2422 © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 2422—2427 (1984) [Vol. 57, No. 9

The Base-Catalyzed Isomerization of the (Iminodiacetato)(*N*-methyliminodiacetato)cobaltate(III) and Bis(iminodiacetato)cobaltate(III) Ions

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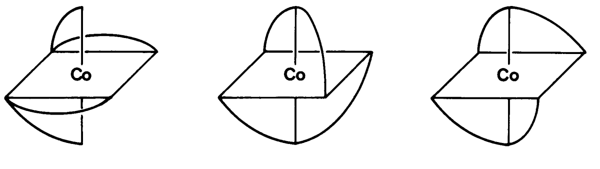
(Received February 16, 1984)

The isomerization reaction among three geometrical isomers of [Co(ida)(mida)]$^-$ was studied in a basic aqueous solution. It has been found that the reaction scheme is *u-fac*$\rightleftharpoons$*mer*$\rightleftharpoons$*s-fac*. The rates of these isomerization paths have been determined as the functions of pH and temperature. The rate of the *u-fac*$\rightleftharpoons$*mer* change is considerably faster than that of the *mer*$\rightleftharpoons$*s-fac* change. The CD loss of the optically active *u-fac* isomer is caused by the isomerization process of *u-fac*$\rightleftharpoons$*mer*. The isomerization of the [Co(ida)$_2$]$^-$ system has also been measured, and the rate data analysed according to the same scheme as that used for the [Co(ida)(mida)]$^-$ system. It is suggested that the isomerizations of the [Co(ida)(mida)]$^-$ and [Co(ida)$_2$]$^-$ systems proceed through a conjugate-base intermediate.

Octahedral complexes containing two symmetrical terdentate ligands, such as dien, ida, and their analogs,[1] provide three possible geometrical isomers: *s-fac, u-fac,* and *mer* (Fig. 1). Legg and Cooke first isolated three geometrical isomers of [Co(ida)(dien)]$^+$.[2] Since then, all geometrical isomers possible in [Co(dien)$_2$]$^{3+}$ and [Co(dien)(mdien)]$^{3+}$ have been prepared by two groups, Keene *et al.*[3] and Kojima *et al.*[4] The series of the geometrical isomers of [Co(ida)$_2$]$^-$ became complete when the *mer* isomer was reported by Koine *et al.*[5] Recently, in our laboratory the *u-fac* isomers of [Co(mida)$_2$]$^-$ and [Co(eida)$_2$]$^-$, which had been considered not to form because of intramolecular repulsions, were prepared under acidic conditions,[6] and the crystal structure of *u-fac*-K[Co(mida)$_2$]·1.5H$_2$O was determined by X-ray analysis.[7]

Although numerous data of the stereochemistry of the terdentate-ligand complexes have been reported,[8] few data on the rearrangement reactions (isomerization and racemization) of these complexes have been reported. Rearrangements in the octahedral complexes can occur by either of two path ways; the intramolecular pathway or the complete ligand-dissociation pathway. The major pathway of the intramolecular rearrangements involves twist and bond-rupture mechanisms, but the choice between twist and bond-rupture alternatives has seldom been unambiguous. It was hoped that the use of the terdentate-ligand complexes in mechanistic studies of rearrangement reactions might offer an opportunity of distinguishing between twist and bond-rupture alternatives, since the coupled chelate rings restrict the number of possible interconversions.



u-fac mer s-fac

Fig. 1. Three geometrical isomers of the [Co(L)$_2$] type complex, where L is a symmetrical terdentate ligand.

Searle *et al.* studied the isomerization of the [Co(dien)(mdien)]$^{3+}$ and [Co(dien)$_2$]$^{3+}$ complexes and proposed a mechanism occurring through a transient five-coordinate intermediate formed by bond-rupture.[9] The racemization rate of *mer*-[Co(dien)$_2$]$^{3+}$ was also measured.[10] This reaction process involves a change in the chiral disposition of two N–H bonds at the secondary nitrogen centers. Cooke has described the *u-fac*- and *s-fac*-[Co(ida)$_2$]$^-$ complexes as being isomerized to each other at a rate depending on the base concentration, and said that the equilibrium distribution of the isomers at room temperature was 28% *u-fac* and 72% *s-fac*.[11] Previously, we ourselves presented preliminary results concerning the reactivities of the [Co(ida)$_2$]$^-$, [Co(ida)(mida)]$^-$,[12] and [Co(mida)$_2$]$^-$ complexes.[6] In the present paper, we will describe a detailed study of the isomerization of the [Co(ida)(mida)]$^-$ and [Co(ida)$_2$]$^-$ systems.

