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An NMR Study of Metal Complexes Containing Acetylacetone and Related Compounds. IV. The NMR Spectra and the Ligand-exchange Reaction of Cobalt(III) Complexes Containing *N,N'*-Ethylenebis(acetylacetonimine) and Amino Acid

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A series of mixed cobalt(III) complexes with the general formula of K[Co(baen)(amino acid anion)$_2$]·nH$_2$O (baen=dianion of *N,N'*-ethylenebis(acetylacetonimine); amino acid =glycine, β-alanine, L-alanine, D-alanine, D,L-alanine, L-valine, D-valine D,L-valine, L-leucine, L-isoleucine, and L-phenylalanine) were newly prepared from a reaction mixture of *trans-N,N'*-ethylenebis(acetylacetoniminato)diaquocobalt(II), [Co(baen)(H$_2$O)$_2$], and the amino acids. Also prepared were mixed cobalt(III) complexes having the general formula of [Co(baen)(X)$_2$]-ClO$_4$(X=glycine ethyl ester, L-alanine ethyl ester, L-leucine ethyl ester, L-phenylethylamine, D-phenylethylamine, and D,L-phenylethylamine). From the elemental analyses, and the IR and NMR spectra, the amino acid anions were found to coordinate as a unidentate ligand, and the structures of all the complexes were determined to be *trans* with respect to the two nitrogen atoms of the coordinated amino groups. The NMR spectral behavior of the complexes containing D,L-amino acid anions and D,L-phenylethylamine was well interpreted in terms of the existence of the following three species in a relative ratio of 1 : 2 : 1; [Co(baen)(L-form ligand)$_2$]$^{\pm n}$, [Co(baen)(L-form ligand)(D-form ligand)]$^{\pm n}$, and [Co(baen)(D-form ligand)$_2$]$^{\pm n}$. A rapid intermolecular exchange reaction of the apical amino acid anion groups was newly found in water: $[\mathrm{Co(baen)(A)_2}]^- + [\mathrm{Co(baen)(B)_2}]^- \rightleftharpoons 2[\mathrm{Co(baen\ (A)(B)}]^-$ (where A and B indicate the apical amino acid anions). Also found was a rapid exchange reaction of the apical amino acid anion groups between the complex and free amino acid anion. Strong support for the rapid inter molecular exchange reaction was obtained in a CD spectral study of them.

It has been well established that the cobalamine (V$_{\mathrm{B}_{12}}$) and its related compounds are labile for the apical ligand substitution reactions, even though the cobalt(III) complexes are generally inert.[1-3] Many anomalous properties of the cobalamines, as compared with the usual cobalt(III) complexes, have been reported by many investigators, and these anomalous properties have been explained in terms of the coordination of the macrocyclic unsaturated corrin to the cobalt(III) ion.[4]

Costa *et al.* found that the cobalt(III) complexes containing *N,N'*-ethylenebis(acetylacetonimine) (baen) and *N,N'*-bis(salicylidene)ethylenediamine (salen) had chemical properties similar to those of the cobalamines.[5-9] Cobalt(III)-baen,-salen complexes make cobalt-carbon bonds, and they show unusual stability in the lower valence state.[10]

In these circumstances, it seemed that it would be very interesting to study the lability of the apical ligands of the cobalt(III)-baen complexes. In this series of studies,[11,12] we found that the cobalt(III)-bean complexes show a rapid intermolecular exchange reaction of the apical ligands. In this paper, we will report the preparation, the NMR spectra, and the rapid intermolecular exchange reaction of the cobalt(III)-baen complexes containing amino acid anions.

Experimental

Preparation of the Complexes. 1) Complexes with the General Formula of K[Co(baen)(amino acid anion)$_2$]·nH$_2$O. *N,N'*-Ethylenebis(acetylacetoniminato)diaquocobalt(II), *trans*-[Co-(baen)(H$_2$O)$_2$][13] (6.3 g, 0.02 mol), was dissolved in 200 m*l* of methanol. Amino acid (0.04 mol) neutralized with an equimolar amount of potassium hydroxide in 100 m*l* of water was then added. After air had been sucked through the solution for three hours, the solution was concentrated to a volume of about 100 m*l*. Acetone (100—200 m*l*) was added, and the mixture was allowed to stand for two days in a refrigerator. Brown crystals separated out; they were subsequently recrystallized from water and acetone. The yield was about 60—80%. The formulas and the elemental analyses data are listed in Table 1.

Complexes with the General Formula of [Co(baen)(amino acid ethyl ester)$_2$]ClO$_4$. Amino acid ethyl ester hydrochloride (0.022 mol), neutralized with an equimolar amount of potassium hydroxide in 50 m*l* of water, was added to a methanol solution (200m*l*) of *N,N'*-ethylenebis(acetylacetoniminato)-diaquocobalt(II) (3.1 g, 0.01 mol). Then, a hydrogen peroxide solution (5%, 5 m*l*) and sodium perchlorate monohydrate (5 g, 0.36 mol) were added to the solution, and the resulting solution was concentrated to about 100—150 m*l*.

