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Stereochemistry and Properties of *unsym-fac-*, *sym-fac-*, and *mer*-(Iminodiacetato)$_n$(*N*-alkyliminodiacetato)$_{2-n}$cobaltate(III) ($n=0$, 1, or 2) Complexes

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Unsymmetrical-facial (*u-fac*) and symmetrical-facial (*s-fac*) isomers of a mixed-ligand type complex, [Co(ida)(Rida)]$^-$ (Rida denotes *N*-methyl- or *N*-ethyliminodiacetate dianion), were prepared and characterized on the basis of their absorption, circular dichroism, ^{1}H NMR, and ^{13}C NMR spectral data. The isomerization and racemization reactions of these isomers were investigated in basic aqueous solution and compared with those of the bis type complexes, [Co(ida)$_2$]$^-$ and [Co(Rida)$_2$]$^-$. The time-course changes in the absorption spectra of [Co(ida)(Rida)]$^-$ and [Co(ida)$_2$]$^-$ indicated that the *mer* isomer exists as a transient labile intermediate in the isomerization reaction of *u-fac* to *s-fac*.

The bis(terdentate) complex of cobalt(III) with *N*-alkyliminodiacetate ion provides three geometrical isomers, as shown in Fig. 1. In a previous paper,[1] we reported the preparation and characterization of the *u-fac* isomers of [Co(mida)$_2$]$^-$ and [Co(eida)$_2$]$^-$, which have large intramolecular steric repulsions. These *u-fac* isomers decomposed in basic aqueous solution; at the same time, the decomposition of the ligands and the reduction of cobalt(III) to cobalt(II) occurred. On the other hand, no such decomposition occurred in the *s-fac* and *mer* isomers of the above two complexes.

In the present paper, the preparation of the mixed-ligand type complexes with both iminodiacetate (ida) and *N*-alkyliminodiacetate (Rida) ions, [Co(ida)(Rida)]$^-$, will be described, and the stereochemistry and the reactivity (isomerization and racemization) in basic aqueous solution will be discussed on the basis of their absorption, circular dichroism (CD), ^{1}H NMR, and ^{13}C NMR spectral data. These results will be compared with those of the bis type complexes, [Co(ida)$_2$]$^-$ and [Co(Rida)$_2$]$^-$.

Experimental

Ligands. Iminodiacetic acid was obtained commercially from Wako Pure Chemical Industries, Ltd. and used without further purification. *N*-Methyl- and *N*-ethyliminodiacetic acids were synthesized by the method in the literature.[2]

Preparation of Complexes. *Potassium Iminodiacetato(*N*-methyliminodiacetato)cobaltate(III)*, u-fac-*K[Co(ida)(mida)]·2H$_2$O*: This isomer was prepared by a method similar to that used for the *u-fac*-K[Co(mida)$_2$] complex reported in our previous paper.[1]

To a solution containing cobalt(II) chloride hexahydrate (5.95 g, 0.025 mol) in 20 cm^3 of water was added a solution containing a mixture of iminodiacetic acid (3.34 g, 0.025 mol) and *N*-methyliminodiacetic acid (3.68 g, 0.025 mol) in 70 cm^3 of water. Lead dioxide (9.0 g, 0.038 mol) was added gradually to the mixed solution adjusting pH to 4.0—4.5, and then the solution was stirred for 1 h at room temperature. After insoluble materials in the reactant solution were removed by filtration, the filtrate was poured into a QAE-Sephadex column (4.7 cm × 90 cm, Cl$^-$ form). The adsorbed band was separated into a broad red-brown band (containing *s-fac* and *mer* isomers of [Co(mida)$_2$]$^-$, [Co(ida)(mida)]$^-$, and [Co(ida)$_2$]$^-$) and a violet one by elution with an 0.1 mol·dm^{-3} KCl solution. The latter band was separated into three bands of blue (*u-fac*-[Co(mida)$_2$]$^-$), violet (*u-fac*-[Co(ida)(mida)]$^-$), and purple (*u-fac*-[Co(ida)$_2$]$^-$) by repeating developments on the same column. The violet eluate containing *u-fac*-[Co(ida)(mida)]$^-$ was acidified by adding a few drops of acetic acid to it and evaporated by use of a rotary evaporator at 35 °C. The complex obtained from the concentrated solution by addition of methanol and acetone was purified by using a Sephadex G-10 column. Needle crystals of violet color were obtained by recrystallization from water to which a methanol–acetone mixture was added. Found: C, 26.39; H, 3.86; N, 7.06%. Calcd for *u-fac*-K[Co(ida)(mida)]·2H$_2$O: C, 26.35; H, 3.93; N, 6.83%.

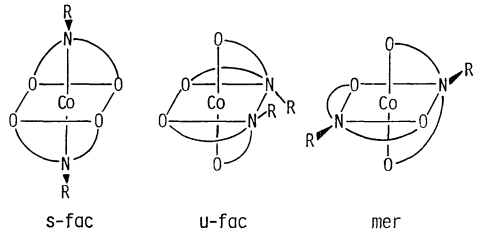

Fig. 1. Three geometrical isomers of [Co(Rida)$_2$]$^-$.