Experimental

Preparation of Complexes. The three geometrical isomers of K[Co(ida)$_2$] and the *u-fac* and *s-fac* isomers of K[Co(ida)(mida)] were prepared according to the method reported in our previous papers[6,12]: *s-fac*-K[Co(ida)$_2$]·2H$_2$O, *u-fac*-K[Co(ida)$_2$]·2.5H$_2$O, *mer*-K[Co(ida)$_2$]·H$_2$O, *u-fac*-K[Co(ida)(mida)]·2H$_2$O, and *s-fac*-Na[Co(ida)(mida)]·H$_2$O.

mer-K[Co(ida)(mida)]·0.5H$_2$O: This complex was obtained by the isomerization of *u-fac*-[Co(ida)(mida)]$^-$ in a weak basic aqueous solution. Five grams of *u-fac*-K[Co(ida)(mida)]·2H$_2$O was dissolved in 250 cm^3 of water, after which the solution was adjusted to pH 8.4—8.5 with potassium hydroxide. An isomerization reaction was carried out at 30 °C for 40 min with constant stirring. The resulting solution was slightly acidified (pH 5—6) with acetic acid and evaporated quickly under reduced pressure at 30—35 °C until crystals of the unreacted *u-fac* isomer deposited. A large amount of methanol was added to them, and the *u-fac* isomer was filtered off. The filtrate was evaporated again, and the remaining *u-fac* isomer was removed. By repeating these procedures several times, the crude *mer* isomer was obtained. Recrystallization was carried out from a small amount of water by adding a mixture of methanol–acetone. The fine red crystals thus deposited were filtered and washed with acetone. Found: C, 28.18; H, 3,82; N, 7.27%. Calcd for K[Co(ida)(mida)]·0.5H$_2$O: C, 28.21; H, 3.42; N, 7.31%.

Optical Resolution. The *u-fac* isomers of [Co(ida)$_2$]$^-$

and [Co(ida)(mida)]$^-$ were resolved into optically active isomers by the methods described in our previous papers[6,12]: $(+)_{589}$-*u-fac*-K[Co(ida)(mida)]·1.5H_2O ($\Delta\varepsilon_{592}=-2.52$, $\Delta\varepsilon_{521}=+2.86$) and $(+)_{589}$-*u-fac*-K[Co(ida)$_2$]·H_2O ($\Delta\varepsilon_{588}=-2.43$, $\Delta\varepsilon_{509}=+2.54$).

Kinetic Studies. All the chemicals were of a reagent grade, and deionized water was degassed before use. The isomerization reactions were studied spectrophotochemically with the use of a Hitachi 557 spectrophotometer. The reaction vessel with jacket and the cell mounted in the cell holder of the spectrophotometer were thermostated at a constant temperature (±0.1 °C) with circulating water from a constant-temperature bath. During the experiments, the temperatures of the reaction vessel and cell were checked with a thermistor thermometer (Takara D221), and the pH of the reaction solution in the vessel by a Toa TSC-10A pH meter.

The reaction was started by stirring a buffer solution (2.0 cm^3) into the complex solution (18.0 cm^3) in the reaction vessel; *ca.* a 3-cm^3 quantity of this solution was then quickly transferred to the cell in order to record the spectral change in the suitable wave-length range at desired time-intervals. All solutions were prepared at the temperature where runs were to be made, and the following conditions were set: pH, 7.5—10.5 (Na_2HPO_4-KH_2PO_4 or Na_2CO_3-$NaHCO_3$ buffer); complex concentration, 2.8—3.0×10^{-3} mol dm^{-3}; ionic strength, 0.1 ($NaClO_4$); temperature, 25—35 °C. In the case of the isomerization between *mer* and *u-fac*, the wave-lengths chosen for kinetic study were 511 and 503 nm for the [Co(ida)(mida)]$^-$ and [Co(ida)$_2$]$^-$ systems respectively. For the isomerization from an equilibrium mixture of *u-fac* and *mer* to *s-fac*, these wave-lengths at the isosbestic points between *u-fac* and *mer* were chosen: 559 and 548 nm for the [Co(ida)(mida)]$^-$ and [Co(ida)$_2$]$^-$ systems respectively.

The rates of the loss of CD magnitude were measured by means of a JASCO J-22 spectrophotometer using the method and conditions described above.

The plots of $\ln(D_0-D_{eq})/(D_t-D_{eq})$ *vs.* the time and ln[CD magnitude] *vs.* the time gave straight lines over three times the half-lives. Analyses of the kinetic data were carried out on a NEC-8800 computer using the least-squares methods. In each of the rate analyses, the value of the standard error was within ±2% of the rate constant.