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TABLE 1. ELEMENTAL ANALYSES OF THE COMPLEXES

	Complex	C (%) Found (Calcd)	H (%) Found (Calcd)	N (%) Found (Calcd)
(I)	K[Co(baen)(gly)$_2$]·2H$_2$O	38.40 (38.09)	5.78 (5.98)	11.19 (11.12)
(II)	K[Co(baen((L-ala)$_2$]·7H$_2$O	34.53 (34.72)	6.88 (7.14)	8.74 (8.94)
(III)	K[Co(baen)(D-ala)$_2$]·7H$_2$O	34.74 (34.72)	7.03 (7.14)	9.04 (8.94)
(IV)	K[Co(baen)(DL-ala)$_2$]·3H$_2$O	38.92 (39.27)	6.63 (6.60)	10.11 (10.19)
(V)	K[Co(baen)(β-ala)$_2$]·3H$_2$O	39.34 (39.27)	6.80 (6.60)	10.33 (10.19)
(VI)	K[Co(baen)(L-val)$_2$]·8H$_2$O	38.16 (37.92)	7.81 (7.83)	7.73 (8.05)
(VII)	K[Co(baen)(D-val)$_2$]·8H$_2$O	37.98 (37.92)	7.95 (7.83)	7.94 (8.05)
(VIII)	K[Co(baen)(DL-val)$_2$]·8H$_2$O	37.68 (37.92)	7.69 (7.83)	7.79 (8.05)
(IX)	K[Co(baen)(L-leu)$_2$]·8H$_2$O	40.00 (39.77)	8.16 (8.10)	7.76 (7.87)
(X)	K[Co(baen)(L-isoleu)$_2$]·8H$_2$O	39.51 (39.77)	7.92 (8.10)	7.58 (7.87)
(XI)	K[Co(baen)(L-phe)$_2$]·6H$_2$O	47.97 (47.61)	6.01 (6.17)	7.47 (7.41)
(XII)	[Co(baen)(glyOEt)$_2$]ClO$_4$	40.82 (40.92)	6.33 (6.19)	9.76 (9.55)
(XIII)	[Co(baen)(L-alaOEt)$_2$]ClO$_4$	42.96 (42.96)	6.73 (6.57)	9.02 (9.11)
(XIV)	[Co(baen)(L-leuOEt)$_2$]ClO$_4$	48.05 (48.09)	7.58 (7.51)	8.17 (8.01)
(XV)	[Co(baen)(L-phenylethylamine)$_2$]ClO$_4$	53.78 (53.97)	6.42 (6.48)	8.86 (8.99)
(XVI)	[Co(baen)(D-phenylethylamine)$_2$]ClO$_4$	53.92 (53.97)	6.54 (6.48)	8.86 (8.99)
(XVII)	[Co(baen)(DL-phenylethylamine)$_2$]ClO$_4$	53.87 (53.97)	6.54 (6.48)	8.88 (8.99)

When the solution was cooled to 0°C, brown crystals separated out; they were subsequently recrystallized from methanol-water. The yield was about 80%. The formulas and the elemental analyses data are summarized in Table 1.

3) *Cobalt(III)-baen Complexes Containing* D-, L-, *and* D,L-*phenylethylamine.* These complexes were prepared by the method employed for the preparation of the complexes containing the amino acid ethyl ester. The yeild was about 80—90%. The phenylethylamine was prepared by a known method[14] and was resolved with acetyl-L-leucine.[15] The (+)-amine had $[\alpha]_D^{25}+39.1°$(without solvent), lit. +39.2°, and the (−)-amine had $[\alpha]_D^{25}-33.4°$, lit. −33.6°. The formulas and the elemental analyses data are listed in Table 1.

Measurements. All the NMR spectra were recorded with a Hitachi R-20 spectrometer (60 MHz) at 35°C. The NMR spectra were measured in D$_2$O or deuterated DMSO, with NaTMS as the internal reference. The IR spectra were measured with a Hitachi EPI-S2 spectrometer, using a potassium bromide disk. The CD spectra were recorded with a Jasco Optical Rotatory Dispersion Recorder, Model ORD/UV-5. All the visible and ultraviolet absorption spectra were recorded with a Hitachi EPS-3 spectrometer.

Results and Discussion

Amino Acid in Unidentate Coordination. It is well known that an amino acid coordinates to a metal ion as a chelate ligand. In some particular complexes, however, the amimo acid acts as a unidentate ligand.[16–18] In the present study, the analytical values of the complexes (in Table 1) suggest that the amino acid in these complexes coordinates to the cobalt(III) ion as a unidentate ligand. Amino acid can coordinate to the cobalt(III) ion as a unidentate ligand in two ways; one is with the oxygen atom of the carboxylate group, and the other, with the nitrogen atom of the amino group. In the present case, the IR spectra suggest that the amino acid anions coordinate in the latter way. All the complexes with the general formula of K[Co(baen)(amino acid anion)$_2$] show the C–O stretching band of the free carboxylate group at about 1600 cm^{-1}, as is shown in Table 2. The carboxylate group of the amino acid anion coordinated to the cobalt(III) ion shows asym. $\nu_{\text{COO-Co}}$ band at about 1650 cm^{-1},[19] and the amino acid anions in these complexes obtained here seem to coordinate to the cobalt(III) ion, with their amino groups. Their absorption and CD spectra give further evidence for the cobalt(III)-nitrogen linkage in the complexes. The absorption and CD spectra of the K[Co(baen)-(amino acid anion)$_2$] complexes are very similar to

TABLE 2. THE INFRARED ABSORPTION SPECTRA (in cm^{-1})

Complex	*asym.* ν_{COO}	*asym.* $\nu_{\text{C=C}}$	*asym.* $\nu_{\text{C=N}}$ and $\nu_{\text{C=O}}$
I	1603	1580	1510
II, III, IV	1603	1560	1510
V	1603	1560	1510
VI, VII, VIII	1603	1603	1515
IX	1603	1603	1511
X	1603	1603	1514
XI	1623	1595	1510
XII	1732 (COOEt)	1595	1512
XIII	1732 (COOEt)	1602	1510
XIV	1740 (COOEt)	1602	1510
XV, XVI, XVII		1590	1510

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Table 3. The NMR spectra of the complexes in D_2O (in δ, ppm)

