Cobalt-59 Nuclear Magnetic Resonance Study of Cobalt(III) Complexes. Empirical Rules for the Cobalt-59 Chemical Shifts and Line Widths of $[Co^{III}(en)_x(NH_3)_{6-2x-y}L_y]$-type Complexes*

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The cobalt-59 chemical shifts and line widths for about seventy cobalt(III) complexes of the $[Co^{III}(en)_x(NH_3)_{6-2x-y}L_y]$ (L=Cl, Br, NO_2, N_3, OH, H_2O, CO_3, and C_2O_4) type have been measured. The cobalt-59 chemical shifts of this type of complex are approximately represented by a simple relation:

$$\delta(\text{ppm}) = 360x + \sum_{i=1}^{y} \delta_i(\text{L}) \qquad (x=0,\ 1,\ \text{and}\ 2),$$

where $\delta_i(\text{L})$ is the i-th ligand shift parameter which represents the contribution of the i-th ligand, L, to the total chemical shift. Three empirical rules can be derived from experimental observations: I. The chemical shift of a *trans*-isomer is higher than that of the corresponding *cis*-isomer. II. The line width of the *trans*-CoA_4B_2 isomer is larger than that of the *cis*-CoA_4B_2 isomer. III. The line width of a *meridional* isomer is larger than that of the corresponding *facial* isomer. Illustrative examples are presented where cobalt-59 NMR is used to identify cobalt (III) complexes and to study the kinetics and equilibrium in solution.

The cobalt-59 chemical shifts and line widths have been reported for a variety of cobalt(III) complexes in solution.[1-8] However, the values of the chemical shifts of the same complexes as measured by different workers are not in good agreement with each other. This inconsistency is assumed to be due to the fact that all the works in the literature are based on one species of chemical shift standard, *i.e.*, $[Co(CN)_6]^{3-}$, which has the highest chemical shift among the cobalt(III) complexes studied so far. Hence, two other complexes ($[Co(en)_3]^{3+}$ and $[Co(acac)_3]$) have here been chosen as the standards besides $[Co(CN)_6]^{3-}$, and used as the standards of chemical shifts in the middle- and low-field regions respectively.

Experimental

Materials. Cobalt(III) complexes were synthesized by standard procedures and purified by recrystallization. Monoethylenediamine-cobalt(III) complexes of the $[Co(en)(NH_3)_2L_2]$ (L=OH, NO_2, and N_3) and $[Co(en)(NH_3)_3L]$ (L=Cl, Br, OH, NO_2, and N_3) types were prepared from $[Co(en)(NH_3)_2Cl_2]Cl$ and $[Co(en)(NH_3)_3H_2O]X_3$,[8] respectively according to the modification of the procedure for the preparation of the corresponding $[Co(NH_3)_{6-x}L_x]$ or $[Co(en)_2(NH_3)_{2-x}L_x]$ type complexes.

NMR Measurements. The cobalt-59 NMR measurements were made at 25.0 °C using a JEOL JNM-WB-20 spectrometer operating at 13.5550 MHz. Some measurements were carried out on a Varian Associates VF-16 spectrometer at several frequencies. For the chemical shift measurements, $[Co(CN)_6]^{3-}$, $[Co(en)_3]^{3+}$, and $[Co(acac)_3]$ were used as the internal or external reference in the high-, middle-, and low-field regions respectively. The difference in chemical shift between the internal and external references was less than 5 ppm. The resonant fields for the above three standards were determined separately from lithium-7 NMR of aqueous lithium chloride solutions using an autodyne oscillator. The standard deviation of the observed values of the chemical shifts was less than 0.5%. In the case of chloro-, bromo-, and aquo-complexes, the standard deviation of the chemical shifts was 2—3% for their large line widths. The line widths were obtained as the peak-to-peak intervals of the first derivatives of the absorption signals, which were recorded under a quite small amplitude of modulation at a frequency of 35 Hz.