*Sodium Iminodiacetato(*N*-methyliminodiacetato)cobaltate(III)*, s-fac-*Na[Co(ida)(mida)]·H$_2$O*. This isomer was obtained by the isomerization reaction of *u-fac* to *s-fac*.

An aqueous solution containing *u-fac*-Na[Co(ida)(mida)], which was converted from the corresponding potassium salt using a small SP-Sephadex column of Na$^+$ form, was adjusted to pH 10—10.5 with NaOH aqueous solution and warmed to *ca.* 50 °C. The color of the solution changed immediately from violet to light brown. The solution was evaporated by use of a rotary evaporator. The desired *s-fac* isomer was isolated as flake crystals of light brown by adding methanol to the concentrated solution. Recrystallization was carried out from warm water by addition of methanol. Found: C, 28.60; H, 3.74; N, 7.60%. Calcd for *s-fac*-Na[Co(ida)(mida)]·H$_2$O: C, 28.74; H, 3.75; N, 7.45%.

An attempt to obtain the *mer* isomer of [Co(ida)(mida)]$^-$ from the red-brown band mentioned above was unsuccessful (*vide post*).

*Potassium Iminodiacetato(*N*-ethyliminodiacetato)cobaltate(III)*, u-fac-*K[Co(ida)(eida)]·H$_2$O*. This isomer was obtained by the same method as that used for *u-fac*-K[Co(ida)(mida)]·2H$_2$O. Found: C, 29.25; H, 4.06; N, 6.95%. Calcd for *u-fac*-K[Co(ida)(eida)]·H$_2$O: C, 29.56; H, 3.97; N, 6.90%.

TABLE 1. ABSORPTION DATA OF THE $[Co(ida)_n(Rida)_{2-n}]^-$ TYPE COMPLEXES

Complex	Structure	First band[a]	Second band[a]	Charge-transfer band[a]
$[Co(ida)_2]^-$	*u-fac*	17.83 (2.18)	26.28 (2.14)	45.35 (4.39)
	s-fac	16.47 (1.10)	27.55 (1.78)	42.0 (4.30) sh)
		20.18 (1.76)		46.37 (4.39)
	mer	16.13 (1.39)	26.39 (2.33)	44.64 (4.31)
		19.88 (2.55)		
$[Co(mida)_2]^-$	*u-fac*	17.24 (2.07)	25.32 (1.98)	42.46 (4.36)
	s-fac	16.4 (1.12) sh)	27.25 (1.85)	44.44 (4.41)
		19.76 (1.79)		
	mer	16.0 (1.40) sh)	25.64 (2.39)	44.05 (4.30)
		19.14 (2.52)		
$[Co(eida)_2]^-$	*u-fac*	17.18 (2.13)	25.00 (2.00)	41.84 (4.32)
	s-fac	16.5 (1.10) sh)	27.25 (1.87)	43.86 (4.33)
		19.49 (1.80)		
	mer	16.0 (1.40) sh)	25.45 (2.42)	43.67 (4.26)
		18.83 (2.48)		
[Co(ida)(mida)]$^-$	*u-fac*	17.70 (2.12)	26.04 (2.06)	44.25 (4.37)
	s-fac	16.69 (1.11)	27.40 (1.81)	45.45 (4.39)
		20.04 (1.76)		
[Co(ida)(eida)]$^-$	*u-fac*	17.64 (2.10)	25.97 (2.02)	43.86 (4.34)
	s-fac	16.67 (1.10)	27.32 (1.83)	45.05 (4.40)
		19.88 (1.80)		

a) Wave numbers and $\log \varepsilon$ values (in parentheses) are given in $10^3\,cm^{-1}$ and $mol^{-1}\,dm^3\,cm^{-1}$, respectively. sh) Shoulder bands.

Sodium Iminodiacetato(N-ethyliminodiacetato)cobaltate(III), s-fac-*Na[Co(ida)(eida)]·H_2O.* This isomer was obtained by the same method as that used for *s-fac*-Na[Co(ida)(mida)]·H_2O. Found: C, 30.97; H, 4.17; N, 7.08%. Calcd for *s-fac*-Na[Co(ida)(eida)]·H_2O: C, 30.78; H, 4.13; N, 7.18%.

The preparations of the *u-fac*, *s-fac*, and *mer* isomers of $K[Co(mida)_2]$ and $K[Co(eida)_2]$ are described in our previous paper.[1] The three isomers of $K[Co(ida)_2]$ were prepared by the same method as that used for the isomers of $K[Co(mida)_2]$.[1] The *mer* isomer, which is easily soluble and unstable in water, was obtained as red needle crystals. Recrystallization was carried out from slightly acidic water by adding methanol. Found: C, 25.49; H, 3.02; N, 7.62%. Calcd for *mer*-$K[Co(ida)_2]\cdot H_2O$: C, 25.41; H, 3.20; N, 7.41%.

