Studies of the Metal Complexes of Cyclohexane Derivatives. VII.[1] Preparation and Properties of Platinum(II) and Cobalt(III) Complexes of (1*R*,2*S*)-1-Aminomethyl-2-methylcyclohexylamine

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Optically active (1*R*,2*S*)-1-aminomethyl-2-methylcyclohexylamine (*R*,*S*-2m-amcha) was synthesized and two Pt(II) and two types of Co(III) complexes containing this ligand were prepared. ^{1}H-NMR and ^{13}C-NMR spectra of the Pt(II) complexes and CD spectrum of *trans*-$[CoCl_2(R,S\text{-2m-amcha})_2]^+$ indicated that the chelate ring takes predominantly the λ conformation with the equatorial C_1–C_2 bond of the cyclohexane ring. The absolute configuration of the ligand has been assigned on the basis of the conformation of the complexes. All possible isomers of the tris Co(III) complex, *fac*-$\Delta(lel_3)$, *mer*-$\Delta(lel_3)$, *mer*-$\Lambda(ob_3)$, and *fac*-$\Lambda(ob_3)$, were isolated and characterized.

It is widely known that a chelated 1,2-diamine having mono- or disubstitution at the carbon atom of the chelate ring, such as 1,2-propanediamine or racemic 2,3-butanediamine, preferentially adopts the conformation with the substituent disposed equatorially.[2-4] However, there have been few reports on complex formation with 1,2-diamines which have two different substituents at the same carbon atom. (1*R*,2*S*)- or (1*S*,2*R*)-1-Aminomethyl-2-methylcyclohexylamine (abbreviated as 2m-amcha) is regarded as a *C*,*C*-unsymmetrically disubstituted 1,2-ethanediamine. These compounds are considered to take a fixed chair conformation with the methyl group equatorial. By virture of this group, the 2m-amcha chelate ring prefers a conformation in which C_1–C_2 bond of the cyclohexane ring lies in the equatorial position with regard to the chelate ring. In this paper we describe the preparation of (1*R*,2*S*)-1-aminomethyl-2-methylcyclohexylamine (*R*,*S*-2m-amcha), the four isomers of $[Co(R,S\text{-2m-amcha})_3]^{3+}$, *trans*-$[CoCl_2(R,S\text{-2m-amcha})_2]^+$, as well as $[Pt(NH_3)_2(R,S\text{-2m-amcha})]^{2+}$ and $[Pt(bpy)(R,S\text{-2m-amcha})]^{2+}$ (bpy=2,2′-bipyridine). Characterization of the ligand and the complexes was made by means of CD and NMR spectral analysis.

Experimental

Preparation and Resolution of the Ligand. 1-Amino-2-methylcyclohexanecarbonitrile was obtained by a slight modification of the method of Steiger.[5] To a mixture containing NaCN (50 g) and NH_4Cl (59 g) in water (240 cm^3) was added aqueous ammonia (70 cm^3, 25—28%). The resulting solution was stirred at 10—20 °C, and to this was added 2-methylcyclohexanone (112 g) in methanol (160 cm^3) dropwise. After the addition ,the mixture was stirred vigorously at 50—55 °C for 5 h. The reaction mixture was cooled, diluted with water (200 cm^3), and then extracted with ether. The ether extract was evaporated to a smalll volume. The concentrate was diluted with ethanol (100 cm^3) and cooled. Then 4 mol/dm^3 HCl (300 cm^3) was added to this ice chilled solution with stirring. The resulting amino nitrile hydrochloride was filtered by suction and washed with a small amount of cold 4 mol/dm^3 HCl.

To a cold aqueous suspension of the amino nitrile hydrochloride so obtained, was added 7 mol/dm^3 NaOH solution (200 cm^3). The oil which separated was extracted with ether. After removal of the ether, the amino nitrile was dried over K_2CO_3. The amino nitrile was reduced with $LiAlH_4$ by the usual manner.[6] In a typical reduction, 36.2 g of amino nitrile yielded 30.7 g of crude *trans*-diamine which contained small amounts of unreduced amino nitrile and *cis*-diamine.