Results and Discussion

Chemical Shift. All the cobalt(III) complexes studied were of the $[Co(en)_x(NH_3)_{6-2x-y}L_y]$ type, where L is Cl, Br, NO_2, N_3, OH, H_2O, CO_3, and C_2O_4. The chemical shifts and line widths of these complexes are listed in Table 1. The chemical shift of the $[Co(NH_3)_6]^{3+}$ ion is taken as zero in the present study. Figures 1-a—1-e show that the chemical shifts change regularly with the combination of ligands. On the basis of these results, the chemical shift of the complexes of the $[Co(en)_x(NH_3)_{6-2x-y}L_y]$ type can be approximately represented as follows:

$$\delta(\text{ppm}) = 360x + \sum_{i=1}^{y} \delta_i(\text{L}),\ (x=0,\ 1,\ \text{and}\ 2) \qquad (1)$$

where $\delta_i(\text{L})$ represents the contribution from the i-th ligand, L, to the total chemical shift. Hereafter, $\delta_i(\text{L})$ will be referred to as the i-th ligand shift parameter.

Table 1-a. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x}]$ type of complexes

Complex	Chemical shift (ppm)	Line width (G)
$[Co(NH_3)_6]^{3+}$	0[a]	0.05
$[Co(en)(NH_3)_4]^{3+}$	360	0.23
trans-$[Co(en)_2(NH_3)_2]^{3+}$	760	0.43
cis-$[Co(en)_2(NH_3)_2]^{3+}$	710	0.27
$[Co(en)_3]^{3+}$	1030[b]	0.05

a) $[Co(NH_3)_6]^{3+}$ is taken as a standard for the chemical shift. b) The resonant field was determined using Li-7 NMR; 13320.2 G at 13.5550 MHz.

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Table 1-b. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}Cl_y]$ type of complexes

Complex	Chemical shift[a] (ppm)	Line width (G)
$[Co(NH_3)_5Cl]^{2+}$	−700	1.0
trans-$[Co(NH_3)_4Cl_2]^+$	−1660[b]	4.0
cis-$[Co(NH_3)_4Cl_2]^+$	−1660[b]	2.0
$[Co(en)(NH_3)_3Cl]^{2+}$	−270	2.5
cis-$[Co(en)_2(NH_3)Cl]^{2+}$	100	2.5
trans-$[Co(en)(NH_3)_2Cl_2]^+$ [c]	−1150	4.0
cis-trans-$[Co(en)(NH_3)_2Cl_2]^+$ [d]	−1170	3.0
trans-$[Co(en)_2Cl_2]^+$	−820	8.0
cis-$[Co(en)_2Cl_2]^+$	−820	4.5

a) The standard deviation of observed values of chemical shifts was 3%. b) The difference in chemical shift between *cis* and *trans* isomers could not be obtained because of their large line widths. c) *trans*-dichloro-*cis*-diammine(ethylenediamine)cobalt(III) ion. d) *cis*-dichloro-*trans*-diammine(ethylenediamine)cobalt(III) ion.

Table 1-c. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}Br_y]$ type of complexes

Complex	Chemical shift[a] (ppm)	Line width (G)
$[Co(NH_3)_5Br]^{2+}$	−670	1.0
$[Co(en)(NH_3)_3Br]^{2+}$	−240	2.5
trans-$[Co(en)(NH_3)_2Br_2]^+$	−1160	4.8
cis-$[Co(en)_2NH_3Br]^{2+}$	110	2.0
trans-$[Co(en)_2Br_2]^+$	−810	5.5
cis-$[Co(en)_2Br_2]^+$	−810	3.0

a) The standard deviation of observed values of chemical shifts was 3%.

Table 1-d. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}(NO_2)_y]$ type of complexes

Complex	Chemical shift (ppm)	Line width (G)
$[Co(NH_3)_5NO_2]^{2+}$	525	0.15
mer-$[Co(en)(NH_3)_3NO_2]^{2+}$	915	0.28
fac-$[Co(en)(NH_3)_3NO_2]^{2+}$	895	0.17
cis-$[Co(en)_2NH_3NO_2]^{2+}$	1265	0.29
trans-$[Co(NH_3)_4(NO_2)_2]^+$	960	0.28
cis-$[Co(NH_3)_4(NO_2)_2]^+$	895	0.15
trans-$[Co(en)(NH_3)_2(NO_2)_2]^+$ [a]	1275	0.50
cis-trans-$[Co(en)(NH_3)_2(NO_2)_2]^+$ [b]	1260	0.34
trans-$[Co(en)_2(NO_2)_2]^+$	1880	1.1
cis-$[Co(en)_2(NO_2)_2]^+$	1700	0.7

a) *trans*-dinitro-*cis*-diammine(ethylenediamine)cobalt(III) ion.
b) *cis*-dinitro-*trans*-diammine(ethylenediamine)cobalt(III) ion.