Results and Discussion

mer-*K[Co(ida)(mida)] Complex.* The absorption spectrum of *mer*-[Co(ida)(mida)]$^-$, which was newly prepared, is shown in Fig. 2, together with those of the *u-fac* and *s-fac* isomers reported in a previous paper;[12] the numerical data are as follows. 1st band ($^1A_1\rightarrow{}^1T_1$), $\lambda_{sh}\simeq625$ nm ($\log\varepsilon\simeq1.39$) and $\lambda_{max}=511$ nm ($\log\varepsilon=2.53$); 2nd band ($^1A_1\leftrightarrow{}^1T_2$). $\lambda_{max}=384$ nm ($\log\varepsilon=2.36$); CT band, $\lambda_{max}=226$ nm ($\log\varepsilon=4.29$). The spectral behavior of *mer*-[Co(ida)(mida)]$^-$ is quite similar to that of *mer*-[Co(ida)$_2$]$^-$ and *mer*-[Co(mida)$_2$]$^-$. In these *mer* isomers, the 1st and 2nd absorption maxima shift to the lower-energy side in the order of [Co(ida)$_2$]$^-$<[Co(ida)(mida)]$^-$<[Co(mida)$_2$]$^-$, while the 1st and 2nd bands increase in intensity in the order of [Co(mida)$_2$]$^-$<[Co(ida)(mida)]$^-$<[Co(ida)$_2$]$^-$. These trends are in agreement with those observed in the *u-fac* isomers of [Co(ida)$_2$]$^-$, [Co(ida)(mida)]$^-$, and [Co(mida)$_2$]$^-$.[12]

As the *mer* isomers of [Co(ida)(mida)]$^-$ and [Co(ida)$_2$]$^-$ are not so stable in an aqueous solution (extremely unstable in a basic aqueous solution) and easily isomerize to the *u-fac* and/or *s-fac* isomers, the procedure of separating the *mer* isomer from the others should be carried out quickly at a low temperature. This is one of the reasons for the lower yields of *mer*-K[Co(ida)(mida)] and *mer*-K[Co(ida)$_2$]. These *mer* isomers have the dissymmetrical structure which arises from a chiral disposition of two noncoplanar ligands, but have not yet been resolved into optically active isomers. On the other hand, *mer*-[Co(mida)$_2$]$^-$ is quite stable, even in a weak basic aqueous solution, and has been resolved into optically active isomers.[5,13]

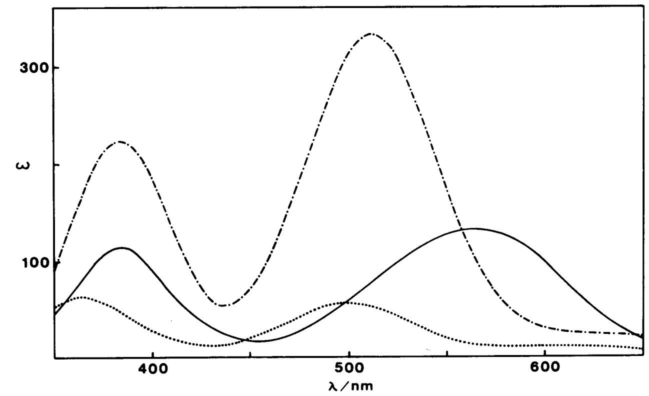


Fig. 2. Absorption spectra of three geometrical isomers of [Co(ida)(mida)]$^-$ in aqueous solution: *u-fac* (——), *mer* (—·—), and *s-fac* (······).

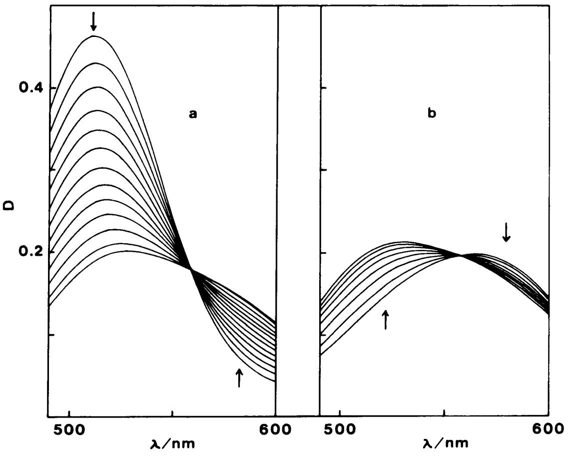


Fig. 3. The time-course changes of absorption spectra of *mer*- and *u-fac*-[Co(ida)(mida)]$^-$ in weak basic aqueous solutions at 30.0 °C. The record intervals are arbitrary: (a) *mer* (2.81×10^{-3} mol dm^{-3}), pH=8.02; (b) *u-fac* (2.98×10^{-3} mol dm^{-3}), pH=7.80.