The reaction product was purified as follows. To a solution of the crude diamine (25 g in 30 cm^3 of ethanol), a solution of (2*R*, 3*R*)-tartaric acid (52 g in 40 cm^3 of H_2O) was added. The solution was kept standing at about 60 °C for 5 min and then cooled. The product which deposited was collected by filtration and washed with ethanol. It was recrystallized from ethanol to give 33 g of colorless powder. Found: C, 41.02; H, 7.32; N, 6.04%. Calcd for $C_{16}H_{30}O_{12}\cdot 3/2\ H_2O$: C, 40.94; H, 7.09; N, 5.97%. Free racemic *trans*-2m-amcha was obtained from the diamine-hydrogentartrate as described in the literature.[7] To a solution of this salt (30 g in 70 cm^3 H_2O) was added a solution of KCl (12 g in 30 cm^3 H_2O). After heating for a while and succesive ice-cooling, the precipitated potassium hydrogentartrate was filtered off. To the filtrate, KOH (60 g) was added . The oil thus separated was extracted with ether. Racemic *trans*-diamine (9 g) was obtained by evaporationg the extract.

To a solution of (2*R*, 3*R*)-di-*O*-benzoyltartaric acid monohydrate (30.4 g in 200 cm^3 of 2-propanol), a solution of racemic 2m-diamine (11.2 g in 60 cm^3 H_2O) was added. The mixed solution was boiled for a few minutes, then cooled to afford 31.9 g of crystals (mp: 156—163 °C). Twice recrystallization of this salt from water gave 12.0 g of the less soluble (2*R*, 3*R*)-di-*O*-benzoyltartarate, mp: 156 °C, $[\alpha]_D=-74.0°$ (1.0 g in 100 cm^3 of methanol). Found: C, 51.87; H, 7.38; N, 4.72%. Calcd for $C_{26}H_{32}N_2O_8\cdot 6H_2O$: C, 51.31; H, 7.38; N, 4.60%. Treatment of this salt (12 g) with 70 cm^3 of 3 mol/dm^3 HCl gave the dihydrochloride of *R*,*S*-2m-amcha (4.5 g) whose absolute configuration was assigned by the CD spectrum of *trans*-$[CoCl_2(R,S\text{-2m-amcha})_2]^+$ as described later. Found: C, 41.57; H, 9.91; H, 11.62%. Calcd for $C_8H_{18}N_2\cdot 2HCl\cdot H_2O$: C, 41.21, H, 9.51; H, 12.01%. $[\alpha]_D=-6.2°$ (2.7 g in 100 cm^3 of H_2O). The optically active free diamine was obtained from this dihydrochloride by adding a stoichiometric quantity of sodium methoxide. It was used for the preparation of the complexes without further purification.

Preparation of Complexes. $[Pt(NH_3)_2(R,S\text{-2}m\text{-amcha})]Cl_2$ *and* $[Pt(bpy)(R,S\text{-2}m\text{-amcha})]Cl_2$: $[Pt(NH_3)_2(R,S\text{-2m-amcha})]Cl_2$ was synthesized by a method similar to that described in the literature.[8] $[Pt(bpy)(R,S\text{-2m-amcha})]Cl_2$ was prepared from $[PtCl_2(bpy)]$ and the ligand, according to the literature method.[9]

trans-$[CoCl_2(R,S\text{-2}m\text{-amcha})_2]Cl$: This complex was prepared by the usual method. To a methanol solution of

Table 1. Analytical data of complexes prepared

Complex	Found (Calcd) (%)		
	C	H	N
$[Pt(NH_3)_2(R,S\text{-2m-amcha})]Cl_2 \cdot 3/2\ H_2O$	20.58(20.47)	5.84(5.80)	11.73(11.94)
$[Pt(bpy)(R,S\text{-2m-amcha})]Cl_2 \cdot 4\ H_2O$	33.73(33.97)	5.04(5.38)	8.61(8.80)
trans-$[CoCl_2(R,S\text{-2m-amcha})_2]Cl \cdot H_2O \cdot CH_3OH \cdot 3/2$ HCl	39.41(39.49)	8.07(8.09)	10.90(10.84)
B-1: $[Co(R,S\text{-2m-amcha})_3]Cl_3 \cdot 2H_2O \cdot 3/2$ HCl	42.08(42.22)	8.97(8.79)	12.21(12.31)
B-2: $[Co(R,S\text{-2m-amcha})_3]Cl_3 \cdot 5/2\ H_2O$	45.33(45.25)	9.77(9.34)	13.25(13.19)
B-3: $[Co(R,S\text{-2m-amcha})_3]Cl_3 \cdot 5/2\ H_2O \cdot 1/2$ HCl	44.02(43.99)	9.13(9.15)	12.95(12.82)
B-4: $[Co(R,S\text{-2m-amcha})_3]Cl_3 \cdot 3\ H_2O$	44.33(44.62)	9.67(9.36)	13.10(13.01)