Table 1-e. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}(N_3)_y]$ type of complexes

Complex	Chemical shift (ppm)	Line width (G)
$[Co(NH_3)_5N_3]^{2+}$	−530	0.20
fac-$[Co(en)(NH_3)_3N_3]^{2+}$	−90	0.37
$[Co(en)_2NH_3N_3]^{2+}$	255	0.7
trans-$[Co(NH_3)_4(N_3)_2]^+$	−1070	0.30
cis-$[Co(NH_3)_4(N_3)_2]^+$	−1110	0.21
$[Co(en)(NH_3)_2(N_3)_2]^+$	−670	0.6
cis-$[Co(en)_2(N_3)_2]^+$	−250	0.5
mer-$[Co(NH_3)_3(N_3)_3]$	−1750[a]	0.71[a]
fac-$[Co(NH_3)_3(N_3)_3]$	−1820[a]	0.17[a]

a) NMR measurements were made in DMSO.

Table 1-f. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}(OH)_y]$ type of complexes

Complex	Chemical shift (ppm)	Line width (G)
$[Co(NH_3)_5OH]^{2+}$	−990	0.23
mer-$[Co(en)(NH_3)_3OH]^{2+}$	−635	0.43
fac-$[Co(en)(NH_3)_3OH]^{2+}$	−560	0.18
trans-$[Co(en)_2NH_3OH]^{2+}$	−110	0.18
cis-$[Co(en)_2NH_3OH]^{2+}$	−220	0.29
cis-$[Co(NH_3)_4(OH)_2]^+$	−1940	0.14
trans-$[Co(en)(NH_3)_2(OH)_2]^+$ [a]	−1580	0.23
cis-trans-$[Co(en)(NH_3)_2(OH_2)]^+$ [b]	−1660	0.59
cis-cis-$[Co(en)(NH_3)_2(OH)_2]^+$ [b]	−1670	0.23
trans-$[Co(en)_2(OH)_2]^+$	−1130	0.15
cis-$[Co(en)_2(OH)_2]^+$	−1150	0.23
$[Co(en)NH_3(OH)_3]$	−2710	0.20

a) *trans*-dihydroxo-*cis*-diammine(ethylenediamine)cobalt(III) ion. b) *cis*-dihydroxo-*trans*-diammine(ethylenediamine)cobalt(III) ion. c) *cis*-dihydroxo-*cis*-diamminecobalt(III) ion.

Table 1-g. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}(H_2O)_y]$ type of complexes

Complex	Chemical shift[a] (ppm)	Line width (G)
$[Co(NH_3)_5H_2O]^{3+}$	−930	2.8
fac-$[Co(en)(NH_3)_3H_2O]^{3+}$	−550	5.0
mer-$[Co(en)(NH_3)_3H_2O]^{3+}$	−550	8.0
trans-$[Co(en)_2(NH_3)H_2O]^{3+}$	−100	7.3
cis-$[Co(en)_2(NH_3)H_2O]^{3+}$	−200	7.0
cis-$[Co(NH_3)_4(H_2O)_2]^{3+}$	−1810	3.0
trans-$[Co(en)_2(H_2O)_2]^{3+}$	−950	—
cis-$[Co(en)_2(H_2O)_2]^{3+}$	−1000	6.5
fac-$[Co(NH_3)_3(H_2O)_3]^{3+}$	−2630	0.20

a) The standard deviation of observed values of chemical shifts was 2%.