Isomerization Reactions of the [Co(ida)(mida)]⁻ System. Figure 3 shows the spectral changes in *mer*- and *u-fac*-[Co(ida)(mida)]$^-$ in weak basic solutions. The *u-fac* isomer changed its spectrum with an isosbestic point at 559 nm, and it gave the final curve in Fig. 3-b after *ca.* 2 h. (We use the term "pseudo-equilibrium state" to describe this state.) However, after that time the intensity of the spectrum (at the pseudo-equilibrium state) began to decrease very slowly under the conditions of pH 7.80 at 30 °C. The prolonged reaction

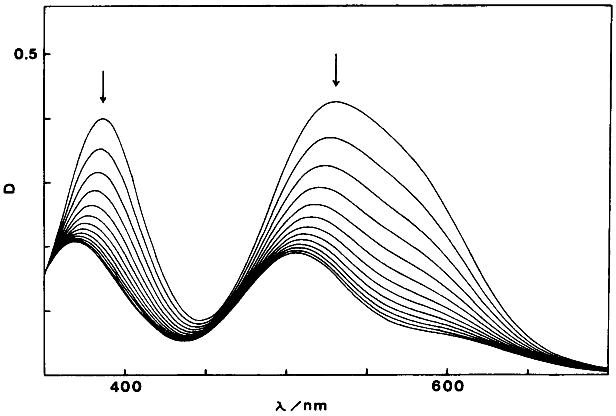


Fig. 4. The time-course change of absorption spectra of *u-fac*-[Co(ida)(mida)]$^-$ in basic aqueous solution (pH=10.10) at 30.0 °C. Record interval is 10 min.

gave the same spectral change as that shown in Fig. 4. The *mer* isomer also showed the spectral change with the passage of time in a weak basic solution, giving an isosbestic point at 559 nm (Fig. 3-a). The final curve in Fig. 3-a, recorded after *ca.* 1.5 h, is identical with that in Fig. 3-b. The subsequent spectral change was the same as that observed in the case of the *u-fac* isomer. The isosbestic point at 559 nm shown in Fig. 3 quite agrees with the point of intersection of the absorption curves of the *mer* and *u-fac* isomers in Fig. 2.

The spectral change in the second step, as shown in Fig. 4, occurred at a considerable rate in the higher-pH region (pH>10). The spectral pattern at the final equilibrium state is fairly close to that of the *s-fac* isomer. The same final spectral pattern was also observed for the final solution starting from the *s-fac* isomer. The resulting mixture at the final equilibrium state was chromatographed on a QAE-Sephadex column, but no other species except for the three geometrical isomers of [Co(ida)(mida)]$^-$ were detected. The *mer* isomer could not be clearly detected on the column chromatograph, because the *mer* isomer is present in a very small amount at the final equilibrium state and is not easily separated from the *s-fac* isomer on the QAE-Sephadex column.

With each spectral curve in Fig. 4, the intensities of absorption ($D(\lambda_x)$) at an arbitrary wave-length (λ_x) due to only *mer* and *u-fac* can be estimated using the following formulas.

$$D(\lambda_x) = D_{\text{obsd}}(\lambda_x) - \varepsilon_{s\text{-}fac}(\lambda_x)\cdot[s\text{-}fac]$$

$$D_{\text{obsd}}(559) = \varepsilon_{s\text{-}fac}(559)\cdot[s\text{-}fac] + \varepsilon_{u\text{-}fac}(559)\cdot[u\text{-}fac + mer]$$

$$[u\text{-}fac + mer] + [s\text{-}fac] = [\text{complex}]_0$$

where [complex]$_0$ is the initial concentration of the complex, where $D_{\text{obsd}}(\lambda_x)$ denotes the observed optical density at λ_x nm in Fig. 4, and where $\varepsilon(\lambda_x)$ is molar absorptivity at λ_x nm of the isomer shown as a subscript. The values of $D(\lambda_x)$ at various wave-lengths decrease in the same ratio to each other (Table 1). This suggests that the [*mer*]/[*u-fac*] ratio can be regarded as constant during the isomerization reaction from the *u-fac-mer* mixture to the *s-fac* isomer except for the very first stage of the reaction. Therefore, the reaction scheme of the isomerization reaction can be described as follows:

Table 1. The intensities of absorption ($D(\lambda_x)$) at several wave-lengths (λ_x) attributably to only *mer*- and *u-fac*-[Co(ida)(mida)]$^-$, as calculated from the spectral data in Fig. 4

λ_x/nm	$D_t(\lambda_x)$			$D_t(\lambda_x)/D_{60}(\lambda_x)$		
	Time/min			Time/min		
	10	30	60	10	30	60
600	0.206	0.138	0.080	2.58	1.73	1
550	0.328	0.221	0.129	2.54	1.71	1
500	0.269	0.181	0.106	2.54	1.70	1
450	0.071	0.048	0.028	2.53	1.71	1
400	0.278	0.187	0.109	2.55	1.72	1

