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Base-Catalyzed Isomerization and Racemization Reactions of $[Co(L_1)(L_2)]^+$-Type Complexes (L_1=Iminodiacetato or *N*-Methyliminodiacetato and L_2=3-Azapentane-1,5-diamine or 3-Methyl-3-azapentane-1,5-diamine)

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The isomerization and racemization reactions of the $[Co(ida)(dien)]^+$ and $[Co(ida)(mdien)]^+$ systems were studied in an aqueous solution. The main isomerization path of the $[Co(ida)(dien)]^+$ system was *u-fac*$\rightleftharpoons$*mer*$\rightleftharpoons$*s-fac* and the rate law for each of the processes could be described as $R=k[\text{complex}][OH^-]$. In the $[Co(ida)(mdien)]^+$ system, there was an additional isomerization path of *u-fac*$\longrightarrow$*s-fac*. The equilibrium mole ratio of three isomers was *u-fac*:*mer*:*s-fac*=25:19:56% for $[Co(ida)(dien)]^+$ and *u-fac*:*mer*:*s-fac*=3:3:94% for $[Co(ida)(mdien)]^+$. In the isomerization of $(+)^{CD}_{564}$-*u-fac*-$[Co(mida)(mdien)]^+$, $(+)^{CD}_{582}$-*mer* isomer was stereoselectively produced. The racemization mechanisms of *mer*-$[Co(ida)(dien)]^+$ and *mer*-$[Co(mida)(dien)]^+$ are also discussed.

As part of a study of the structure-reactivity pattern in octahedral complexes, our attention was drawn to cobalt(III) complexes containing two terdentate ligands such as dien, ida, and their analogs.1) This type complex provides three possible geometrical isomers; *s-fac, u-fac,* and *mer* (Fig. 1). Each isomer of $[Co(dien)_2]^{3+}$ isomerized in water at high temperature (82 °C), giving a mixture of all three isomers. The isomerization reaction was thought to proceed through three intramolecular paths; *u-fac*$\rightleftharpoons$*mer*, *mer*$\rightleftharpoons$*s-fac*, and *s-fac*$\rightleftharpoons$*u-fac*.2) We previously studied the isomerization reactions of the $[Co(ida)_2]^-$ and $[Co(ida)(mida)]^-$ systems and found that the reactions proceeded through two intramolecular paths, as shown in Scheme 1. All of the reactions are base-catalyzed and probably involve conjugate base intermediates.3) The isomers of $[Co(mida)_2]^-$, which have no N–H proton to deprotonate, did not isomerize under the same conditions as those for the isomers of $[Co(ida)_2]^-$.4) The isomers of $[Co(edma)_2]^+$ also isomerized to other ones in a basic aqueous solution; however, the main reaction paths are quite different from those of the $[Co(ida)_2]^-$ system.5)

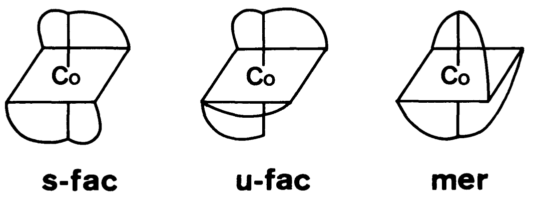


Fig. 1. Three geometrical isomers of the [Co(L)(L′)] type complex, where L and L′ are symmetrical terdentate ligands.

Scheme 1.

Recently, we presented preliminary results concerning the reactivities of the $[Co(ida)(dien)]^+$, $[Co(ida)(mdien)]^+$, $[Co(mida)(dien)]^+$, and $[Co(mida)(mdien)]^+$ complexes.6) In this paper, we describe a detailed study of the isomerization reaction of those complexes. In addition, we also report on rate data regarding racemization for the *mer* isomers of $[Co(ida)(dien)]^+$ and $[Co(mida)(dien)]^+$.

Experimental

Complexes and Reagents. The complexes examined here were prepared according to the methods described in previous papers.7) They are *u-fac*-$[Co(ida)(dien)]Cl\cdot 0.5H_2O$, *mer*-$[Co(ida)(dien)]Cl\cdot H_2O$, *s-fac*-$[Co(ida)(dien)]Cl\cdot 0.5H_2O$, *u-fac*-$[Co(ida)(mdien)]Cl\cdot 1.5H_2O$, *mer*-$[Co(ida)(mdien)]Cl\cdot 2H_2O$, *u-fac*-$[Co(mida)(dien)]Cl\cdot 1.5H_2O$, *mer*-$[Co(mida)(dien)]Cl\cdot 1.5H_2O$, *u-fac*-$[Co(mida)(mdien)]Cl\cdot 3H_2O$, *mer*-$[Co(mida)(mdien)]Cl\cdot 2H_2O$, $(+)^{CD}_{538}$-*u-fac*-$[Co(ida)(dien)]Cl\cdot 2H_2O$ ($\Delta\varepsilon_{538}=+2.014$), $(-)^{CD}_{550}$-*u-fac*-$[Co(ida)(mdien)]Cl\cdot 1.5H_2O$ ($\Delta\varepsilon_{550}=-1.804$), $(+)^{CD}_{544}$-*u-fac*-$[Co(mida)(dien)]Cl\cdot 0.5H_2O$ ($\Delta\varepsilon_{544}=+2.441$), $(+)^{CD}_{564}$-*u-fac*-$[Co(mida)(mdien)]Cl\cdot 3H_2O$ ($\Delta\varepsilon_{564}=+1.658$), $(+)^{CD}_{560}$-*mer*-$[Co(ida)(dien)]Cl\cdot 1.5H_2O$ ($\Delta\varepsilon_{560}=+0.214$), and $(-)^{CD}_{570}$-*mer*-$[Co(mida)(dien)]Cl\cdot 1.5H_2O$ ($\Delta\varepsilon_{570}=-0.205$).