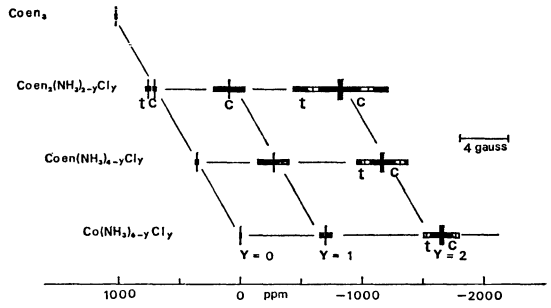
Table 1-h. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-2y}(CO_3)_y]$ type of complexes

Complex	Chemical shift (ppm)	Line width (G)
$[Co(NH_3)_4(CO_3)]^+$	−1580	1.1
$[Co(en)_2(CO_3)]^+$	−730	1.9
$[Co(en)NH_3)_2(CO_3)]^+$	−1180	1.9
$[Co(NH_3)_2(CO_3)_2]^-$	−3550	1.6
$[Co(en)(CO_3)_2]^-$	−2940	2.4
$[Co(CO_3)_3]^{3-}$	−5770	0.25

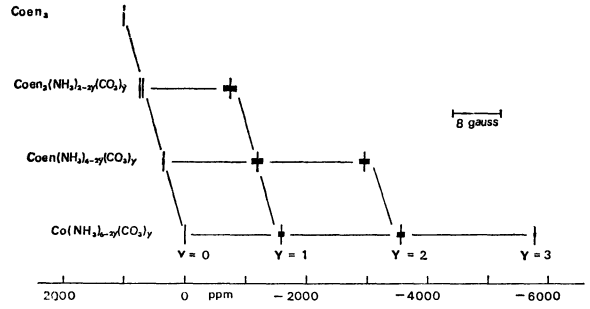
Table 1-i. Chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-2y}(C_2O_4)_y]$ type of complexes

Complex	Chemical shift (ppm)	Line width (G)
$[Co(NH_3)_4(C_2O_4)]^+$	−1850[a]	—
$[Co(en)_2(C_2O_4)]^+$	−460[b]	2.0[b]
$[Co(NH_3)_2(C_2O_4)_2]^-$	−2780	1.5
$[Co(en)(C_2O_4)_2]^-$	−2250	3.2
$[Co(C_2O_4)_3]^{3-}$	−4700	0.25

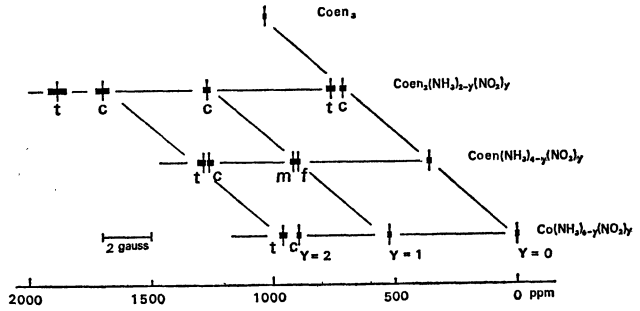
a) This signal may be ascribed to $[Co(NH_3)_4(H_2O)_2]^{3+}$ ion. b) NMR measurements were made at 45 °C.



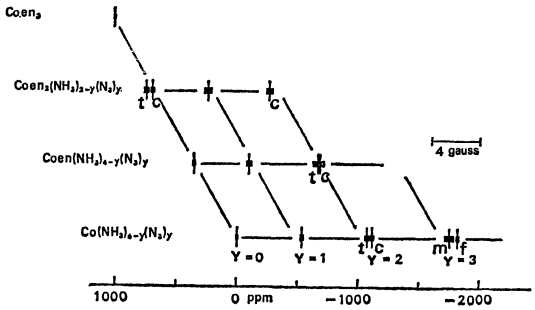
(a) $[Co(en)_x(NH_3)_{6-2x-y}Cl_y]$ type of complexes



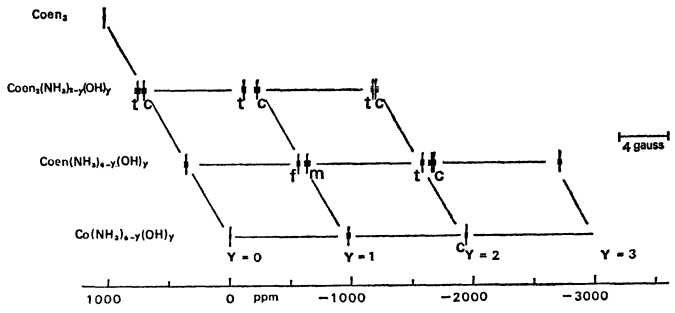
(b) $[Co(en)_x(NH_3)_{6-2x-2y}(CO_3)_y]$ type of complexes