Optical Resolution. *$(+)_{589}$-u-fac-K[Co(ida)(mida)]*: Resolving agent, $(+)_{589}$-$[Co(ox)(en)_2]Br\cdot H_2O$ (1.83 g, 5 mmol) was dissolved in 400 cm^3 of warm water (40 °C) and the bromide ion was converted to the acetate one using a small column containing Dowex 1×8 resin (200—400 mesh, CH_3COO^- form). The solution eluted from the column was concentrated to a volume of *ca.* 30 cm^3. This concentrated solution was mixed with an aqueous solution containing *u-fac*-H[Co(ida)(mida)] (this acidic complex was prepared in solution by loading *u-fac*-K[Co(ida)(mida)]·$2H_2O$ (2.05 g, 5 mmol) on a small column containing Dowex 50W×8 resin of H^+ form). The mixed solution was evaporated to a volume of 20 cm^3 using a rotary evaporator. To the concentrated solution was added 90% methanol until the purple crystals of diastereomer ($(+)_{589}$-$[Co(ox)(en)_2]$-$(+)_{589}$-[Co(ida)(mida)]·$2H_2O$) began to appear. The solution was cooled in a refrigerator for 1—2 h. The crystals which deposited were filtered and washed with water–methanol mixture (1:1), methanol, and then acetone. Yield was 1.40 g. Recrystallization was carried out twice from the concentrated aqueous solution by adding methanol. $[\alpha]_{589}^{15}$ +1274°.

The diastereomer was dissolved in a small amount of water and loaded on a small SP-Sephadex column (K^+ form) to remove $(+)_{589}$-$[Co(ox)(en)_2]^+$. To the solution obtained by elution with water was added a few drops of acetic acid, and the solution was evaporated to a few milliliters. A mixture of methanol–acetone (1:1) was added to the concentrated solution until crystals began to appear, and the solution was allowed to stand in a refrigerator for a few hours. The crystalline powder which deposited was filtered and washed with methanol and then acetone. Recrystallization was carried out from water by adding a methanol–acetone mixture. Found: C, 26.94; H, 3.77; N, 6.98%. Calcd for $(+)_{589}$-*u-fac*-K[Co(ida)(mida)]·$1.5H_2O$: C, 26.75; H, 3.78; N, 7.07%.

The $(-)_{589}$-isomer was obtained from the filtrate of the less soluble diastereomer.

$(+)_{589}$-u-fac-K[Co(ida)(eida)]·2.5H_2O. The diastereomer ($(+)_{589}$-$[Co(ox)(en)_2]$$(+)_{589}$-*u-fac*-[Co(ida)(eida)], $[\alpha]_{589}^{15}$ +1165°) and the $(+)_{589}$-isomer were obtained in the same way as that used for the resolution of *u-fac*-K[Co(ida)-(mida)]·$2H_2O$. Found: C, 27.93; H, 4.17; N, 6.52%. Calcd for $(+)_{589}$-*u-fac*-K[Co(ida)(eida)]·$2.5H_2O$: C, 27.72; H, 4.42; N, 6.47%.

Measurements. The absorption and CD spectra were measured by a Hitachi 557-type spectrometer and a JASCO J-22 spectropolarimeter, respectively. The ^1H NMR spectra were recorded on a JEOL MH-100 NMR spectrometer using DSS as an internal standard. The ^{13}C NMR spectra at 25 MHz were recorded on a JEOL JNM-FX100 spectrometer, in pulsed Fourier transform/proton noise decoupled mode. Peak positions were measured relative to internal dioxane (δ=67.44 ppm).

TABLE 2. OBSERVED CD DATA OF THE $[Co(ida)_n(Rida)_{2-n}]^-$ TYPE COMPLEXES

Complex	First band region[a)]	Second band region[a)]	Charge-transfer band region[a)]
$(+)_{589}$-*u-fac*-$[Co(ida)_2]^-$	17.01 (−2.430)	24.69 (−0.57) sh)	37.45 (−0.70) sh)
	19.65 (+2.541)	26.67 (−0.697)	41.84 (−3.211)
			46.08 (+12.49)
$(+)_{589}$-*u-fac*-$[Co(mida)_2]^-$	16.31 (−2.234)	23.53 (−0.83) sh)	37.31 (−5.034)
	18.32 (+3.155)	25.45 (−0.954)	41.49 (+7.180)
			46.08 (−14.44)
$(+)_{546}$-*mer*-$[Co(mida)_2]^-$	16.3 (−0.17) sh)	25.13 (−0.104)	34.72 (+0.450)
	18.32 (−0.570)	27.55 (+0.112)	43.48 (−2.069)
	20.45 (+0.868)		
$(+)_{589}$-*u-fac*-$[Co(eida)_2]^-$	16.13 (−2.420)	23.26 (−0.802)	36.36 (−4.922)
	18.15 (+3.053)	25.32 (−0.885)	40.65 (+7.981)
			45.05 (−17.39)
$(+)_{589}$-*u-fac*-$[Co(ida)(mida)]^-$	16.89 (−2.521)	24.27 (−0.779)	38.91 (−5.625)
	19.19 (+2.863)	26.11 (−0.829)	44.25 (+10.05)
			48.54 (−13.26)
$(+)_{589}$-*u-fac*-$[Co(ida)(eida)]^-$	16.75 (−3.117)	24.10 (−0.792)	38.91 (−3.513)
	13.98 (+3.101)	26.2 (−0.72) sh)	43.86 (+4.960)
			47.62 (−3.720)

a) Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively. sh) Shoulder bands.