All the chemicals used were of reagent grade, and the deionized water was degassed before use.

Isomerization. ***u-fac*-$[Co(ida)(dien)]^+$:** The following reaction conditions were set: complex concentration, 4.0×10^{-3} M (M=mol dm^{-3}); pH, 10.00±0.03, 10.30±0.03, and 10.60±0.03 (Na_2CO_3–$NaHCO_3$ buffer); ionic strength (*I*), 0.1 M ($NaClO_4$); temperature, 40.0±0.1 °C. The isomerization reaction was started by dissolving the isomer (540.20 mg) in 400 cm^3 of the buffer solution in a reaction vessel kept in a thermostated bath. The temperature and pH of the reaction solution were checked with a thermistor thermometer (TAKARA D221) and a pH meter (TOA TSC-10A), respectively. At prescribed time intervals, a constant volume (30.0 cm^3) of the reaction solution was taken out and acidified to pH 6 in order to stop the reaction, and then applied to a column (3.0 cm×60 cm) of SP-Sephadex C-25 (K^+ form) cation exchanger. On elution with 0.2 M KCl, two bands, el. 1 (*mer*) and el. 2 (*s-fac* and *u-fac*), were separated.

The two eluates were collected separately and concentrated to constant volumes (10 or 20 cm^3) and the amounts of the isomers were spectrophotometrically determined with a JASCO UVIDEC-670 spectrophotometer. The amounts of *u-fac* and *s-fac* were calculated from binary-curve analyses of the absorption spectrum of the concentrated el. 2 eluate. (In this curve analysis, the spectral data at 25 points in the visible region were used.) The analysis calculations were carried out on an NEC PC-9801F computer using the least-squares method. The isomerization reactions of *s-fac-* and *mer*-$[\mathrm{Co(ida)(dien)}]^+$ were carried out by a procedure similar to that used for *u-fac* isomer.

The isomerization reactions for the $[\mathrm{Co(ida)(mdien)}]^+$, $[\mathrm{Co(mida)(dien)}]^+$, and $[\mathrm{Co(mida)(mdien)}]^+$ systems were also conducted according to a similar method as described above.

CD Decrease of *u-fac* Isomers and Racemization of *mer* Isomers. The rates of CD decrease of optically active *u-fac* isomers were measured with a JASCO J-22 spectropolarimeter. A reaction vessel with a jacket and a water-jacket cell mounted in the cell compartment of the spectropolarimeter were thermostated at 40.0 °C with circulating water. The reaction was started by dissolving the complex in 20.0 cm^3 of a buffered solution in the reaction vessel. About 3 cm^3 of this solution was quickly transferred into the cell in order to record the decrease of the CD intensity. The reaction conditions were as follows: complex concentration, 5.0×10^{-3} M; pH, 10.30 ± 0.05 ($\mathrm{Na_2CO_3}$-$\mathrm{NaHCO_3}$ buffer); I, 0.1 M ($\mathrm{NaClO_4}$); temperature, 40.0 ± 0.1 °C.

The racemization reactions of *mer*-$[\mathrm{Co(ida)(dien)}]^+$ and *mer*-$[\mathrm{Co(mida)(dien)}]^+$ were carried out by a procedure similar to that described above. The following reaction conditions were set: complex concentration, 5.02×10^{-3} M; pH, 4.2—6.0 ($\mathrm{CH_3COOH}$-$\mathrm{CH_3COONa}$ buffer); I, 1.0 M ($\mathrm{NaNO_3}$); temperature, 30—40 °C. The ionic product of water at the appropriate temperature was obtained from the literature[8] and the appropriate activity coefficient corrections for ionic strength were made using the same source. The hydroxide concentration could then be calculated. Plots of ln[CD intensity] vs. time gave a straight line over three half-lives, from which the pseudo-first-order rate constant k_{obsd} (s^{-1}) was obtained. Analyses of the kinetic data were carried out using the least-squares method. In each of the kinetic data analyses, the value of the standard deviation was within ±1% of the rate constant.