Complex	C=CH	CH$_2$-CH$_2$	CH(R) (amino acid)	CH$_3$ (C=O)	CH$_3$ (C=N)	R (amino acid)
I	5.18	3.69	2.51	2.27	2.11	
II, III	5.17	3.69	2.90 2.78 2.66 2.54	2.25	2.11	$\left.\begin{matrix}1.14\\1.02\end{matrix}\right\}$ (CH$_3$)
IV	5.20 5.17 5.13	3.69	2.90 2.78 2.66 2.54	2.28 2.25 2.22	2.12 2.11 2.08	$\left.\begin{matrix}1.14\\1.02\end{matrix}\right\}$ (CH$_3$)
V	5.18	3.69	2.19	2.27	2.11	
VI, VII	5.17	3.72	2.48 2.40	2.25	2.12	1.80 (center of -CH(Me)$_2$ peaks) $\left.\begin{matrix}0.84\\0.72\end{matrix}\right\}$ (CH$_3$), $\left.\begin{matrix}0.80\\0.68\end{matrix}\right\}$ (CH$_3$)
VIII	5.21 5.17 5.14	3.73	2.48 2.40	2.28 2.25 2.22	2.13 2.12 2.11	1.80 (center of -CH(Me)$_2$ peaks) $\left.\begin{matrix}0.84\\0.72\end{matrix}\right\}$ (CH$_3$), $\left.\begin{matrix}0.80\\0.68\end{matrix}\right\}$ (CH$_3$)
IX	5.17	3.69	2.70 2.60 2.50	2.25	2.12	1.35 (center of -CH$_2$-CH(Me)$_2$ peaks) $\left.\begin{matrix}0.89\\0.80\end{matrix}\right\}$ (CH$_3$)
X	5.17	3.69	2.51 2.44	2.25	2.12	2.15 (center of -CH(Me)-CH$_2$(Me) peaks) $\left.\begin{matrix}0.99\\0.90\\0.79\end{matrix}\right\}$ (CH$_3$), $\left.\begin{matrix}0.93\\0.90\end{matrix}\right\}$ (CH$_3$)
XI	4.82	3.36	2.96 2.57 2.82 2.50 2.71 2.36 2.63 2.22	2.08	1.86	$\left.\begin{matrix}7.46 & 7.29\\7.39 & 7.19\\7.36 & 7.13\\7.32 & 7.07\end{matrix}\right\}$ (C$_6$H$_5$)

Table 4. The NMR spectra of the complexes (in δ, ppm)

Complex	Solvent	Baen				Axial ligand
		C=CH	CH$_2$-CH$_2$	CH$_3$ (C=O)	CH$_3$ (C=N)	
XII	D_2O	5.02	3.69	2.25	2.08	2.76 (CH$_2$ of gly) $\left.\begin{matrix}3.95\\4.08\\4.20\\4.32\end{matrix}\right\}$ (CH$_2$-Me of OEt), $\left.\begin{matrix}1.30\\1.18\\1.06\end{matrix}\right\}$ (CH$_3$ of OEt)
XIII	D_2O	4.98	3.69	2.23	2.04	$\left.\begin{matrix}1.17\\1.05\end{matrix}\right\}$ CH$_3$ of ala) $\left.\begin{matrix}3.96\\4.08\\4.20\\4.32\end{matrix}\right\}$ (CH$_2$-Me of OEt), $\left.\begin{matrix}1.29\\1.17\\1.05\end{matrix}\right\}$ (CH$_3$ of OEt)
XIV	DMSO	5.02	3.69	2.17	1.94	2.94 (center of CH(R) of leu) 1.26 (center of CH$_2$-CH(Me)$_2$ of leu) $\left.\begin{matrix}0.81\\0.76\end{matrix}\right\}$ (CH$_3$ of leu) $\left.\begin{matrix}4.33\\4.11\\3.99\\3.87\end{matrix}\right\}$ (CH$_2$-Me of OEt), $\left.\begin{matrix}1.26\\1.14\\1.02\end{matrix}\right\}$ (CH$_3$ of OEt)
XV, XVI	DMSO	4.99	3.47	2.13	2.03	7.31 (C$_6$H$_5$), $\left.\begin{matrix}1.18\\1.08\end{matrix}\right\}$ (CH$_3$)
XVII	DMSO	5.14 4.99 4.81	3.47	2.21 2.13 2.03	2.13 2.03 1.92	7.31 (C$_6$H$_5$), $\left.\begin{matrix}1.18\\1.08\end{matrix}\right\}$ (CH$_3$)

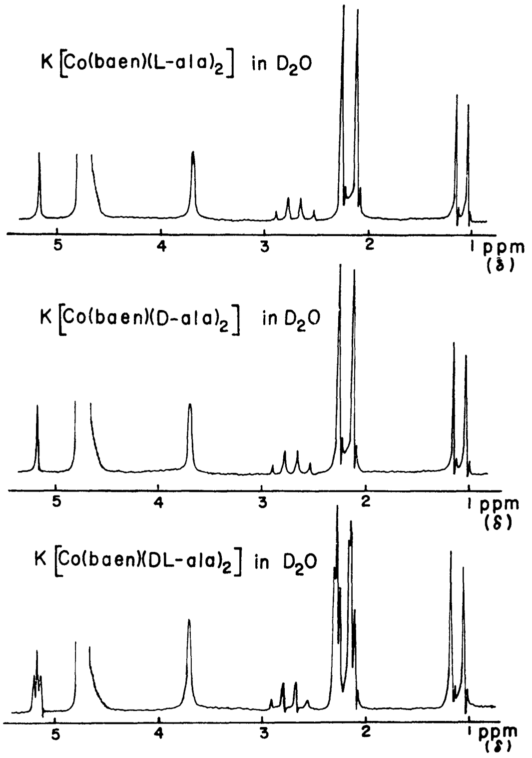

Fig. 1. The NMR Spectra of K[Co(baen)(L-ala)$_2$], K[Co(baen)(D-ala)$_2$], and K[Co(baen)(DL-ala)$_2$] complexes in D_2O.

those of the [Co(baen)(amino acid ethyl ester)$_2$]ClO$_4$, in which the amino acid ethyl ester coordinated to the cobalt(III) ion, with its amino group.

An attempt to prepare a cobalt(III)-baen complex in which unidentate amino acid coordinates to the cobalt(III) ion with its carboxylate group was not successful. It is well known that the amino acid in a unidentate coordination generally prefers the formation of a bond to the cobalt(III) ion with its carboxylate group than one with its amino group.20) Therefore, this unusual chemical property of the cobalt(III)-baen complex that the cobalt(III)-baen complex prefers the coordination-bond formation with an amino group of the amino acid anion, may be thought to be due to the anomalous chemical properties of the cobalt(III) complexes containing an unsaturated planar quadridentate ligand.

NMR Spectra of Complexes I, II, III, V, VI, VII, IX, X, XI, XII, XIII, XIV, XV, and XVI. The NMR spectral data of all the complexes are summarized in Tables 3 and 4, while some typical NMR spectra are shown in Fig. 1.