Results and Discussion

Absorption Spectra. The absorption spectral data of the newly prepared mixed-ligand type complexes are listed in Table 1, together with those of the bis type complexes reported in a previous paper.[1] The comparison of absorption spectra among the three different geometrical isomers of the bis type complexes are shown in Fig. 2. Each isomer exhibits a considerably different spectrum behavior in the d-d transition region. The first ($^1A_1 \rightarrow {}^1T_1$) and second ($^1A_1 \rightarrow {}^1T_2$) bands increase the intensities in the order *s-fac* < *u-fac* < *mer*. This trend is in agreement with that observed in the three geometrical isomers of $[Co(ida)(dien)]^+$.[3] Legg and Cooke have attributed an increment of absorption intensity to the following elements: the removal of the center of the symmetry and the strained structure.[3] If their proposal is applied to the present bis type complexes, the *u-fac* isomer (C_2 symmetry) which lacks the center of symmetry would give a more intense spectrum than the *s-fac* isomer (C_{2h}), which has a plane of symmetry, and the *mer* isomer (C_2), containing both the elements: removal of the center of symmetry and the strained structure would give the most intense spectrum.

In each geometrical isomer, the first and second absorption maxima shift to the lower energy side in the order of $[Co(ida)_2]^-$, $[Co(mida)_2]^-$, and $[Co(eida)_2]^-$ (Fig. 2). This fact indicates that the ligand field strength decreases in the order of ida, mida, and eida, and that the terdentate ligand (ida) containing secondary nitrogen is located at a higher position in the spectrochemical series than the terdentate ligand (mida or eida) containing tertiary nitrogen. This trend agrees with those observed in the *s-fac* and *mer* isomers of $[Co(ida)(dien)]^+$ and $[Co(mida)(dien)]^+$ [3] and in

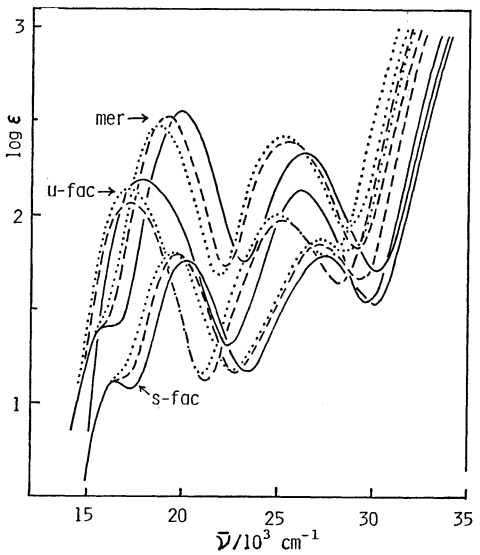

Fig. 2. Absorption spectra of three geometrical isomers of $[Co(ida)_2]^-$ (——), $[Co(mida)_2]^-$ (----), and $[Co(eida)_2]^-$ (·····).

the *s-fac* isomers of the $[Co(dien)_2]^{3+}$ and $[Co(dema)_2]^{3+}$ (dema = 3-methyl-3-azapentane-1,5-diamine) complexes, which contain secondary and tertiary nitrogens, respectively.[4]

As mentioned in the experimental section, for the mixed-ligand type complexes, $[Co(ida)(mida)]^-$ and $[Co(ida)(eida)]^-$, two geometrical isomers with violet and light brown colors were obtained by utilizing the preparative method of acidic conditions. As Fig. 3 shows, the absorption spectra of the violet isomers are identical in band shape and intensity with those of the *u-fac* isomers of the bis type complexes, while the spectra of the light brown isomers are identical with those of the *s-fac* isomers. These facts make it pos-

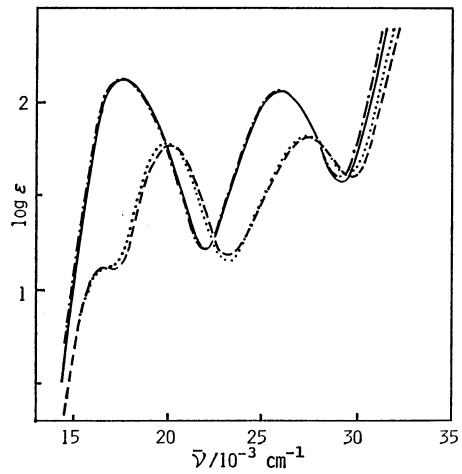

Fig. 3. Absorption spectra of the mixed-ligand complexes: *u-fac* (——) and *s-fac* (----) of [Co(ida)(mida)]⁻; *u-fac* (—·—) and *s-fac* (·····) of [Co(ida)(eida)]⁻.

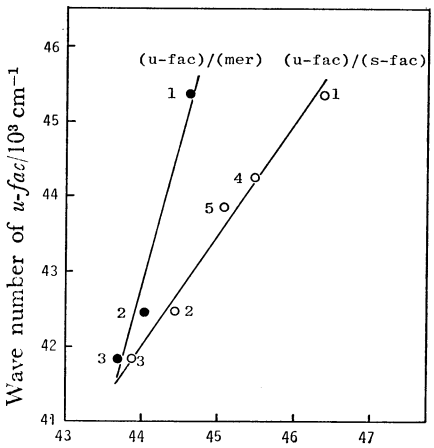

Fig. 4. Correlations of CT band maxima between two geometrical isomers. 1 $[Co(ida)_2]^-$, 2 $[Co(mida)_2]^-$, 3 $[Co(eida)_2]^-$, 4 [Co(ida)(mida)]⁻, and 5 [Co(ida)(eida)]⁻.

sible to assign the structures of the violet and light brown isomers of the mixed complexes to *u-fac* and *s-fac*, respectively.