Results and Discussion

Isomerization of the $[\mathrm{Co(ida)(dien)}]^+$ System. The isomerization reaction of *u-fac*-$[\mathrm{Co(ida)(dien)}]^+$ was carried out under the conditions of pH 10.30 and I=0.1 M at 40.0 °C. Figure 2-a shows the concentration changes of the starting material and reaction products. A part of the numerical data are listed in Table 1.[9] In this reaction, *mer* was first formed and *s-fac* was subsequently formed. After about 25 h, the amount of *mer* began to decrease. The *s-fac* isomer gradually increased in its amount, and was a major product at the final stage of the reaction. Isomerization reactions using *mer* and *s-fac* as the starting materials were also carried out under the same conditions as used for *u-fac*. The results are shown in Figs. 2-b and 2-c and a part of the numerical data are listed in Table 1. The isomerization of *mer* proceeded rapidly, and *u-fac* and *s-fac* were formed simultaneously. The amount of *u-fac* formed was maximal about 30 h after the start of the reaction; it then gradually decreased. However, the isomerization of

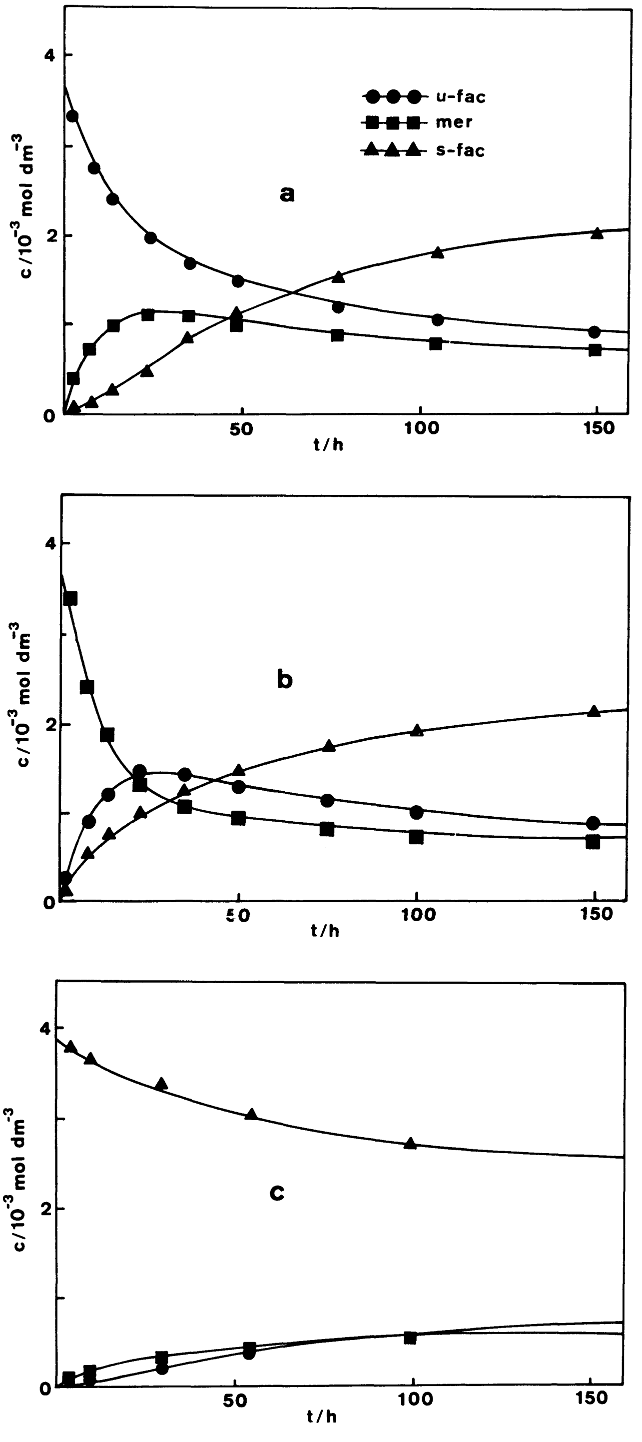


Fig. 2. The isomerization reaction of $[\mathrm{Co(ida)(dien)}]^+$ in a basic aqueous solution (pH 10.30) at 40.0°C. Starting isomers are *u-fac (a), mer* (b), and *s-fac* (c). Each of the lines is the curve calculated from the data at Table 2 by using Runge-Kutta method.

Table 1. Concentration Changes of the Starting Materials and Products in the Isomerization Reaction (40.0 °C, pH 10.30)

(i) *u-fac*-[Co(ida)(dien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
1.5	3.43	0.28	0.01
8.0	2.75	0.70	0.10
23.5	1.95	1.04	0.45
49.0	1.51	0.98	1.13
150.0	0.89	0.68	1.83

(ii) *mer*-[Co(ida)(dien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
1.5	0.23	3.43	0.18
8.0	0.87	2.42	0.51
14.0	1.16	1.87	0.82
35.0	1.37	1.10	1.24
100.5	0.91	0.73	1.90

(iii) *s-fac*-[Co(ida)(dien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
4.0	0.03	0.06	3.83
10.0	0.09	0.14	3.75
30.0	0.25	0.30	3.51
55.0	0.36	0.38	3.11
100.0	0.55	0.48	2.86