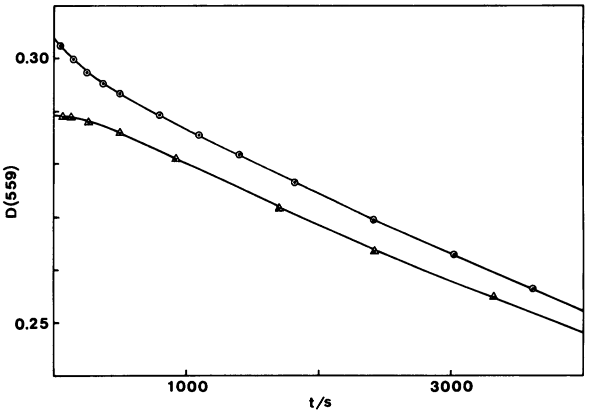


Fig. 5. The time-course changes of absorbance at 559 nm for *mer*- and *u-fac*-[Co(ida)(mida)]$^-$ in basic aqueous solutions: *mer* (—⊙—) 2.35×10^{-3} mol dm^{-3}, pH=9.09, 30.7 °C; *u-fac* (—△—△—) 2.30×10^{-3} mol dm^{-3}, pH=8.98, 30.4 °C.

$$\begin{array}{c}\underbrace{\textit{mer} \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} \textit{u-fac}} \\ k_s' \downarrow\uparrow k_{-s}' \\ \textit{s-fac}\end{array} \tag{1}$$

Thus, in order to study the isomerization of the [Co(ida)(mida)]$^-$ system, two independent experiments were carried out: The examinations of the *mer*⇄*u-fac* isomerization at pH 7.5—8.5 and of the (*mer*+*u-fac*)⇄*s-fac* isomerization at pH 9.5—10.5. The progress of the *mer*⇄*u-fac* isomerization was followed at 511 nm, and the D_t data for the analysis of kinetics were obtained during the isosbestic point at 559 nm was maintained. Each of the *mer* and *u-fac* isomers was used as a starting material under the same conditions, and the average value of D_{eq} (absorbance at the pseudo-equilibrium state) was used for the kinetic analysis.

The pseudo-first-order rate constants, k_s' and k_{-s}', can be determined from the intensity loss of absorption at 559 nm. However, it is ambiguous which isomer, *mer* or *u-fac*, in an equilibrium mixture isomerized to *s-fac*. Figure 5 shows the plots of absorbance at 559 nm

(D(559)) *vs.* the time using *mer* and *u-fac* as starting materials at pH 9 and 30 °C. In the run using *mer* as the starting material, the D(559) change in the very first stage of the reaction, where the equilibrium between *mer* and *u-fac* should not be achieved, is faster than that observed in the successive time-course. On the other hand, in the run using *u-fac* as the starting material, the initial D(559) change is slower than the subsequent change. These results support the idea that *s-fac* is produced from *mer*, and that Reaction Scheme (1) should be modified as follows:

$$\begin{tikzcd} \textit{mer} \arrow[r, shift left, "k_1'"] \arrow[d, shift right, "k_3'"'] & \textit{u-fac} \arrow[l, shift left, "k_2'"] \\ \textit{s-fac} \arrow[u, shift right, "k_4'"'] & \end{tikzcd} \qquad (2)$$

The relationships between the rate constants for Schemes (1) and (2) are $k_4'=k_{-\mathrm{s}}'$ and $k_3'=(K+1)k_\mathrm{s}'$, where K is equal to k_1'/k_2'. The pseudo-first-order and second-order rate constants for Scheme (2), k' and $k=k'/[\mathrm{OH}^-]$, are listed in Table 2. The rate law for each isomerization path can be described as $R=k[\text{complex}][\mathrm{OH}^-]$, judging from the constancy of the k obtained in the runs with various pHs at a constant temperature (Table 2). The reaction rates for the $(\textit{mer}+\textit{u-fac})\rightleftharpoons\textit{s-fac}$ change were independent of the sort of buffer (carbonate or phosphate buffer); however, an increase in the ionic strength from 0.1 to 1.0 increased the reaction rate (about 35%).

Isomerization Reactions of the [Co(ida)₂]⁻ System. The *mer*-[Co(ida)₂]⁻ complex showed spectral change in a weak basic solution (pH *ca.* 8.0) at 30 °C, giving an isosbestic point at 548 nm; this is consistent with the point of the intersection of the absorption curves of the *mer* and *u-fac* isomers. This implies that the spectral change is due to the *mer*→*u-fac* isomerization. After about 1.5 h, the spectra of the solution showed a nearly constant pattern (pseudo-equilibrium state), and the subsequent spectral change, which was attributed to the isomerization from a mixture of *u-fac* and *mer* to *s-fac*, was very slow under the conditions of pH *ca.* 8.0 and 30 °C. The spectral pattern at the pseudo-equilibrium state was almost identical with that of *u-fac*. Under the same conditions, the *u-fac* isomer showed a tendency of spectral change attributably to the isomerization to the *mer* isomer, but the change was very small. The equilibrium distribution of *u-fac* and *mer* is more favorable for *u-fac* than that in the case of the [Co(ida)(mida)]⁻ complex.