Both the bis and mixed-ligand complexes exhibit charge transfer (CT) bands with the intensities of log ε=4.26—4.40 in the region 42000—46000 cm^{-1} (Table 1). The maximum positions of these bands vary with the ligands and the geometrical structures. As Fig. 4 shows, all the complexes show linear relationships between the maximum positions of two different isomers. These correlations suggest that the alkyl substituent on the nitrogen atom of coordinated ida brings about a shift of CT band maximum to lower energy in the order *u-fac*>*s-fac*>*mer*.

Circular Dichroism Spectra. The CD data of the *u-fac* isomers of the mixed-ligand type complexes are listed in Table 2, together with those of the bis type complexes. All the $(+)_{589}$-*u-fac* isomers exhibit similar CD patterns in the visible region; that is, these isomers give two component CD bands with (−) and (+) signs at the lower and higher energy sides in the first band region, respectively, and with (−) sign in the second band region. Figure 5 shows the comparison of the CD curves among $(+)_{589}$-*u-fac*-[Co(ida)(mida)]⁻, -$[Co(ida)_2]^-$, and -$[Co(mida)_2]^-$. The shift trend of the CD bands is identical with that of the absorption bands.

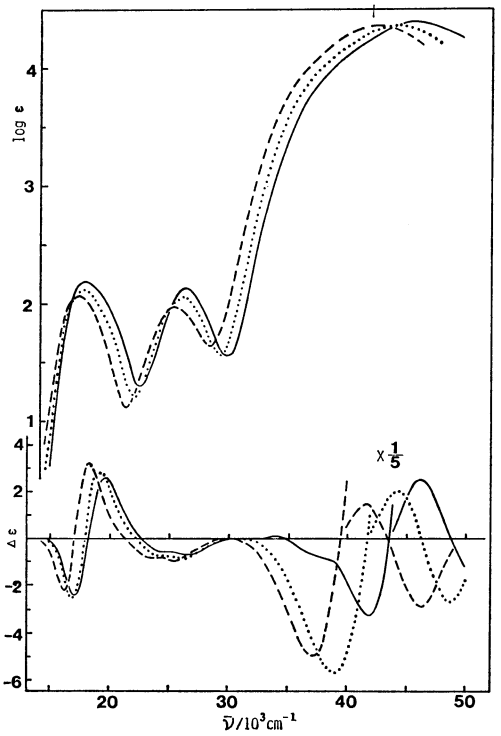

Fig. 5. Absorption and CD spectra of the $(+)_{589}$-*u-fac* isomers: $[Co(ida)_2]^-$ (——), [Co(ida)(mida)]⁻ (·····), and $[Co(mida)_2]^-$ (----).

In a previous study,[1] the absolute configuration of the $(-)_{589}$-isomer in *u-fac*-$[Co(mida)_2]^-$ and -$[Co(eida)_2]^-$ was assigned to $\Lambda\Lambda\Lambda$ (or Λ) from the comparison of CD spectra in the visible region with that of the $(-)_{546}$-isomer of *u-fac*-$[Co(ida)_2]^-$ whose the absolute configuration had been determined as $\Lambda\Lambda\Lambda$.[5,6] Similarly, the absolute configuration of the mixed-ligand complexes can be determined by comparing the CD patterns with those of the bis complexes; that is, the $\Lambda\Lambda\Lambda$ (or Λ) configuration is assigned to the $(+)_{589}$-isomers of *u-fac*-[Co(ida)(mida)]⁻ and -[Co(ida)(eida)]⁻, whose CD spectra give patterns similar to those of $(+)_{589}$-*u-fac*-$[Co(ida)_2]^-$, -$[Co(mida)_2]^-$, and -$[Co(eida)_2]^-$.

Koine *et al.* succeeded in resolving *mer*-$[Co(mida)_2]^-$ into optically active isomers.[7] The optical activity of this isomer arises from a chiral disposition of the two non-coplanar ligands. Therefore, the CD intensity of the *mer* isomer is expected to be lower than that of the *u-fac* isomer, which has the configurational chirality. Actually, the $(+)_{546}$-*mer* isomer give considerably lower CD intensity than those of the $(+)_{589}$-*u-fac* isomers (Table 2). Similar phenomena have been observed for the complexes containing other terdentate ligands, such as dien[7,8] and dema.[4]

^1H NMR Spectra. Cooke measured the ^1H NMR spectra of the *s-fac* and *u-fac* isomers of $[Co(ida)_2]^-$ and the *s-fac* isomer of $[Co(mida)_2]^-$ and as-

Table 3. ^{13}C Chemical shifts (ppm) of the $[Co(ida)_n(Rida)_{2-n}]^-$ type complexes