(iv) *u-fac*-[Co(ida)(mdien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}			
	u-fac	*mer*	*s-fac*	pink
0.2	3.62	0.19	0.34	0.12
0.5	3.11	0.25	0.85	0.15
1.2	2.47	0.41	1.30	0.15
4.0	1.04	0.30	3.06	0.04
6.0	0.62	0.25	3.57	0

(v) *mer*-[Co(ida)(mdien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}			
	u-fac	*mer*	*s-fac*	pink
0.2	0.16	3.11	0.33	0.14
0.5	0.49	2.12	0.98	0.24
1.2	0.79	1.00	1.75	0.29
3.5	0.57	0.31	2.83	0.16
5.0	0.44	0.20	3.13	0.12

(vi) *u-fac*-[Co(mida)(dien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
1.0	2.81	0.92	0.09
4.0	1.52	1.75	0.10
6.0	1.21	1.77	0.10
12.0	1.08	1.49	0.04
24.0	1.00	1.05	0.05

(vii) *mer*-[Co(mida)(dien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
1.0	0.58	3.42	0.22
2.0	0.82	2.92	0.10
8.0	1.22	2.10	0.07
13.0	1.08	1.55	0.04
24.0	0.90	1.06	0.10

(viii) *u-fac*-[Co(mida)(mdien)]$^+$

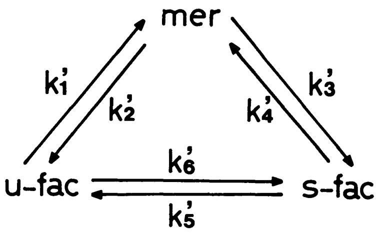
t/min	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
10	2.55	0.38	0.21
30	1.04	0.70	0.21
50	0.47	0.86	0.16
70	0.29	0.83	0.17
90	0.13	0.75	0.13

(ix) *mer*-[Co(mida)(mdien)]$^+$

t/h	Concn/10^{-3} mol dm^{-3}		
	u-fac	*mer*	*s-fac*
0.5	0.10	3.25	0.17
2.0	0.14	2.44	0.46
6.0	0.11	1.25	0.87
14.0	0.31	0.38	1.10
25.0	0.35	0.14	1.12

s-fac (Fig. 2-c), of which the rate was very slow, produced *mer* at first and then *u-fac*. The amount of *u-fac* exceeded that of *mer* after about 70 h. The equilibrium mole ratio of the three isomers was *u-fac*: *mer*:*s-fac*=25:19:56%.

In the isomerization of the [Co(ida)(dien)]$^+$ system, the reaction paths are described as Scheme 2. The rate constants (k_1'—k_6') were obtained on the basis of the following procedure. Tentative values of the rate constants, k_1'—k_6', were estimated from the initial rates and the equilibrium mole ratio of the three isomers. Curves of the concentration change of each isomer was obtained by Runge–Kutta method[10] using these tentative rate constants. The calculation of Runge–Kutta method was repeated using the modified values of the rate constants until the difference between the calculated curves and the observed ones was minimized. The results are listed in Table 2 and the best-fit curves are shown in Fig. 2. The *u-fac*$\rightleftharpoons$*s-fac* change hardly occurs (Table 2). Thus, the main



Scheme 2.

Table 2. The Rate Constants for the Isomerization of the $[Co(ida)(dien)]^+$ and $[Co(ida)(mdien)]^+$ Systems (40.0 °C, $I=0.1$ M)

		$[Co(ida)(dien)]^+$						Co(ida)(mdien)]$^+$	
		pH[a)] 10.00		pH[a)] 10.30		pH[a)] 10.60		pH[a)] 10.30	
		k_n'[b)]	k_n[c)]	k_n'[b)]	k_n[c)]	k_n'[b)]	k_n[c)]	k_n'[b)]	k_n[c)]
u-fac ⟶ *mer*	(1)	6.2	17	11	15	22	15	38	51
mer ⟶ *u-fac*	(2)	8.0	22	14	19	28	19	83	112
mer ⟶ *s-fac*	(3)	3.2	8.4	5.6	7.5	12	8.4	132	117
s-fac ⟶ *mer*	(4)	1.0	2.8	1.8	2.5	6.0	4.0	2.1	2.8
s-fac ⟶ *u-fac*	(5)	0	0	0	0	0	0	3.1	4.2
u-fac ⟶ *s-fac*	(6)	0.5	1.4	0.9	1.2	1.9	1.2	101	135

a) Na_2CO_3-$NaHCO_3$ buffer. b) $\times 10^{-6}\ s^{-1}$. c) $\times 10^{-3}\ M^{-1}\ s^{-1}$.

isomerization paths of $[Co(ida)(dien)]^+$ system can be described as in Scheme 1, which is found in the isomerization reaction of the $[Co(ida)_2]^-$ system.