(c) $[Co(en)_x(NH_3)_{6-2x-y}(NO_2)_y]$ type complexes



(d) $[Co(en)_x(NH_3)_{6-2x-y}(N_3)_y]$ type of complexes



(e) $[Co(en)_x(NH_3)_{6-2x-y}(OH)_y]$ type of complexes

Fig. 1. The diagram for chemical shifts and line widths for $[Co(en)_x(NH_3)_{6-2x-y}L_y]$ type of complexes. The chemical shift and line width are represented by longitudinal and transverse bars, respectively. *Trans*, *cis*, *meridional*, and *facial* isomers are represented by t, c, m, and f, respectively.

The ligand shift parameters obtained are listed in Table 2.

The chemical shifts for ammine–ethylenediamine mixed complexes are listed in Table 1-a. The chemical shifts are proportional to the number of the ethylenediamine(or ammine) groups. The replacement of two NH_3 by one (en) results in a high-field shift of 360 ppm.

Figure 1-a shows the relation between the chemical shifts and the combinations of ligands for chloroammine complexes. From this diagram, the first and the sec-

Table 2. Ligand shift parameter

Ligand	first (ppm)	second (ppm)	third (ppm)
NO_2^-	530± 20	420±100	—
N_3^-	−480± 50	−540± 50	−660± 50
Cl^-	−650± 50	−900± 50	—
Br^-	−620± 50	−900± 50	—
OH^-	−950±100	−950±100	−1100±100
H_2O	−900±100	−870±100	−830±100
Ligand	second (ppm)	fourth (ppm)	sixth (ppm)
CO_3^{2-}	−1500±100	−1900±100	−2200
$C_2O_4^{2-}$	−1200±100	−1500±100	−2000

ond ligand shift parameters are estimated as $\delta_1(Cl) = -(650+50)$ and $\delta_2(Cl) = -(900\pm50)$ ppm respectively. A quite similar diagram is obtained for bromoammine complexes, which show a slightly higher shift than to the chloroammine complexes.

The diagram for the carbonato species is shown in Fig. 1-b. The second, fourth, and sixth ligand shift parameters are estimated to be $-(1500\pm100)$, $-(1900\pm100)$, and -2200 ppm respectively. The absolute values for the ligand shift parameters become large with the increase in the number of substituted carbonato groups. Similar trends are observed for the Cl, Br, N_3, and C_2O_4 series. According to these results, it may be concluded that the absolute values of ligand shift parameters becomes smaller with an increase in the resonant fields of complexes. The diagrams for the NO_2 and N_3 series are shown in Figs. 1-c and 1-d respectively.

As Fig. 1-e shows, the contribution of the OH radical to the chemical shifts of cobalt-59 is additive: *i.e.*, the first, second, and third ligand shift parameters are almost equal ($\delta_1 \cong \delta_2 \cong \delta_3 \cong -(950\pm100)$ ppm). The chemical shifts of aquo-complexes also show a similar trend. The line width for aquo-complexes is much larger than that for the corresponding hydroxo-complexes: this certainly reflects the difference in the quadrupolar interactions of cobalt-59 between Co–OH and Co–OH_2 bonds.

Empirical Rules for the Chemical Shifts and Line Widths of Geometrical Isomers. The following rules have been deduced from the results of the present experiment concerning the relations between the geometrical isomers and their chemical shifts or line widths.

Rule I. The chemical shift of the trans*-isomer is higher than that of the corresponding* cis *isomer.* This rule holds for the complexes of the CoA_4B_2, $CoA_2A'_2B_2$, and CoA_4BC types, where A, B, and C refer to the different ligand atoms directly coordinate with cobalt, and where A and A′ represent the ligands of the same ligand atoms, such as NH_3 and (en). Shimura[9] presented an empirical rule for d-d absorption bands of *cis* and *trans* isomers of CoA_4B_2 type complexes: if A is in a higher rank than B in the spectroschemical series, $\nu_{max(cis)} - \nu_{max(trans)} > 0$, while if B is in a higher rank than A, $\nu_{max(cis)} - \nu_{max(trans)} < 0$. However, as has been described above, the chemical shift of a *trans* isomer, the chemical shift of a *trans* isomer is always higher than that of the corresponding *cis* isomer, regardless of the strength of the ligand fields for A and B. Simple calculation suggests that the difference in radial parameters and orbital reduction factors[10] is reponsible for the difference in chemical shifts between the *cis* and *trans* isomers.