All the complexes except IV, VIII, and XVII show NMR spectral patterns with one C=CH and two CH$_3$ signals in a relative ratio of 1 : 3 : 3. Although there are three possible geometrical structures, *trans*-planar, *cis*-α, and *cis*-β, these spectral patterns clearly correspond to the *trans*-planar or *cis*-α structures. Since the cobalt(III)-baen complexes containing such unidentate ligands as ammonia, pyridine, and nitro group take the *trans*-planar structure,12) we can safely assign the *trans*-planar structure to the complexes synthesized in this study.

NMR Spectra of Complexes IV, VIII, and XVII. The NMR spectra of the complexes IV, VIII, and XVII, however, show split patterns for the C=CH and two CH$_3$ signals of baen. The C=CH signal splits into three peaks with a relative intensities of 1 : 2 : 1, and, the two CH$_3$ signals, into a pair of three peaks with relative intensities of 3 : 6 : 3 respectively. Since these complexes were prepared by using D,L-racemic amino acid or amine as the starting materials, if the reaction between [Co(baen)(H$_2$O)$_2$] and the D,L-racemic ligand proceeded statistically it can be thought that Complexes IV, VIII, and XVII are obtained as a 1 : 2 : 1 mixture product of the following three species: [Co(baen)(L-form ligand)$_2$]$^{\pm n}$, [Co(baen)(L-form ligand)(D-form ligand)]$^{\pm n}$, and [Co(baen)(D-form ligand)$_2$]$^{\pm n}$. Complexes II and III, Complexes VI and VII, and Complexes XV and XVI show the same NMR spectra with one another, and the central peak of the C=CH signal and the two central peaks of two CH$_3$ signals of Complexes IV, VIII, of and XVII coincide with the corresponding peaks Complexes II, VI, and XV respectively. Therefore, we can assign these signals to those based on the [Co(baen)(L-form ligand)$_2$]$^{\pm n}$ and [Co(baen)(D-form ligand)$_2$]$^{\pm n}$ complexes. Thus, we can conclude that the split of two C=CH peaks and the split of four CH$_3$ peaks of Complexes IV, VIII, and XVII are based on the [Co(baen)(L-form ligand)(D-form ligand)]$^{\pm n}$ complex. The relative ratio between the central C=CH peak and the split of the two C=CH peaks of these complexes is estimated to be 1 : 1. Therefore, we can determine the relative ratio of the three species, [Co(baen)(L-form ligand)$_2$]$^{\pm n}$, [Co(baen)(L-form ligand)(D-form ligand)]$^{\pm n}$, and [Co(baen)(D-form ligand)$_2$]$^{\pm n}$, to be 1 : 2 : 1, which is in agreement with the above statistical considerations. The origin of the peak splitting is thought to be based on the asymmetric

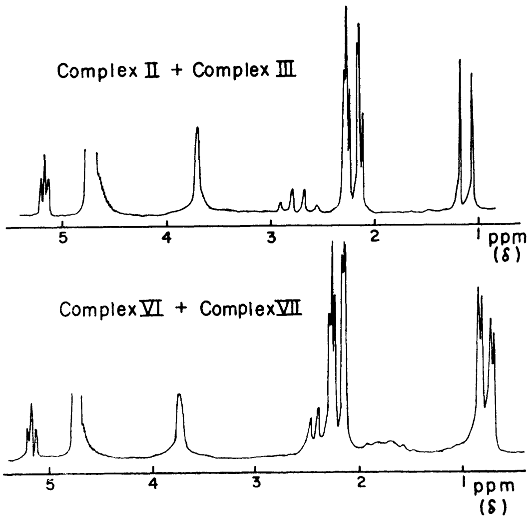

Fig. 2. The NMR spectra of 1 : 1 mixtures of complexes II and III, and VI and VII in D_2O. The pH of the solutions is about 11. The compounds are referred to Table 1.

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20) A. Nakahara and M. Shibata, ed. A special number of "Kagaku no Ryoiki," **90**, Nankodo, Tokyo (1970), p. 9.

Table 5. The NMR spectra of the 1 : 1 mixtures (in δ, ppm)

Mixture of complexes	C=CH	CH_2-CH_2	CH_3(C=O)	CH_3(C=N)
II+III	5.20 5.17 5.13	3.69	2.28 2.25 2.22	2.12 2.11 2.08
II+V	5.18 5.17	3.69	2.27 2.25	2.11
II+VI	5.17	3.71	2.25	2.11
II+VII	5.20 5.17 5.14	3.71	2.27 2.25 2.22	2.11
II+IX	5.17	3.69	2.25	2.11
II+X	5.17	3.69	2.25	2.11
II+XI	5.17 5.04 4.96 4.82	3.69 3.55 3.36	2.25, 2.22, 2.18, 2.11 2.08, 2.02, 1.95, 1.86	

Table 6. The NMR spectra of the 1 : 1 mixtures (in δ, ppm)

Mixture of complexes	C=CH	CH_2-CH_2	CH_3(C=O)	CH_3(C=N)
III+V	5.18 5.17	3.69	2.27 2.25	2.11
III+VI	5.20 5.17 5.14	3.71	2.27 2.25 2.22	2.11
III+VII	5.17	3.71	2.25	2.11
III+IX	5.20 5.17 5.14	3.69	2.27 2.25 2.22	2.11
III+X	5.20 5.17 5.14	3.69	2.27 2.25 2.22	2.11
III+XI	5.17 5.02 4.99 4.82	3.69 3.52 3.36	2.25, 2.20, 2.15, 2.13 2.11, 2.01, 1.86	

nature of these complexes, as will be mentioned latter.

Exchange Reaction of the Apical Amino Acid Anions in Cobalt(III)-baen Complexes. The NMR spectra of 1 : 1 mixtures of Complexes II and III and of Complexes VI and VII are shown in Fig. 2, while their numerical values are tabulated in Tables 5 and 6. Both NMR spectra show peak splitting for C=CH and two CH_3 signals respectively, and the NMR spectra are the same as those of Complexes IV and VIII respectively. If there were no intermolecular interaction between the complexes, the NMR spectrum of the 1 : 1 mixture should be a superposition of the spectra of their original complexes. Therefore, some kind of intermolecular interaction is thought to occur in these complexes in water.