The isomerization reaction of the $[Co(ida)(dien)]^+$ system was also carried out under the conditions of pH 10.00 and 10.60 at 40.0 °C, and analyzed by the same method as described above. The pseudo-first-order rate constants (k_n') and second-order rate constants ($k_n=k_n'/[OH^-]$) are listed in Table 2. Judging from the constancy of k_n, the rate law for each isomerization path can be described as $R=k_n[\text{complex}][OH^-]$. It is probable that the isomerization of the $[Co(ida)(dien)]^+$ system proceeds through the conjugate base intermediate. In the isomerization reaction of the $[Co(ida)(dien)]^+$ system, other species except for three geometrical isomers were little detected. This fact suggests that the ligand dissociation is not involved in the reaction; if such dissociation was involved, the reaction should provide hydrolysis products. Thus, the isomerization must involve only the intramolecular paths. We can consider two possibilities for the intramolecular rearrangement; twist proceeding through the trigonal prismatic transition state and bond rupture forming a five-coordinate intermediate and followed by rearrangement within the intermediate by a subsequent recoordination of the COO^- group. The *mer*$\rightleftharpoons$*s-fac* change (in Scheme 2) can be sufficiently explained in terms of only the bond-rupture mechanism, whereas the *u-fac*$\rightleftharpoons$*mer* (and also *u-fac*$\rightleftharpoons$*s-fac*) change may be described by the mechanisms of both bond rupture and twist.

Isomerization of the $[Co(ida)(mdien)]^+$ System. The isomerization reactions using *u-fac*- and *mer*-$[Co(ida)(mdien)]^+$ as the starting materials were carried out under the conditions of pH 10.30 and $I=0.1$ M at 40.0 °C. The reaction rate was relatively faster in the $[Co(ida)(mdien)]^+$ system than in the $[Co(ida)(dien)]^+$ system. The concentration changes in the starting materials and products are shown in Figs. 3-a and 3-b. A part of the numerical data (five data points) are listed in Table 1.[9)] In the isomerization reactions of both *u-fac* and *mer*, a small amount of pink by-product was formed together with the other isomers in the initial stage of the reactions. The pink by-product was eluted prior to the mixture of *u-fac* and *s-fac* but posterior to *mer* on SP-Sephadex column chromatograph. Therefore, the pink by-product must be +1 charged one. The pink by-product could not be isolated, because it was unstable and was formed only in a small amount. During the concentration of a solution containing the pink by-product under reduced pressure at 35—40 °C, the pink by-product changed to *s-fac*. The amount of the pink by-product was esti-

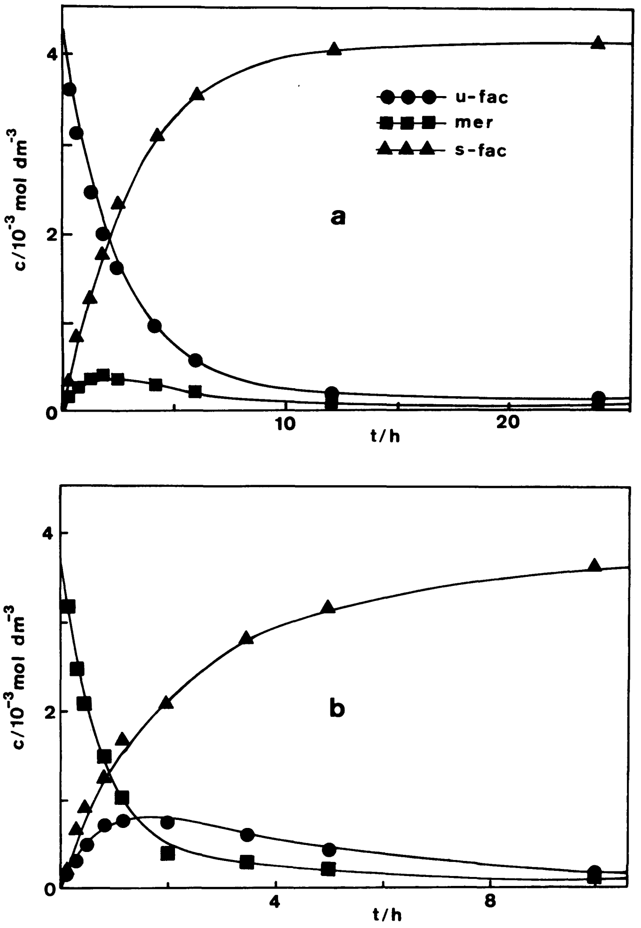


Fig. 3. The isomerization reaction of $[Co(ida)(mdien)]^+$ in a basic aqueous solution (pH 10.30) at 40.0 °C. Starting isomers are *u-fac* (a) and *mer* (b). Each of the lines is the curve calculated from the data in Table 2 by using Runge-Kutta method.

mated on the basis of the absorption spectrum of the *s-fac* formed from the pink by-product. The amount of the pink by-product was maximal about 30 min after the start of the reaction. It is likely that the pink by-product was a monoaqua species whose formation competes with isomerization in a bond-rupture process. No other species, except for three geometrical isomers and pink by-product, were detected in the isomerization reaction of the [Co(ida)(mdien)]$^+$ system. At the final stage of the reaction, *s-fac* was the main product.