Complex[a] and free ligand[b]	δ (C_{oxy})	Shift non-equivalence	Δ[c] (C_{oxy})	δ (C_α)	Shift non-equivalence	Δ[c] (C_α)	δ (N-$\underline{C}H_3$)	δ (N-$\underline{C}H_2CH_3$)	δ (N-$CH_2\underline{C}H_3$)
$[Co(ida)_2]^-$									
s-fac	185.66		+16.50	58.32		+10.44			
u-fac	184.93	0.74	+15.77	59.59	1.61	+11.71			
	184.19		+15.03	57.98		+10.10			
mer	184.53	0.19	+15.37	57.05	0.14	+9.17			
	184.34		+15.18	56.91		+9.03			
H_3ida	169.16			47.88					
$[Co(mida)_2]^-$									
s-fac	183.42		+15.20	69.29		+12.28	51.41		
u-fac	183.66	1.60	+15.44	71.39	3.46	+14.38	50.24		
	182.06		+13.84	67.93		+10.92			
mer	183.32	0.58	+15.10	68.42	0.54	+11.41	51.36		
	182.74		+14.52	67.88		+10.87			
H_3mida	168.22			57.01			44.34		
$[Co(eida)_2]^-$									
s-fac	183.86		+15.35	65.35		+10.28		58.28	8.63
u-fac	184.25	1.36	+15.74	67.25	2.78	+12.18		57.55	8.43
	182.89		+14.38	64.47		+9.40			
mer	183.66	0.34	+15.15	65.15	0.88	+10.08		57.06	9.60
	183.32		+14.81	64.27		+9.20			
H_3eida	168.51			55.07				58.80	9.94
$[Co[ida)(mida)]^-$									
s-fac	185.27	(ida)	+16.11	68.81	(mida)	+11.80	51.65		
	183.86	(mida)	+15.64	58.92	(ida)	+11.04			
u-fac	185.22	1.36 (ida)	+16.06	70.02	1.80 (mida)	+13.01	50.14		
	183.86		+14.70	68.22		+11.21			
	183.17	0.72 (mida)	+14.95	59.65	2.20 (ida)	+11.77			
	182.45		+14.23	57.45		+9.57			
$[Co(ida)(eida)]^-$									
s-fac	185.27	(ida)	+16.11	65.05	(eida)	+9.98		(58.67)[d]	8.92
	184.25	(eida)	+15.74	(58.82)	(ida)	+10.94			
u-fac	185.27	1.46 (ida)	+16.11	66.03	1.80 (eida)	+10.96		(57.36)[d]	8.43
	183.81		+14.65	64.23		+9.16			
	183.62	0.69 (eida)	+15.11	59.65	2.10 (ida)	+11.77			
	182.92		+14.42	(57.55)[d]		+9.67			

a) Measured in D_2O. b) Measured in 7.5 M DCl. c) $\Delta(C_{oxy}) = (\delta(C_{oxy})$ of coordinated ligand$) - (\delta(C_{oxy})$ of free ligand); $\Delta(C_\alpha) = (\delta(C_\alpha)$ of coordinated ligand$) - (\delta(C_\alpha)$ of free ligand). d) Values in parentheses are assigned tentatively.

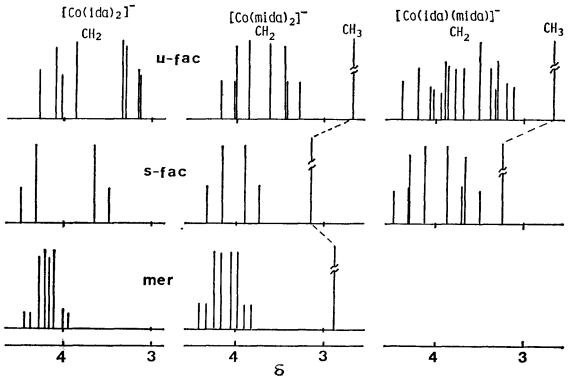

Fig. 6. The ^{1}H NMR spectra of the bis and mixed-ligand complexes in D_2O solution.

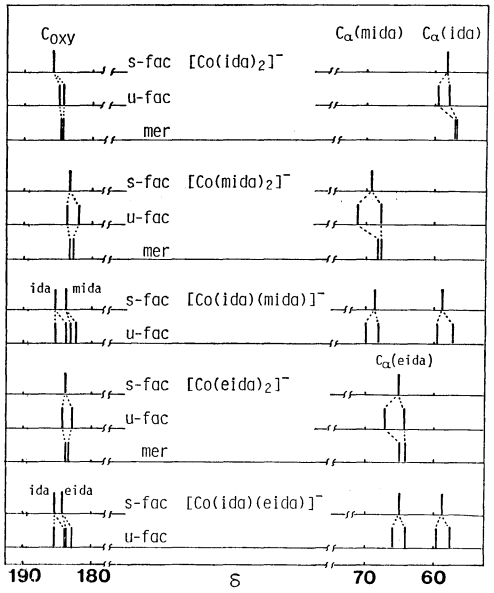

Fig. 7. ^{13}C NMR spectra of bis- and mixed-ligand complexes. The signals of *N*-methyl and -ethyl carbons are omitted.

signed the resonance peaks observed as one or two sets of AB quartets to the acetate-methylene protons.[9] Similar AB patterns (J_{AB}=16.0—18.0 cps) are also observed for the *mer* isomer of $[Co(ida)_2]^-$ and the *u-fac* and *mer* isomers of $[Co(mida)_2]^-$ in the range 3.3—4.3 ppm, as Fig. 6 shows.