Since the split peaks of the C=CH and CH_3 signals are based on the [Co(baen)(L-form ligand)(D-form ligand)]$^{\pm n}$ complex, as mentioned above, we can interpret the NMR spectral behavior of the 1 : 1 mixtures of Complexes II and III and of Complexes VI and VIII by assuming that the following intermolecular exchange reaction of the apical amino acid anions occurs rapidly and that the corresponding three species exist as a 1 : 1 : 2 equilibrium mixture:

$$\begin{aligned}&[\mathrm{Co(baen)(L\text{-}from\ amino\ acid\ anion)_2}]^- \\ &\quad + [\mathrm{Co(baen)(D\text{-}form\ amino\ acid\ anion)_2}]^- \rightleftharpoons \\ &2[\mathrm{Co(baen)(L\text{-}form\ amino\ acid\ anion)}\text{-} \\ &\quad \mathrm{(D\text{-}form\ amino\ acid\ anion)}]^-. \qquad (1)\end{aligned}$$

NMR Spectra of 1 : 1 Mixtures of the Complexes. In order to confirm the above assumption in detail, we measured the NMR spectra of 1 : 1 mixtures of the complexes. The NMR spectral data are summarized in Tables 5, 6, 7, and 8, while some representative NMR spectra are shown in Fig. 3.

The NMR spectra of the 1 : 1 mixtures of [Co(baen)(A)$_2$]$^-$ and[Co(baen)(B)$_2$]$^-$ complexes (where A and B indicate the apical amino acid anions) show peaks based on the two original complexes. Furthermore, when the optical forms of A and B are different, the peaks of the [Co(baen)(A)(B)]$^-$ complex also appear. Therefore, these experimental facts strongly support the above assumption. When the optical forms of A and B are identical, however, the peaks of the [Co(baen)(A)(B)]$^-$ complex can not be clearly distinguished except in the cases of the complexes containing the phenylalanine anion. In phenylalanine complexes, [Co(baen)-

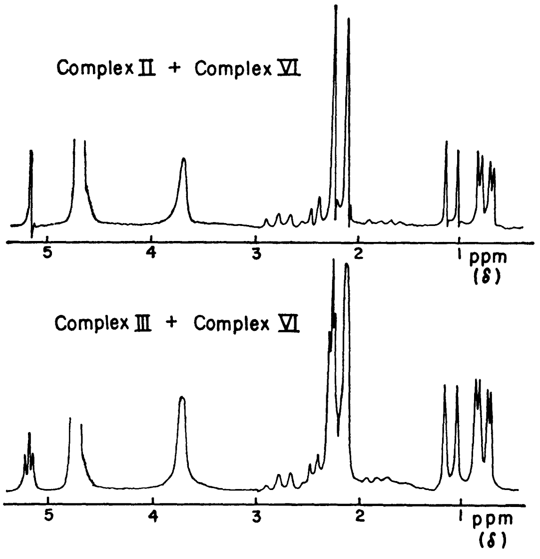

Fig. 3. The NMR spectra of 1 : 1 mixtures of complexes II and VI, and III and VI in D_2O. The solution pH is about 11. The compounds are referred to Table 1.

Table 7. The NMR spectra of the 1 : 1 mixtures (in δ, ppm)

Mixture of complexes	C=CH	CH_2-CH_2	CH_3(C=O)	CH_3(C=N)
I+II I+III	5.18 5.17	3.69	2.27 2.25	2.11
I+VI I+VII	5.18 5.17	3.70	2.27 2.25	2.11
I+IX	5.17	3.69	2.27 2.25	2.11
I+XI	5.18 5.00 4.82	3.69 3.51 3.36	2.27, 2.19, 2.11, 2.08 2.01, 1.98, 1.86	

(phenylalanine anion)(A)]$^-$, a large peak splitting resulting from the large magnetic anisotropy effect of a phenyl group is observed regardless of the optical form of A. Therefore, when the optical forms of A and B are identical, the formation of the [Co(baen)-(A)(B)]$^-$-type complexes can also be assumed.

TABLE 8. THE NMR SPECTRA OF 1 : 1 MIXTURES (in δ, ppm)

Mixture of complexes	C=CH	CH_2-CH_2	CH_3(C=O)	CH_3(C=N)
VI+VII	5.21 5.17 5.14	3.72	2.28 2.25 2.22	2.13 2.12 2.11
VI+IX	5.17	3.70	2.25	2.11
VI+X	5.17	3.70	2.25	2.11
VI+XI	5.17 5.03 4.93 4.82	3.70 3.56 3.36	2.25, 2.17, 2.15, 2.12 2.08, 2.01, 1.92, 1.86	
VII+IX	5.20 5.17 5.14	3.70	2.27 2.25 2.22	2.11
VII+X	5.20 5.17 5.14	3.70	2.27 2.25 2.22	2.11
VII+XI	5.17 5.02 4.98 4.82	3.70 3.56 3.36	2.25, 2.17, 2.12, 2.08, 2.01, 1.92, 1.86	
IX+XI	5.17 5.02 4.94 4.82	3.69 3.53 3.36	2.25, 2.18, 2.14, 2.12 2.08, 2.03, 1.96, 1.86	

NMR Spectra of the Mixtures of the Complexes and the Free Amino Acid Anion. If the exchange reaction of the apical amino acid anions occur rapidly and if all the possible products exist as equilibrium mixtures, we can expect that the following reactions between the complex and the free amino acid anion also occur rapidly, and that the corresponding products exist as equilibrium mixtures:

$$[\mathrm{Co(baen)(A)_2}]^- + \mathrm{B}^- \rightleftharpoons [\mathrm{Co(baen)(A)(B)}]^- + \mathrm{A}^- \qquad (2)$$

$$[\mathrm{Co(baen)(A)(B)}]^- + \mathrm{B}^- \rightleftharpoons [\mathrm{Co(baen))B)_2}]^- + \mathrm{A}^- \qquad (3)$$

We can confirm the above assumption by observing the peaks of the free amino acid anion A$^-$.