Rule II. The line width of the trans-CoA_4B_2 *isomer is larger than that of the* cis-CoA_4B_2 *isomer.* It is well established that the cobalt-59 line widths for the species in solution are determined by quadrupolar interaction. A calculation based on a simple point-charge model has shown that the electric field gradient of a *trans* isomer is twice as that of the corresponding *cis* isomer.[6] The line widths of *cis*- and *trans*-$[Co(en)_2(NH_3)_2]^{3+}$, $[Co(en)_2(NO_2)_2]^+$, $[Co(en)_2Cl_2]^+$, $[Co(en)_2Br_2]^+$, $[Co(NH_3)_4(NO_2)_2]^+$, $[Co(NH_3)_4(N_3)_2]^+$, and $[Co(NH_3)_4Cl_2]^+$ are consistent with this rule. $[Co(en)_2(OH)_2]^+$ ion is the only exception among all the complexes studied which does not obey the general trends cited above. The relatively large line width of the *cis*-$[Co(en)_2(OH)_2]^+$ ion suggests a distortion of the field, resulting in a significant deviation from the regular octahedral structure.

Rule III. The line width of the mer*-isomer is larger than that of* fac*-isomer.* The electric field gradient at the site of the central cobalt nucleus in the *fac*-triaquotriamminecobalt(III) complex is estimated to be very small, as we see a sharp spectrum with a line width of 0.20 G. This value is in contrast to the broad spectra (about 2G) of the other aquoammine-complexes.[6] It can also be predicted from the point-charge model that *mer*-CoA_3B_2C complexes should give larger line widths than *fac*-CoA_3B_2C complexes. In fact, the line width of the *mer*-$[Co(en)(NH_3)_3NO_2]^{2+}$ ion is twice as large as that of the corresponding *fac*-isomer.

The Application of Cobalt-59 NMR to the Kinetics and Equilibria in Solution. The ligand shift parameters given in Table 2 can be used, along with the empirical rules presented above, to identify the cobalt(III) complexes and to study the kinetics and equilibria in solution. Illustrative examples will be presented and briefly discussed below.

Example 1. It is well established that the $[Co(NH_3)_5OH]^{2+}$, $[Co(NH_3)_4(OH)_2]^+$, $[Co(en)_2(NH_3)(OH)]^{2+}$, and $[Co(en)_2(OH)_2]^+$ ions exist in an alkaline solution.[11–13] However, the corresponding monoethylenediamine hydroxo-complexes, such as $[Co(en)(NH_3)_3(OH)]^{2+}$ and $[Co(en)(NH_3)_2(OH)_2]^+$ ions, have not yet been identified. In a concentrated alkaline solution, *trans*-$[Co(en)(NH_3)_2Br_2]Br$ shows two cobalt-59 NMR signals which do not coincide with that of the *trans*-$[Co(en)(NH_3)_2Br_2]^+$ ion (Fig. 2-a). The chemical shifts of these two signals are -1670 and -1580 ppm, which are very close to the value, -1540 ppm, estimated by means of Equation (1). This suggests that *trans*-$[Co(en)(NH_3)_2Br_2]^+$ is hydrolyzed to yield $[Co(en)(NH_3)_2(OH)_2]^+$ ion in an alkaline solution. On the basis of Rule I, the high- and low-field signals of the doublet can be assigned to the *trans*-dihydroxo and *cis*-dihydroxo isomers respectively. Figure 2-b shows an NMR spectrum of *trans*-$[Co(en)(NH_3)_2Br_2]$-Br dissolved in 10% aqueous ammonia and heated at 40 °C for 10 minutes. A high-field doublet in Fig. 2-b