The *u-fac* and *s-fac* isomers of $[Co(ida)(mida)]^-$ give the spectra consisting of four and two sets of AB quartets, respectively, in the acetate region (3.1—4.5 ppm), suggesting that the two acetate rings of each ligand are nonequivalent and equivalent in the former and latter isomers, respectively. The spectral patterns of these two isomers are nearly identical with the superimposed spectra of each corresponding isomer in both $[Co(ida)_2]^-$ and $[Co(mida)_2]^-$.

^{13}C NMR Spectra. The ^{13}C NMR chemical shifts of the present complexes are listed in Table 3 and the shift patterns are shown in Fig. 7. In the previous papers,[10,11] we reported that the chelation of α-amino acids to cobalt(III) ion brings about down-field changes (Δ values in Table 3) in the ^{13}C chemical shifts of their carboxyl-carbon (C_{oxy}) and α-carbon (C_α). All the present complexes exhibit down-field shift changes

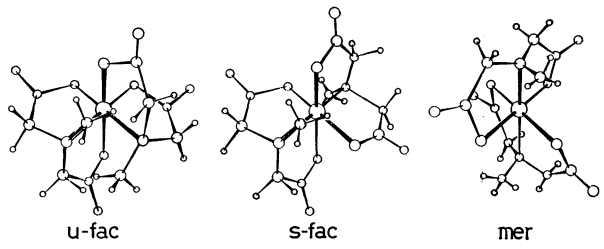

Fig. 8. Molecular models of *u-fac*-, *s-fac*-, and *mer*-$[Co(mida)_2]^-$.

in the range +13.84—+16.50 ppm for carboxyl-carbons, and the values are comparable with those of α-amino acid complexes.[10,11] However, the Δ values (+9.03—+14.38 ppm) of α-carbons for all the present complexes are considerably larger than those (+4.44—+8.29) for the α-amino acid complexes.

It is well-known that ^{13}C resonance patterns reflect the symmetries of the complexes.[12-15] In the cases of $[Co(ida)_2]^-$ and $[Co(Rida)_2]^-$, the ^{13}C signals of the α- and carboxyl-carbons appear as single peaks in the *s-fac* isomer (C_{2h}) and as double peaks in the *u-fac* and *mer* isomers (C_2). The double peaks of the latter isomers indicate that the two acetate rings of each ligand are nonequivalent in chemical environment. As given in Table 3, the shift nonequivalences[13] (resonance separations of the double peaks) are larger in the *u-fac* isomer than in the *mer* one and larger in $[Co(Rida)_2]^-$ than in $[Co(ida)_2]^-$. The difference in shift nonequivalences between these two isomers may be related to the difference in interligand steric repulsions. The molecular model of *u-fac*-$[Co(mida)_2]^-$ (Fig. 8) suggests an existence of large steric repulsions between the *N*-methyl group of one ligand and the methylene and methyl groups of the other ligand. The large steric repulsions can also be related to the fact that the *u-fac*-$[Co(mida)_2]^-$ complex decomposes easily in weakly basic aqueous solution[1] (*vide post*). A similar argument can also be made for the $[Co(eida)_2]^-$ complex.

The assignments of the ^{13}C resonance peaks of $[Co(ida)(Rida)]^-$ were made in comparison with the resonance peaks of $[Co(ida)_2]^-$ and $[Co(Rida)_2]^-$. The α- and carboxyl-carbons of the ida and Rida ligands in *u-fac*-$[Co(ida)(Rida)]^-$ exhibit different behaviors in chemical shift changes from those in *u-fac*-$[Co(ida)_2]^-$ and -$[Co(Rida)_2]^-$ (Fig. 7). For example, the shift nonequivalences of ida (C_α, 2.20 ppm; C_{oxy}, 1.36 ppm) in *u-fac*-$[Co(ida)(mida)]^-$ are larger than those of ida (C_α, 1.61 ppm; C_{oxy}, 0.74 ppm) in *u-fac*-$[Co(ida)_2]^-$. Contrary to this behavior, the shift nonequivalences of mida (C_α, 1.80 ppm; C_{oxy}, 0.72 ppm) in the former complex are smaller than those of mida (C_α, 3.46 ppm; C_{oxy}, 1.60 ppm) in *u-fac*-$[Co(mida)_2]^-$. These observations indicate that the shift nonequivalences of the paired carbons on a ligand are remarkably influenced by the interligand steric repulsions.