In order to confirm this again, we measured the NMR spectra of mixtures of the complex and the free amino acid anion. The NMR spectral data of 1 : 2 mixtures are listed in Tables 9 and 10, while some typical NMR spectra are shown in Fig. 4.

Through these measurements, we can clearly observe the peaks corresponding to A$^-$. The following facts are also observed. When the ratio between the complex and the free amino acid anion is kept at 1 : 2, the observed NMR spectra for these mixtures coincide with the corresponding NMR spectra of the 1 : 1 mixtures of the complexes, except for the additional peaks of the free amino acid anions. In these cases, the NMR spectra correspond to those of the possible species in the relative ratio of 1 : 2 : 1 : 4 : 4; [Co-

TABLE 9. THE NMR SPECTRA OF THE 1 : 2 MIXTURES OF COMPLEX AND FREE AMINO ACID ANION AT pH 13 (in δ, ppm)

1 : 2 mixture of complex and free amino acid anion	C=CH	CH_2-CH_2	CH_3(C=O)	CH_3(C=N)	Peaks of axial amino acid anion	Peaks of free amino acid anion
I+L-ala$^-$ I+D-ala$^-$ II+gly$^-$ III+gly$^-$	5.18 5.17	3.69	2.27 2.25	2.11	2.51 (CH_2 of gly) 2.90, 2.78, 2.66, 2.54 (CHMe of ala) 1.14, 1.02 (CH_3 of ala)	3.23 (CH_2 of gly) 3.27, 3.38, 3.49, 3.60 (CHMe of ala) 1.20, 1.31 (CH_3 of ala)
I+L-val$^-$ I+D-val$^-$ VI+gly$^-$ VII+gly$^-$	5.18 5.17	3.70	2.27 2.25	2.11	2.51 (CH_2 of gly) 2.48, 2.40 (CHR of val) 1.80 (center of -CH(Me)$_2$ of val) 0.84, 0.72 (CH_3 of val) 0.80, 0.68 (CH_3 of val)	3.23 (CH_2 of gly) 3.08, 3.17 (CHMe of val) 0.99, 0.88 (CH_3 of val) 0.92, 0.81 (CH_3 of val)
I+L-leu$^-$ IX+gly$^-$	5.17	3.60	2.27 2.25	2.11	2.51 (CH_2 of gly) 2.70, 2.60, 2.50 (CHR of leu) 1.35 (center of $CH_2CH(Me)_2$ of leu) 0.89, 0.80 (CH_3 of leu)	3.23 (CH_3 of gly) 3.45, 3.33, 3.21 (CH(R) of leu) 0.93, 0.84 (CH_3 of leu)
I+L-phe$^-$ XI+gly$^-$	5.18 5.01 4.98 4.82	3.69 3.50 3.35	2.27, 2.19, 2.11, 2.08 2.01, 1.98, 1.86		2.51 (CH_2 of gly) 2.39 (CH_2 of gly) 7.46—7.07 (C_6H_5 of phe)	3.23 (CH_2 of gly) 7.48 (C_6H_5 of phe)

Table 10. The NMR spectra of the 1 : 2 mixtures of complex and free amino acid anion at pH 13 (in δ, ppm)

1 : 2 mixture of complex and free amino acid anion	C=CH	CH_2-CH_2	CH_3(C=O)	CH_3(C=N)	Peaks of axial amino acid anion	Peaks of free amino acid anion
II+D-ala$^-$ III+L-ala$^-$	5.20 5.17 5.13	3.69	2.28 2.25 2.22	2.12 2.11 2.08	2.90, 2.78, 2.66, 2.54 (CHMe of ala) 1.14, 1.02 (CH_3 of ala)	3.27, 3.38, 3.49, 3.60 (CHMe of ala) 1.32, 1.20 (CH_3 of ala)
II+L-val$^-$ VI+L-ala$^-$	5.17	3.71	2.25	2.11	2.90, 2.78, 2.66, 2.54 (CHMe of ala) 1.14, 1.02 (CH_3 of ala) 2.48, 2.40 (CHR of val)	3.27, 3.38, 3.49, 3.60 (CHMe of ala) 1.32, 1.20 (CH_3 of ala) 3.08, 3.17 (CHR of val)
II+D-val$^-$ VI+D-ala$^-$	5.20 5.17 5.14	3.71	2.27 2.25 2.22	2.11	1.80 (center of -CH(Me)$_2$ of val) 0.84, 0.72 (CH_3 of val) 0.80, 0.68 (CH_3 of val)	0.99, 0.88 (CH_3 of val) 0.92, 0.82 (CH_3 of val)
II+L-leu$^-$ XI+L-ala$^-$	5.17	3.69	2.25	2.11	2.90, 2.78, 2.66, 2.54 (CHMe of ala) 1.14, 1.02 (CH_3 of ala) 2.70, 2.60, 2.50 (CHR of leu) 1.35 (center of CH_2-CH(Me)$_2$ of leu) 0.89, 0.80 (CH_3 of leu)	3.27, 3.38, 3.49, 3.60 (CHMe of ala) 1.32, 1.20 (CH_3 of ala) 3.45, 3.33, 3.21 (CHR of leu) 0.93, 0.84 (CH_3 of leu)
II+L-phe$^-$ XI+L-ala$^-$	5.17 5.04 4.96 4.82	3.69 3.55 3.36	2.25, 2.25, 2.22, 2.18, 2.11, 2.11, 2.08, 2.02, 1.95, 1.95		2.90, 2.78, 2.66, 2.54 (CHMe of ala) 1.14, 1.02 (CH_3 of ala) 1.22, 1.12 (CH_3 of ala) 2.57 (center of CHR of phe) 7.46 7.07 (C_6H_5 of phe)	3.27, 3.38, 3.49, 3.60 (CHMe of ala) 1.32, 1.20 (CH_3 of ala) 7.48 (C_6H_5 of phe)

(baen)(A)$_2$]$^-$, [Co(baen)(A)(B)]$^-$, [Co(baen)(B)$_2$]$^-$, A$^-$, and B$^-$. When the ratio is kept at 1 : 20, the observed NMR spectra are the same as those of the complexes corresponding to [Co(baen)(B)$_2$]$^-$, except for the additional peaks of the free amino acid anions. These facts indicate that Reactions 1, 2, and 3 occur and that the corresponding equilibria are made up at the same time; the equilibrium constants in Reactions 1, 2, and 3 are all estimated to be about 1 for all the cases.