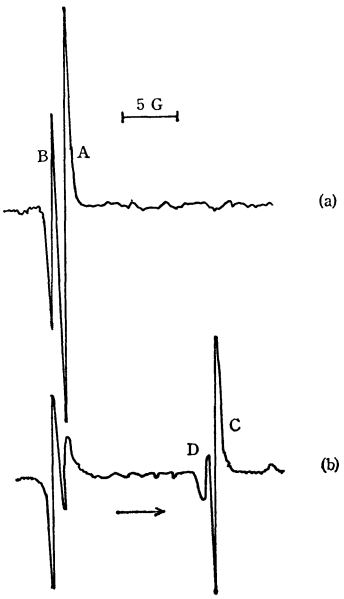


Fig. 2(a). Co-59 NMR spectra of *trans*-$[Co(en)(NH_3)_2Br_2]Br$ in concentrated ammonia solution. A and B correspond to *trans*- and *cis*-$[Co(en)(NH_3)_2(OH)_2]^+$ ions, respectively.
(b). Co-59 NMR spectra of *trans*-$[Co(en)(NH_3)_2Br_2]Br$ is ammonia solution which is heated at 40 °C for 10 minutes. C and D correspond to *fac*- and *mer*-$[Co(en)(NH_3)_3OH]^{2+}$ ions, respectively.

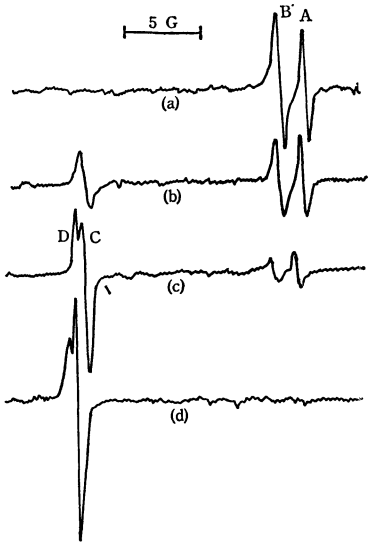


Fig. 3. Time variation of Co-59 NMR spectra of *cis*-$[Co(en)_2NH_3Br]Br_2$ in alkaline solution;
(a) at initial state, (b) after 5 min, (c) after 15 min, and (d) after 60 min.
The base hydrolysis reaction proceeded at 60 °C. NMR measurements were made at 25 °C after the reaction was quenched by cooling.
A, B, C, and D correspond to *trans*- and *cis*- $Co(en)_2NH_3OH]^{2+}$ and *trans*- and *cis*-$[Co(en)_2(OH)_2]^+$ ions, respectively.

with chemical shifts of −560 and −635 ppm is assigned to *mer*- and *fac*-$[Co(en)(NH_3)_3(OH)]^{2+}$. The chemical shift for $[Co(en)(NH_3)_3(OH)]^{2+}$ estimated from Equation (1) is −590 ppm. The broad and sharp signals of the doublet can be assigned to the *mer*- and *fac*-isomers respectively by means of Rule III.

Example 2. A doublet signal was observed in an alkaline solution of *cis*-$[Co(en)_2(NH_3)Br]Br_2$ which does not coincide with that of the *cis*-$[Co(en)_2(NH_3)Br]^{2+}$ ions itself. The high- and low-field signals of the doublet coincide with those of the *trans*- and *cis*-$[Co(en)_2(NH_3)(OH)]^{2+}$ ions respectively, suggesting that Br^- is replaced by OH^- to yield the *cis*- and *trans*-$[Co(en)_2(NH_3)(OH)]^{2+}$ ions. The fact that the initial concentrations of the *cis*- and *trans*-$[Co(en)_2(NH)_3(OH)]^{2+}$ ions (*cis* 80%, *trans* 20%) gradually change to reach the equilibrium concentrations (*cis* 70%, *trans* 30%) shows that the isomerization takes place between the *cis*- and *trans*-isomers.[8] If a large excess of the OH^- ion exists, the signal intensities of *cis*- and *trans*-$[Co(en)_2(NH_3)(OH)]^{2+}$ decrease and a new doublet corresponding to *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ appears (Fig. 3). These results clearly indicate that the *cis*- and *trans*-$[Co(en)_2(NH_3)(OH)]^{2+}$ ions are hydrolyzed to yield the *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ ions. The intensity measurements of each signal[8] would make it possible to determine the rate constants for the base hydrolysis. A quantitative treatment of this system is now under study and will be discussed in detail in a coming paper.

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