The base-catalyzed isomerization reaction of the [Co(ida)(mdien)]$^+$ system was also analyzed by the Runge–Kutta method assuming Scheme 2. In this calculation, the formation of the pink by-product was neglected. The results are listed in Table 2, indicating that the reactions proceed through three intramolecular paths. The calculated curves of the concentration changes by Runge-Kutta method are shown in Fig. 3. It is worth noting that the *u-fac*⟶*s-fac* change occurs very easy in the [Co(ida)(mdien)]$^+$ system but hardly in the [Co(ida)(dien)]$^+$ system.

The *u-fac*$\rightleftharpoons$*mer* change can be explained in terms of both bond rupture and twist. However, the fact that the isomerization rate is faster in the mdien complex than in the dien complex (Tables 1 and 2) is not favorable to the twist mechanism, judging from the view point of the intramolecular steric factor. The equilibrium mole ratio of three isomers of [Co(ida)(mdien)]$^+$ were *u-fac*:*mer*:*s-fac*=3:3:94%. The equilibrium further shifts to *s-fac* side compared with that of the [Co(ida)(dien)]$^+$ system. Similarly, the equilibriums of [Co(ida)(mida)]$^-$ and [Co(dien)(mdien)]$^{3+}$ systems shift more to *s-fac* side compared with those of the [Co(ida)$_2$]$^-$ and [Co(dien)$_2$]$^{3+}$ systems respectively.[2,3] These tendencies may be explained by the intramolecular steric repulsion.

Isomerization of the [Co(mida)(dien)]$^+$ and [Co(mida)(mdien)]$^+$ Systems. The isomerization reactions of the [Co(mida)(dien)]$^+$ and [Co(mida)(mdien)]$^+$ systems were studied under the conditions of pH 10.30 at 40.0 °C. A part of the numerical data are listed in Table 1. The *s-fac* isomer of [Co(mida)(dien)]$^+$ was stable under the reaction conditions; other species, such as isomerization and/or hydrolysis products, were scarcely detected throughout a reaction of over 80 h. As shown in Table 1, the *u-fac*- and *mer*-[Co(mida)(dien)]$^+$ interconverted each other accompanying the formation of unknown by-products with more than 2+ charge in a considerable amount. The *s-fac* isomer was scarcely formed in the isomerization reactions of *u-fac* and *mer*. In the isomerization of *mer*-[Co(mida)(mdien)]$^+$, *u-fac* and *s-fac* were formed simultaneously, while in the isomerization of *u-fac*-[Co(mida)(mdien)]$^+$, *mer* was mainly formed. The isomerization of *s-fac* was very slow. In these isomerization reactions, considerable amounts of unknown by-products with more than 2+ charge were formed. The isomerization reactions of the [Co(mida)(dien)]$^+$ and [Co(mida)(mdien)]$^+$ systems were complicated, so that the reaction processes could not be analyzed.

The CD Decrease of Optically Active *u-fac* Isomers. The rates of CD decrease of optically active *u-fac* isomers were measured under the conditions of pH 10.30 at 40.0 °C. In each case of [Co(ida)(dien)]$^+$, [Co(ida)(mdien)]$^+$, and [Co(mida)(dien)]$^+$, the intensities of CD at two arbitrary wavelengths decreased in the same ratio, and the isocircular dichroism points lay on the base line. This fact indicates that no optically active products are formed. The rate constants of the CD decrease, k_{CD} (s^{-1}), for $(+)^{CD}_{538}$-*u-fac*-[Co(ida)(dien)]$^+$ is 24×10^{-6} s^{-1}, which is larger than the sum of values of k_1' and k_6' (Table 2), probably indicating that racemization of *u-fac* itself occurs. The value of k_{CD} for $(-)^{CD}_{550}$-*u-fac*-[Co(ida)(mdien)]$^+$ is 128×10^{-6} s^{-1}, which is nearly equal to the sum of the values of k_1' and k_6'. Therefore, the CD decrease of *u-fac*-[Co(ida)(mdien)]$^+$ is attributed to the isomerization reaction. The rate of CD decrease for $(+)^{CD}_{544}$-*u-fac*-[Co(mida)(dien)]$^+$ ($k_{CD}=84\times10^{-6}$ s^{-1}) was also close to the rate of the decrease of the *u-fac* due to isomerization and decomposition.

For each of [Co(ida)(dien)]$^+$, [Co(ida)(mdien)]$^+$, and [Co(mida)(dien)]$^+$, no optically active *mer* isomer was obtained from the isomerization reaction of optically active *u-fac* (as described above). However, this fact does not imply that the path of the *u-fac*$\rightleftharpoons$*mer* change is not stereoselective, because the racemizations of these *mer* are very fast under the present reaction conditions (vide post).