Peak Splitting and the Conformation of the Apical Amino Acid Anions. The fact that the NMR spectra of the complexes containing L-form amino acid anions are the same as those of the corresponding complexes containing D-form amino acid anions indicates that both complexes have the same symmetrical nature (C_2) and that both complexes have the same conformation for the apical ligand groups, although they are in the relation of an optical isomer. From the molecular-model test, it is found that the mobility of the apical ligand groups is somewhat restricted by the steric hindrance between the apical ligand groups and the coordinated baen. Although, in the cases of Complexes II, III, VI, VII, XV, and XVI, the symmetry of these complexes belongs to C_2, in the cases of Complexes IV, VIII, and XVII, in which both D- and L-form ligands are present, as the configurational effect of the optically-different forms of the apical ligands are not averaged because of the restriction of the mobility of the apical ligand groups, the symmetry of these complexes belongs to C_1. Perhaps this lowering of the symmetry from C_2 to C_1 may make

Table 11. The CD spectra of the complexes (in c/s×10^{-13})

Complex	Solvent	ν ($\Delta\varepsilon_{max}$)	ν ($\Delta\varepsilon_{max}$)	ν ($\Delta\varepsilon_{max}$)	ν ($\Delta\varepsilon_{max}$)
II	H_2O	49.2 (+0.20)	55.6 (−0.63)	62.5 (+2.42)	71.0 (−1.87)
	MeOH	49.2 (−0.45)	55.6 (−2.28)	62.5 (+2.05)	71.0 (−1.34)
III	H_2O	49.2 (−0.21)	55.6 (+0.64)	62.5 (−2.43)	71.0 (+1.88)
	MeOH	49.2 (+0.45)	55.6 (+2.28)	62.5 (−2.05)	71.0 (+1.34)
VI	H_2O	49.2 (+0.80)	55.6 (0.00)	62.5 (+4.87)	71.0 (−3.51)
	MeOH	49.2 (+0.43)	55.6 (−1.75)	62.5 (+4.33)	71.0 (−3.33)
VII	H_2O	49.2 (−0.80)	55.6 (0.00)	62.5 (−4.88)	71.0 (+3.51)
	MeOH	49.2 (−0.44)	55.6 (+1.75)	62.5 (−4.33)	71.0 (+3.32)
IX	H_2O	49.0 (−0.73)	55.6 (−0.72)	62.5 (+4.80)	71.0 (−3.40)
	MeOH	49.0 (+0.31)	55.6 (−2.26)	62.5 (+4.36)	71.0 (−2.80)
X	H_2O	49.0 (+1.20)	55.6 (−1.25)	62.5 (+4.54)	71.0 (−3.55)
	MeOH	49.0 (+0.41)	55.6 (−2.28)	62.5 (+4.94)	71.0 (−3.69)
XI	H_2O	49.0 (+0.73)	55.6 (−0.27)	62.5 (+2.92)	71.0 (−2.25)
	MeOH	49.0 (+0.69)	55.6 (−0.68)	62.5 (+2.17)	71.0 (−1.95)
XIIII	MeOH	49.0 (+0.31)	55.6 (−0.16)	62.5 (+1.81)	71.4 (−1.79)
XIV	MeOH	49.0 (+0.97)	55.6 (+0.76)	62.5 (+3.70)	71.4 (−2.92)
XV	MeOH	49.0 (+0.76)	55.6 (+2.02)	66.6 (−0.31)	74.0 (+0.82)
XVI	MeOH	49.0 (−0.65)	55.6 (−1.73)	66.6 (+0.25)	74.0 (−0.70)

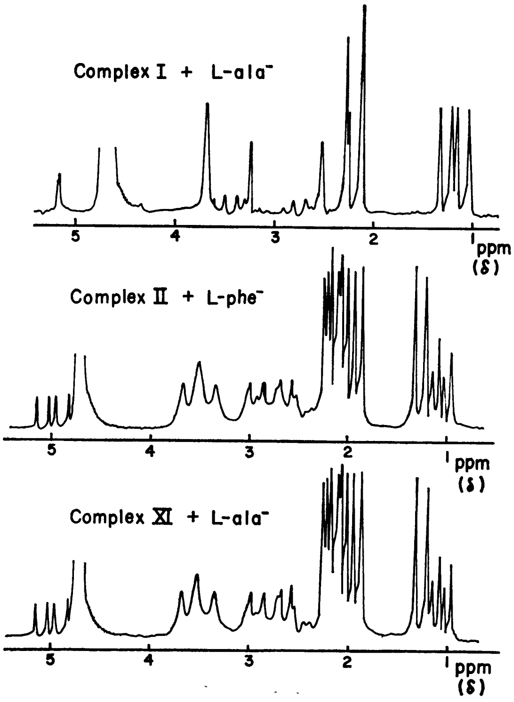

Fig. 4. The NMR spectra of 1 : 2 mixture of complex and potassium salt of amino acid in D_2O. The solution pH is adjusted to about 13 by adding NaOD solution. The compounds are referred to Table 1.