In an aqueous solution buffered at pH *ca.* 10.0 at 30 °C, the isomerization from a mixture of *u-fac* and *mer* to *s-fac* occurred at a considerable speed, giving isosbestic points at about 474 and 445 nm, which are different from the points of intersection (481 and 443 nm) of the absorption curve of *u-fac* and that of *mer*. Judging from the observation of the isosbestic points, the [*mer*]:[*u-fac*] ratio can be regarded as constant in this process. The ratio ([*mer*]:[*u-fac*]=2.3:97.7) which was calculated using the molar absorptivities of three geometrical isomers at 474 nm was consistent with the ratio ([*mer*]:[*u-fac*]=1.8:98.2) calculated from the absorption data at the pseudo-equilibrium state, within the limits of experimental error.

The isomerizations of the [Co(ida)₂]⁻ system were examined by the same method as that used in the case of the [Co(ida)(mida)]⁻ system. Even though there was no obvious experimental fact supporting the idea that *s-fac* was produced from *mer*, it seems reasonable to assume that the isomerization scheme for the [Co(ida)₂]⁻ system is the same as that for the [Co(ida)(mida)]⁻ system. Thus, the data observed were analyzed according to

TABLE 2. THE RATE CONSTANTS FOR THE ISOMERIZATION OF THE [Co(ida)(mida)]⁻ AND [Co(ida)₂]⁻ SYSTEMS IN BASIC AQUEOUS SOLUTIONS

		[Co(ida)(mida)]⁻			
T/°C	pH	$\frac{k_1'\times10^3}{\mathrm{s}^{-1}}$	$\frac{k_2'\times10^4}{\mathrm{s}^{-1}}$	$\frac{k_1\times10^{-2}}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$	$\frac{k_2\times10^{-2}}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$
24.8	8.03	0.282	0.735	2.66	0.693
27.2	8.03	0.403	1.08	3.17	0.850
30.0	7.47	0.193	0.537	4.46	1.24
30.0	8.02	0.647	1.80	4.21	1.17
30.0	8.27	1.19	3.32	4.37	1.21
30.0	8.45	1.81	5.03	4.37	1.21
32.5	8.04	1.07	3.01	5.58	1.57
34.4	8.06	1.48	4.14	6.45	1.80
T/°C	pH	$\frac{k_3'\times10^3}{\mathrm{s}^{-1}}$	$\frac{k_4'\times10^5}{\mathrm{s}^{-1}}$	$\frac{k_3\times10^{-1}}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$	$\frac{k_4\times10}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$
24.7	9.72	0.340	0.366	0.662	0.712
27.3	9.71	0.508	0.548	0.828	0.895
30.0	9.51	0.483	0.607	1.02	1.28
30.1	9.71	0.793	0.897	1.04	1.18
30.0	10.08	1.68	2.11	0.949	1.19
32.7	9.71	1.26	1.45	1.38	1.59
34.7	9.74	1.84	2.25	1.64	2.00

		[Co(ida)₂]⁻			
T/°C	pH	$\frac{k_1'\times10^3}{\mathrm{s}^{-1}}$	$\frac{k_2'\times10^5}{\mathrm{s}^{-1}}$	$\frac{k_1\times10^{-2}}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$	$\frac{k_2}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$
25.2	8.03	0.221	0.398	2.05	3.65
27.6	8.03	0.352	0.634	2.66	4.79
30.3	7.86	0.382	0.689	3.50	6.31
30.2	8.32	1.05	1.89	3.37	6.07
32.8	8.14	1.07	1.93	4.35	7.83
34.5	8.15	1.48	2.67	5.21	9.38
T/°C	pH	$\frac{k_3'\times10^3}{\mathrm{s}^{-1}}$	$\frac{k_4'\times10^5}{\mathrm{s}^{-1}}$	$\frac{k_3\times10^{-1}}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$	$\frac{k_4\times10}{\mathrm{M}^{-1}\,\mathrm{s}^{-1}}$
25.1	9.66	0.636	0.466	1.38	1.01
27.4	9.68	1.07	0.811	1.85	1.41
30.3	9.43	1.02	0.762	2.50	1.88
30.3	10.03	4.19	3.03	2.59	1.88
30.1	10.61	14.5	11.0	2.41	1.83
32.2	9.64	2.84	2.15	3.16	2.88
34.8	9.64	4.28	3.16	4.78	3.53

Each rate constant, k_n' ($n=1-4$), corresponds to that in Scheme (2). The 2nd-order rate constant, k_n, represents $k_n'/[\mathrm{OH}^-]$.

Scheme (2). The kinetic parameters are listed in Table 2. As the reaction rates depend on the $[OH^-]$ concentrations with the first-order, the second-order rate constants can be calculated from $k=k'[OH^-]$ (Table 2).