Figure 4 shows the CD spectral change of $(+)^{CD}_{564}$-*u-fac*-[Co(mida)(mdien)]$^+$ with the passage of time under the conditions of pH 10.30 at 40.0 °C. The isocircular

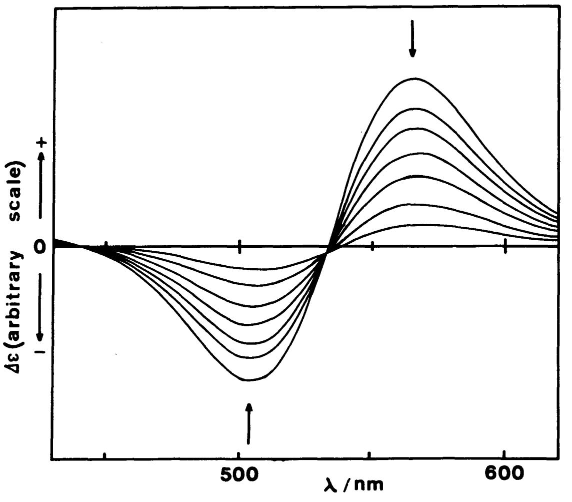


Fig. 4. The CD spectral change of $(+)^{CD}_{564}$-*u-fac*-[Co(mida)(mdien)]$^+$ in a basic aqueous solution (pH 10.30) at 40.0 °C. Each of the curves was recorded at 2, 12, 19, 28, 39, 60, and 101 min, respectively.

dichroism points do not lie on the base line. This observation indicates the formation of an optically active product (*mer*). The reaction solution was acidified in order to stop the reaction 30 min after its start; then, optically active *mer* in the reaction solution was isolated by SP-Sephadex column chromatography. As shown in Fig. 5, the *mer* formed from $(+)^{\mathrm{CD}}_{564}$-*u-fac* isomer is $(+)^{\mathrm{CD}}_{582}$ form, and its optical purity is presumed to be considerably high, because its CD strength is comparable to that of pure $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$. The absolute configuration of $(+)^{\mathrm{CD}}_{564}$-*u-fac* has been determined to *ΛΔΛ*.[7a] The absolute configuration of $(+)^{\mathrm{CD}}_{582}$-*mer* can be assigned to *λ*-spiral by a comparison of the CD spectral pattern with that of $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$, the absolute configuration of which has been determined to be *δ*-spiral by the X-ray diffraction method.[12] The stereoselectivity in the *u-fac*⟶*mer* change (Scheme 3) may be attributed to the steric repulsion of two CH_3 groups in the isomerization process.

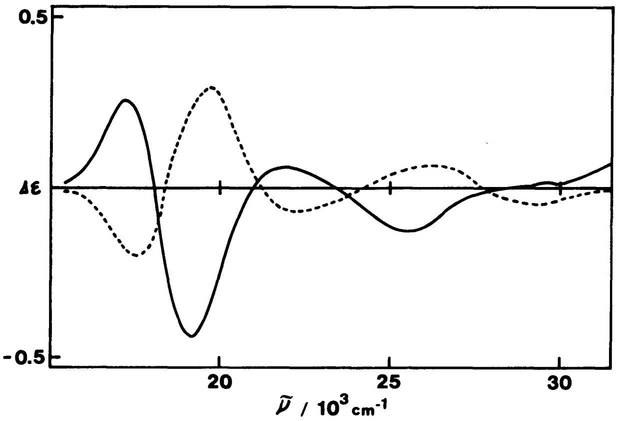
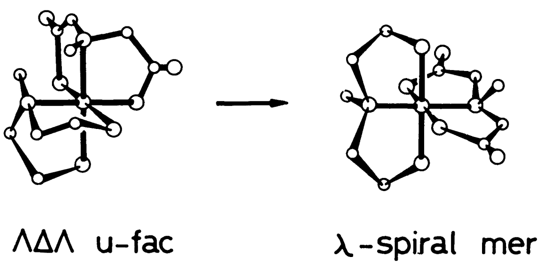


Fig. 5. CD spectral measured in 0.1 M HCl: $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$ (……) and $(+)^{\mathrm{CD}}_{582}$-*mer*-[Co(mida))(mdien)]$^+$ (—) formed from $(+)^{\mathrm{CD}}_{564}$-*u-fac* isomer.

Racemization of *mer*-[Co(ida)(dien)]$^+$ and *mer*-[Co(mida)(dien)]$^+$. Two *mer* isomers, *mer*-[Co(ida)(dien)]$^+$ and *mer*-[Co(mida)(dien)]$^+$, have been resolved into optically active ones; however, we have not yet been successful with *mer*-[Co(ida)(mdien)]$^+$. The enantiomer of these *mer* are designated by the *δ*- or *λ*-spiral configuration, due to the arrangement of the two trans N–H groups in *mer*-[Co(ida)(dien)]$^+$ or due to the arrangement of the trans N–H and N–CH_3 groups in *mer*-[Co(mida)(dien)]$^+$; the absolute configurations of $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$ and $(-)^{\mathrm{CD}}_{560}$-*mer*-[Co(ida)(dien)]$^+$ are assigned to the *δ*-spiral configuration.[12] The CD spectra of $(+)^{\mathrm{CD}}_{560}$-*mer*-[Co(ida)(dien)]$^+$ and $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$ changed with time in an acetate buffer solution (pH 4.20—6.00 at 30—40 °C). The isocircular dichroism points lay on the base line and the values of the CD intensities at various wavelengths decreased in the same ratio. The absorption spectra did not change during a CD measurement, indicating that no isomerization and/or hydrolysis oc-



Scheme 3.