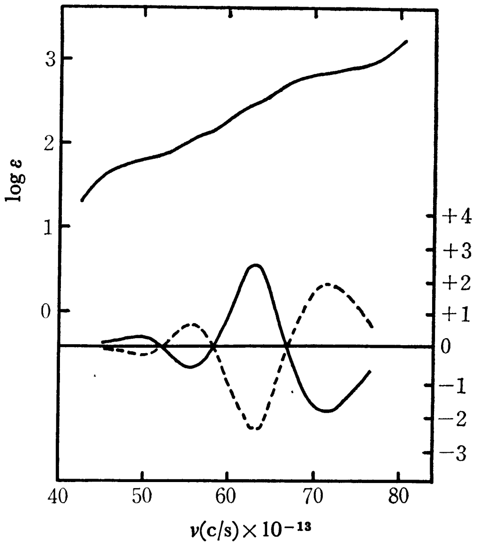

Fig. 5. The AB and CD spectra of K[Co(baen)(L-ala)$_2$] (——) and) K[Co(baen)(D-ala)$_2$] (----) in water.

the main contribution to the peak splitting for the NMR spectra of the complexes containing both D- and L-form ligands. The [Co(baen)(A)(B)]$^-$ complexes (where A and B have the same optical form) show no distinctive peak splitting in their NMR spectra, except when A or B is a phenylalanine anion. These facts indicate that the contribution of the conformation of the apical ligand groups for the peak splitting is bigger than that of the variation in the alkyl group of the amino acid groups. When the complexes contain phenylalanine and the other amino acid anions, because of the big magnetic shielding effect of the phenyl group, the peak splitting is observed in their complexes regardless of the optical forms of the apical ligands. For these complexes, the peak splitting is observed not only in the C=CH and CH_3 signals, but also in the CH_2–CH_2 signal.

On the other hand, when the complexes contain gylcine and β-alanine anions, there is no optically-active form in them. Therefore, no peak splitting is observed for the NMR spectra concerning those of glycine and β-alanine anions.

Table 12. The electronic absorption spectra of the complexes (in c/s$\times 10^{-13}$)

Complex	ν_{sh} (log ε)	ν_{sh} (log ε)	ν_{sh} (log ε)	ν_{sh} (log ε)	ν_{sh} (log ε)	ν_{max} (log ε)
I	49.0 (1.70)	55.0 (1.96)	62.0 (2.45)	71.4 (2.90)	83.0 (3.63)	89.2 (3.86)
II, III, IV	49.2 (1.80)	55.6 (2.05)	62.5 (2.52)	71.4 (2.90)	85.2 (3.76)	89.6 (3.92)
V	49.0 (1.74)	55.5 (2.04)	62.3 (2.48)	71.4 (2.90)	85.2 (3.75)	89.5 (3.89)
VI, VII, VIII	49.0 (1.74)	55.5 (2.06)	62.5 (2.52)	71.0 (2.90)	85.6 (3.79)	89.3 (3.91)
IX	49.6 (1.74)	55.6 (2.04)	62.5 (2.49)	71.0 (2.90)	85.5 (3.74)	89.3 (3.89)
X	49.6 (1.76)	55.6 (2.04)	62.5 (2.48)	71.0 (2.89)	85.2 (3.70)	89.3 (3.88)
XI	49.2 (1.70)	55.6 (2.05)	62.5 (2.50)	71.5 (2.90)	85.2 (3.70)	89.2 (3.88)
XII	49.0 (1.62)	55.5 (1.98)	62.5 (2.56)	71.0 (2.89)	83.3 (3.70)	88.2 (3.86)
XIII	49.0 (1.64)	55.5 (2.00)	62.5 (2.58)	71.0 (2.90)	83.3 (3.72)	88.2 (3.86)
XIV	49.0 (1.62)	55.5 (2.00)	62.5 (2.57)	71.0 (2.90)	83.3 (3.71)	88.2 (3.87)
XV, XVI, XVII	48.0 (1.67)	55.0 (2.08)	64.0 (2.67)	71.0 (2.90)	84.0 (3.60)	88.2 (3.70)

The data of complexes I, II, III, IV, V, VI, VII, VIII, IX, X, and XI are those in water.
The data of complexes XII, XIII, XIV, XV, XVI, and XVII are those in methanol.

CD Spectra of the Complexes. Some typical AB and CD spectra of the complexes are shown in Figs. 5 and 6, while their numerical data are listed in Tables 11 and 12.

The absorption and CD spectra of all the complexes are very complicated because of the π–π^* transition of the baen and charge-transfer transitions,[21–23] and so we can not make band assignemnts at this stage. However, since the CD spectra of the complexes containing L-form ligands are symmetric with those of the corresponding complexes containing D-form ligand, and since the two CD spectra differ only in their signs, by using this CD spectral behavior, we can obtain evidence for the rapid intermolecular exchange reaction of the apical amino acid groups. The CD spectra of mixtures of the complexes containing the L-alanine anion and the free D-alanine anion were measured. When the ratio between the L-alanine complex and the free D-alanine anion was kept at 1 : 1, the observed CD spectrum is that of one-half of the L-alanine complex only. When it was 1 : 2, no CD peaks were observed. When it was 1 : 20, the observed CD spectrum corresponded to that of the D-alanine complex only. These CD spectral changes are found to occur within a few sec. Therefore, it can be concluded that the exchange reactions are very rapid for the cobalt(III) complex, but it is sufficiently slow for all the species in the equilibrium condition to be distinguished separately in the NMR spectra.

These exchange reactions are observed in water, but not in dimethylformamide and dimethylsulfoxide; this is in agreement with the results of the polarographic study.[10] These exchange reactions are thought to be based on the unusual chemical properites of the cobalt(III) complexes containing an unsaturated planar quadridentate ligand.

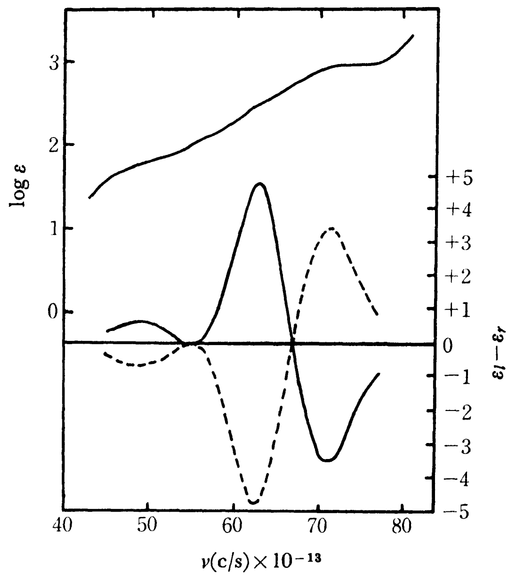

Fig. 6. The AB and CD spectra of K[Co(baen)(L-val)$_2$] (——) and K[Co(baen)(D-val)$_2$] (----) in water.

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