The Loss of Optical Activities in the u-fac *Isomers.* The optically active *u-fac* isomers of the $[Co(ida)(mida)]^-$ and $[Co(ida)_2]^-$ complexes lost their CD strength with the passage of time in a basic aqueous solution. The rates of CD loss in these complexes depended on the $[OH^-]$ concentration with the first-order. Therefore, the rates are described by a rate law in this form: $-d\,[\text{CD strength}]/dt=k_{CD}[\text{complex}][OH^-]$. The rate parameters obtained are given in Table 3. In both the $[Co(ida)(mida)]^-$ and $[Co(ida)_2]^-$ complexes, the comparable values of k_{CD} with k_2 (rate constant for the *u-fac→mer* change) indicate that the loss of CD in the *u-fac* isomer is mainly caused by the isomerization process of *u-fac→mer.*

During the course of the *u-fac→mer* process for the systems of both $[Co(ida)(mida)]^-$ and $[Co(ida)_2]^-$, the CD spectra decreased in magnitude while keeping the spectral patterns of the optically active *u-fac* isomers used as starting materials. Thus, the isoextinct points of the CD change were observed on a base line. Such CD behavior implies that the *mer* isomer produced from optically active *u-fac* is racemate, but this does not exclude the possibility that *u-fac→mer* change might occur through a stereospecific pathway such as *Λ-u-fac→mer-δ*-NH,NCH$_3$ (or *Δ-u-fac→mer-λ*-NH,NCH$_3$). The dissymmetrical structure of the *mer*-$[Co(ida)(mida)]^-$ or *mer*-$[Co(ida)_2]^-$ complex is due to the chirality described by the stereochemical relationship between the N–H and N–CH$_3$ bonds (or two N–H bonds) of the nitrogen atoms in the two ligands. If the rate of the inversion at the N-center (of the coordinated ida) for the *mer* structure is fast enough compared with the rate of the *u-fac→mer* change, the result described above may be expected. (We use the term "inversion" to describe the configurational change about a secondary nitrogen center in *mer*-$[Co(ida)(mida)]^-$ or *mer*-$[Co(ida)_2]^-$ despite the absence of asymmetry.) For the *mer*-$[Co(dien)_2]^{3+}$, $[Co(NH_3)_4(Me\text{-}en)]^{3+}$, $[Co(NH_3)_4(sar)]^{2+}$, and $[Co(en)_2(sar)]^{2+}$ complexes, the rates of the inversion at the secondary nitrogen center have been measured. The observed processes were all described by a rate law of the same form: $R=k[\text{complex}][OH^-]$. The rate constants ($k$) were $2.4\times10^2\ M^{-1}\,s^{-1}$ for both $[Co(dien)_2]^{3+}$[10] (at 35.0 °C) and $[Co(NH_3)_4(Me\text{-}en)]^{3+}$[14] (at 34.3 °C), and $1.9\times10^4\ M^{-1}\,s^{-1}$ and $7.32\times10^4\ M^{-1}\,s^{-1}$ for $[Co(NH_3)_4(sar)]^{2+}$[15] (at 30.0 °C) and $[Co(en)_2(sar)]^{2+}$[16] (at 30.0 °C), respectively. Therefore, for the present *mer* complexes, which have not yet been optically resolved, the rates of inversion can be expected to be sufficiently faster than the rate of *u-fac→mer* isomerization.

Table 3. THE RATE CONSTANTS FOR THE CD LOSS OF THE OPTICALLY ACTIVE *u-fac* ISOMERS OF THE $[Co(ida)(mida)]^-$ AND $[Co(ida)_2]^-$ COMPLEXES IN BASIC AQUEOUS SOLUTIONS AT 30.0 °C

Complex	pH	$\frac{k'_{CD}}{s^{-1}}$	$\frac{k_{CD}}{M^{-1}\,s^{-1}}$
$[Co(ida)(mida)]^-$	8.11	1.90×10^{-4}	1.00×10^{2}
	9.46	4.55×10^{-3}	1.07×10^{2}
	10.05	1.60×10^{-2}	0.97×10^{2}
$[Co(ida)_2]^-$	8.15	1.89×10^{-5}	9.11
	9.76	7.61×10^{-4}	9.01
	10.05	1.53×10^{-3}	9.28

The second-order rate constant, k_{CD}, represents $k'_{CD}/[OH^-]$.