Table 3. Rate Constants and Activation Parameters for Racemization of $(+)^{\mathrm{CD}}_{560}$-*mer*-[Co(ida)(dien)]$^+$ and $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$ Ions (I=1.0 M)

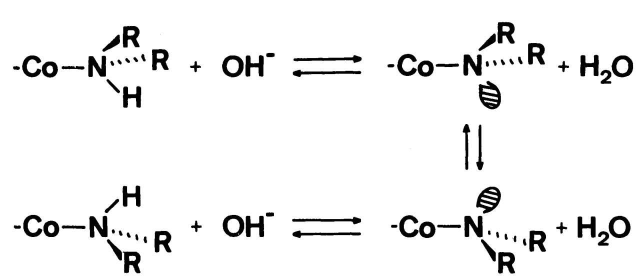
(i) $(+)^{\mathrm{CD}}_{560}$-*mer*-[Co(ida)(dien)]$^+$

T / °C	pH$^{a)}$	k_{rac}' / 10^{-4} s^{-1}	k_{rac} / 10^4 M^{-1} s^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}
30.0	5.10	1.28	5.30	72.7±6.5	85.3±21.1
30.0	5.37	2.34	5.21		
30.0	5.70	5.03	5.23		
30.0	6.00	9.38	4.89		
35.0	5.11	2.87	8.13		
40.0	5.06	6.19	14.0		

(ii) $(-)^{\mathrm{CD}}_{570}$-*mer*-[Co(mida)(dien)]$^+$

T / °C	pH$^{a)}$	k_{rac}' / 10^{-4} s^{-1}	k_{rac} / 10^4 M^{-1} s^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}
30.0	4.20	1.60	52.6	59.7±1.3	61.4±4.3
30.0	4.41	2.63	53.3		
30.0	4.75	5.55	51.4		
30.0	5.34	21.9	52.2		
35.0	4.20	3.40	78.3		
40.0	4.20	7.15	117		

a) CH_3COOH-CH_3COONa buffer.



Scheme 4.

curred. Therefore, the CD decreases can be due to racemizations of *mer*, themselves. The progress of the racemization was followed by monitoring the decrease of the CD intensity at 560 nm for *mer*-[Co(ida)(dien)]$^+$ and at 570 nm for *mer*-[Co(mida)(dien)]$^+$. Kinetic data are summarized in Table 3. The values of the racemization rate constant k_{rac} ($=k_{rac}'/[OH^-]$) for *mer*-[Co(ida)(dien)]$^+$ at 30.0 °C are essentially constant, so that the rate law is described as $R=k_{rac}[\text{complex}][OH^-]$. Activation energies E_a were calculated by a least-squares method of the Arrhenius plots of k_{rac}. The activation parameters calculated for the two complexes are given in Table 3. The racemization rate of *mer*-[Co(mida)(dien)]$^+$ is about one order faster than that of *mer*-[Co(ida)(dien)]$^+$, and the activation enthalpy of the former is smaller than that of the latter. It seemes likely that the electron-donative CH_3 group exerts a trans effect in *mer*-[Co(mida)(dien)]$^+$, enhancing the racemization rate. A similar trans effect (enhancing of the racemization rate) was observed in the racemization of *mer*-[Co(edma)(mdien)]$^{2+}$.[13]

All of the racemization data for the present complexes can be explained according to the mechanism shown in Scheme 4, proposed for the racemizations of *mer*-[Co(dien)$_2$]$^{3+}$[14] and *mer*-[Co(edma)(dien)]$^{2+}$.[13] This proposal can be supported by the fact that optically active *mer*-[Co(mida)(mdien)]$^+$ did not racemize, even in a weakly basic aqueous solution.

The racemization rates for *mer*-type complexes increase in the order of [Co(dien)$_2$]$^{3+}$<[Co(edma)(dien)]$^{2+}$<[Co(ida)(dien)]$^+$. The difference in the racemization rates may be attributed to the electronic property of the chelates. The electronegative carbonyl group decreases the electron density on the secondary amine nitrogen center, in which inversion occurs. Consequently, the pre-equilibrium of Scheme 4 displaces to the deprotonated form and the racemization rate increases.

References

1) Abbreviations used: dien, 3-azapentane-1,5-diamine; ida, iminodiacetate dianion; mdien, 3-methyl-3-azapentane-1,5-diamine; mida, *N*-methyliminodiacetate dianion; edma, ethylenediamine-*N*-acetate anion.

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