Reactions in Basic Aqueous Solution. In a previous paper,[1] we reported that in basic solution the *mer* isomer of $[Co(ida)_2]^-$ isomerizes rapidly to the *u-fac* and/or *s-fac* one and the *u-fac* isomers of $[Co(mida)_2]^-$ and $[Co(eida)_2]^-$ decompose along with

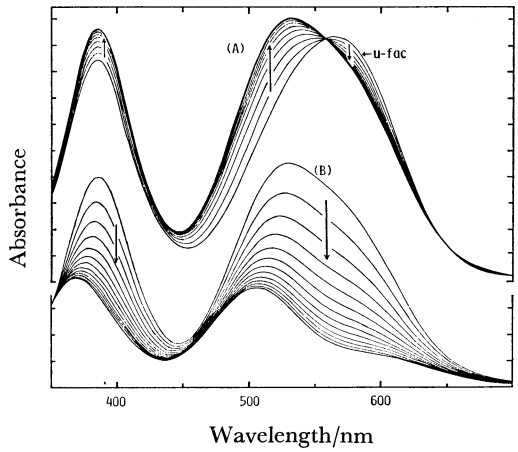

Fig. 9. Time-course changes of absorption spectra of *u-fac*-[Co(ida)(mida)]$^-$ in basic aqueous solutions at 30 °C. Trends of spectral changes with time are shown by arrows. (A): pH, 8.42; record interval, 5 min; time to recording start from pH adjustment, 160 s. (B): pH, 10.10; record interval, 10 min; time to recording start, 40 s.

the decomposition of one ligand per two complex ions and the reduction of cobalt(III) to cobalt(II). Such reactions suggest that the basic conditions are unfavourable to the preparations of the three geometrical isomers of the bis type complexes. Actually, the preparation under basic conditions gave only the *u-fac* and *s-fac* isomers in $[Co(ida)_2]^-$ and only the *s-fac* and *mer* isomers in $[Co(mida)_2]^-$ and $[Co(eida)_2]^-$. The preparation under acidic conditions (pH 4.0—4.5), however, gave all of the three possible isomers in substantial yield; *e.g.* in the case of $[Co(mida)_2]^-$ the formation ratio of the three isomers was *u-fac*:*s-fac*:*mer*=42:34:24. This ratio indicates that the *u-fac* isomer is formed most favourably in an acidic medium, although this isomer is thermodynamically unstable. The preparations of the mixed-ligand complexes have also been performed under the same acidic conditions as used for the bis complexes, but no *mer* isomers were isolated because of the rapid isomerization.

In analogy with the case of *u-fac*-$[Co(ida)_2]^-$ which was described in a previous paper,[1] the *u-fac* isomer of [Co(ida)(mida)]$^-$ also isomerized in basic aqueous solution. Figure 9 shows the spectral changes of *u-fac*-[Co(ida)(mida)]$^-$ in weak and strong basic solutions. In the weak basic solution of pH 8.42, the spectrum changes slowly with the passage of time, giving two isosbestic points at 588 and 647 nm (Fig. 9(A)). A new band peak which is observed near 530 nm is ascribed to the formation of a new complex. However, over about one hour the intensity of the spectrum began to decrease and the prolonged reaction gave a spectrum nearly identical with that of *s-fac*-[Co(ida)(mida)]$^-$. On the other hand, in strong basic solution of pH 10.10, a rapid spectral change is observed (Fig. 9(B)). The pattern of this spectral change is almost identical with that observed in the prolonged reaction of the weak basic solution mentioned above. The spectral changes in these two cases (pH 8.42 and 10.10) suggest that the isomerization of *u-fac* to *s-fac* proceeds in a two-step reaction.

In order to identify the new complex mentioned above, the reactant solution of pH 8.42 was chromatographed by use of a Sephadex G-10 column. The violet band of the unreacted *u-fac* isomer was eluted early and the red band containing the new complex followed as a partially overlapped band. The absorption spectrum of the solution eluted from the red band gave the first and second band maxima at 19490 and 25840 cm^{-1}, respectively. These maximum positions are comparable with those of the *mer* isomers of $[Co(ida)_2]^-$ and $[Co(mida)_2]^-$ (Table 1). This suggests that the new complex takes the *mer* structure. Similar spectral changes were also observed in the basic solutions of *u-fac*-[Co(ida)(eida)]$^-$ and -$[Co(ida)_2]^-$. Therefore, it is expected that the isomerization of these complexes proceeds in a reaction fashion similar to the case of *u-fac*-[Co(ida)(mida)]$^-$.

The preliminary kinetic study of *u-fac*-[Co(ida)(mida)]$^-$ and -$[Co(ida)_2]^-$ in basic aqueous solution give the following results. The rate constants of the racemization and isomerization reactions (*u-fac* to *s-fac*) for [Co(ida)(mida)]$^-$ are 94.8 and 2.03 $M^{-1}\,s^{-1}$ (at 30 °C), respectively; the racemization reaction proceeds more rapid than the isomerization reaction, and these reactions of [Co(ida)(mida)]$^-$ are more rapid than those of $[Co(ida)_2]^-$. These results lead to the following suggestions: the racemization of optically active *u-fac* isomer occurs through the isomerization path of *u-fac* to *mer*; the racemization of *u-fac*-$[Co(ida)_2]^-$ is accelerated by the base catalyzed reaction at the secondary amine nitrogens of coordinated ida,[14] while that of *u-fac*-[Co(ida)(mida)]$^-$ is accelerated by both the base-catalyzed reaction of ida and the steric effect due to *N*-methyl group of mida. A more detailed discussion on the kinetics of the present complexes will be given in the following communication.

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