Mechanism of Isomerization Reactions. As shown in Table 2, the rate constants of the *u-fac→mer* change for $[Co(ida)_2]^-$ are much different from those for $[Co(ida)(mida)]^-$. The equilibrium distributions of the geometrical isomers in both the $[Co(ida)(mida)]^-$ and $[Co(ida)_2]^-$ systems are as follows (at 30 °C):

	u-fac(%)	*mer*(%)	*s-fac*(%)
$[Co(ida)(mida)]^-$	4.1	1.2	94.7
$[Co(ida)_2]^-$	29.0	0.5	70.5

These results indicate that the *u-fac* isomer in the $[Co(ida)(mida)]^-$ system is less stable than the *u-fac* isomer in the $[Co(ida)_2]^-$ system. This fact may be explained by means of the "steric effect" of the N–CH$_3$ group in the mida ligand. Through the examination of the molecular model for *u-fac*-$[Co(ida)(mida)]^-$, we can find the existence of steric repulsion between the N–CH$_3$ group of the mida ligand and the methylene group of the ida ligand. This is also supported by the ^{13}C-NMR data, in which the signals of the two α-carbons in the ida ring appear as more greatly separated doublet peaks in *u-fac*-$[Co(ida)(mida)]^-$ (Δ=2.21 ppm) than in *u-fac*-$[Co(ida)_2]^-$ (Δ=1.61 ppm).[12] The difference (Δ) in the chemical shift between the two acetate rings of an ida ligand is probably related to the difference in inter-ligand steric repulsion. The equilibrium distribution described above also shows that both the ida and mida ligands are liable to adopt the facial structure rather than the meridional one. The distribution value (29.0%) of *u-fac*-$[Co(ida)_2]^-$ is in fair agreement with that (28%) reported by Cooke.[11]

That no other species except for three geometrical isomers were detected in the isomerization reaction of the $[Co(ida)(mida)]^-$ system suggests that the ligand dissociation is not involved in the reaction; if such dissociation were involved, the reaction should provide disproportionation and/or hydrolysis products. Thus, the isomerization must involve only the intramolecular pathway. 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. (Rearrangement occurs in this intermediate and is followed by the recoordination of the -COO$^-$ group.) The *mer⇄s-fac* change in Scheme (2) can be sufficiently explained in terms of only the bond-rupture mechanism, whereas the *mer⇄u-fac* change may be described by the mechanisms of both bond-rupture and twist. The activation energies (E_a) for each process in Scheme (2) were obtained using the Arrhenius plots of the second-order rate constants in Table 2; the activation parameters calculated are given in Table 4. These

Table 4. The activation parameters for the base-catalyzed isomerization of the [Co(ida)(mida)]$^-$ and [Co(ida)$_2$]$^-$ complexes at 30 °C

	ΔH^* kJ mol^{-1}	ΔS^* J K^{-1} mol^{-1}
[Co(ida)(mida)]$^-$		
mer→*u-fac*	69.7 ± 2.9	35.1 ± 9.7
u-fac→*mer*	75.0 ± 3.2	42.0 ± 10.7
mer→*s-fac*	69.5 ± 2.0	4.0 ± 6.4
s-fac→*mer*	77.5 ± 2.8	-6.9 ± 9.2
[Co(ida)$_2$]$^-$		
mer→*u-fac*	73.3 ± 1.6	45.0 ± 5.4
u-fac→*mer*	73.3 ± 1.7	11.6 ± 5.8
mer→*s-fac*	91.3 ± 3.7	82.9 ± 12.3
s-fac→*mer*	99.2 ± 3.6	68.5 ± 11.2

results do not offer any conclusive idea for determining the mechanism of the *mer*$\rightleftarrows$*u-fac* change.

Cooke *et al.* have reported the base-catalyzed racemization of [Co(edta)]$^-$, which does not have protons on nitrogen atoms, and proposed a twist mechanism, the transient intermediate of which is a seven-coordinate species with the OH$^-$ group.[17] Also in the [Co(mida)$_2$]$^-$ system, which does not have protons on nitrogens, the *s-fac* and *mer* isomers were not isomerized; moreover, the optically active *mer* isomer was not racemized under the conditions of the present experiment. Therefore, for the present complexes with acidic secondary amine sites (ida), the base catalysis of the intramolecular isomerization pathway is more satisfactorily accounted for in terms of a rearrangement process which might proceed through the conjugate base species. The difference in activation energy between [Co(edta)]$^-$ (E_a=136.7 kJ mol^{-1}) and the present complexes may be connected with the difference in reaction mechanism between the two systems. Deprotonation seems to facilitate (1) some possibilities of nitrogen-to-cobalt pπ–dπ bonding (π stabilization) and (2) the adjustment of the bond angles at secondary amine sites which necessarily accompanies stereo change. All the experimental data for the present systems can be explained by the transient five-coordinated conjugate-base intermediate formed by bond-rupture, even though the possibility of twist mechanism should also be considered for the *u-fac*$\rightleftarrows$*mer* change.

References

1) Abbreviations used: dien, diethylenetriamine; ida, iminodiacetate dianion; mdien, *N*,*N*-bis(2-aminoethyl)-methylamine; mida, *N*-methyliminodiacetate dianion; eida, *N*-ethyliminodiacetate dianion.

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