-1} and $(3.6 \pm 0.1) \times 10^{-6}$ sec^{-1}, respectively. Using spectrophotometric data Kruse and Taube[3] obtained 3.0×10^{-6} sec^{-1} and 3.6×10^{-6} sec^{-1} at 24.95° for k_1 and k_{-1}, respectively. The rate constants k_{-1} obtained in these two experiments are in good agreement, whereas k_1 obtained from spectrophotometry is larger than that obtained from ^{59}Co nmr. The difference in concentration equilibrium constants may be responsible to this discrepancy.

Co(en)$_2$NH$_3$OH^{2+} Ion.—A change with time of nmr spectra of the Co(en)$_2$NH$_3$OH^{2+} ion is shown in Figure 4. The signals at high and low fields are assigned to the *trans*- and *cis*-Co(en)$_2$NH$_3$OH^{2+} ions, respectively.[13] The first-order rate constant for isomerization from the cis to the trans isomer estimated from eq 1 is $(1.7 \pm 0.1) \times 10^{-6}$ sec^{-1} (25.0°). By using the equilibrium quotient, $K = (cis)/(trans) = 2.5 \pm 0.1$, the rate constant for the reverse reaction is obtained as $(4.3 \pm 0.1) \times 10^{-6}$ sec^{-1}. Martin and Tobe[4] reported the isomerization rate constant from the trans to the cis as 2×10^{-5} sec^{-1} (at 30°).

(13) A signal at high field with a line width of 0.18 G coincides with that of *trans*-[Co(en)$_2$NH$_3$H$_2$O]Br$_3$ in alkaline solution, and a signal at low field with a line width of 0.29 G coincides with that of *cis*-[Co(en)$_2$NH$_3$H$_2$O]Br$_3$ in alkaline solution.