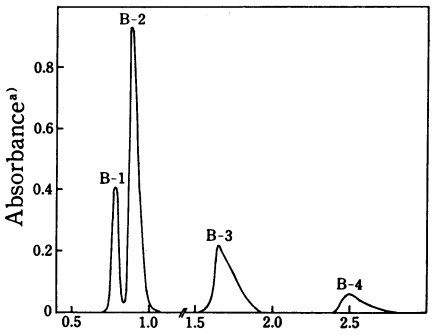

Fig. 1. Elution curve of the isomers of $[Co(R,S\text{-2m-amcha})_3]^{3+}$.
Eluent: 0.20 mol/dm³ Na_2SO_4, a) at 20.8×10^3 cm^{-1}.

$CoCl_2 \cdot 6H_2O$ was added a methanol solution of twice the amount of *R,S*-2m-amcha. The mixture was air-oxidized for 4—5 h and then evaporated. An excess amount of concentrated hydrochloric acid was added to the resulting brown residue. The green powder which formed was collected and washed thoroughly with acetone. The crude complex thus obtained was recrystallized from methanol.

Four Isomers of $[Co(R,S\text{-2m-amcha})_3]Cl_3$: Four isomers of the tris-complex were prepared by the published method[10] with slight modification. To a dimethyl sulfoxide solution (6 cm³) of *trans*-$[CoCl_2py_4]Cl_2 \cdot 6H_2O$(2 mmol) was added *R,S*-2m-amcha (8.4 mmol) dropwise. The resulting solution was stirred for 30 min, diluted with water to 2 dm³ and the pH adjusted to about 3 with hydrochloric acid. The product was adsorbed on SP-Sephadex C-25. A small portion of the adsorbed product was charged on the top of an SP-Sephadex C-25 column (2.7 cm × 65 cm) and the product was eluted with a 0.2 mol/dm³ Na_2SO_4 solution. The four bands which descended were called B-1, B-2, B-3, and B-4 (Fig. 1). Each fraction was adsorbed again on SP-Sephadex and the complex was eluted with 1 mol/dm³ hydrochloric acid solution. The eluent was concentrated on a water bath and then evaporated in a vacuum desiccator over NaOH and P_2O_5. The four complexes named B-1, B-2, B-3, and B-4 were obtained as orange powders. The B-1, B-3, and B-4 complexes were recrystallized from dilute hydrochloric acid. Recrystallization of B-2 in the chloride form was unsuccessfull. It was used without further purification. The analytical data for the complexes are given in Table 1.

Measurements: ^{1}H-NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer with D_2O as a solvent and DSS as an internal reference. ^{13}C-NMR spectra were recorded on a JEOL-FX-100 spectrometer with D_2O as a solvent and TMS as an external reference. CD spectra were measured with a JASCO-J-40 spectropolarimeter, and the absorption spectra with a Shimadzu UV-210-A spectrophotometer. Optical rotations at 589 nm were measured with a JASCO-DIP-4 polarimeter.

Results and Discussion

Conformation of the Ligand. The 2m-amcha ligand has two geometrical isomers, *cis* and *trans*. Chart 1 shows the conformational pairs of the two isomers. Munday[11] reported that 1-amino-2-methylcyclohexanecarboxylic acid obtained by hydrolysis of amino nitrile by Strecker synthesis has an axial carboxyl group. However, Cremlyn[12,13] claimed that the carboxyl group of the same compound is in the equatorial position. As mentioned in the literature,[11] 1-amino-2-methylcyclohexanecarbonitrile resists hydrolysis by an ordinary method. We also obtained a similar experimental result; that hydrolysis of this compound had to be carried out in a sealed vessel at high temperature. This seems to indicate that the cyano group lies in an equatorial position close to the equatorial 2-methyl group. The 2m-amcha obtained *via* Strecker synthesis is considered to have a configuration similar to that of the corresponding amino carboxylic acid. Accordingly, the *trans*-configuration shown in Chart 1, **2a** is a dopted for this diamine.

The 100 MHz ^{1}H-NMR spectrum of amcha·2HCl is shown in Fig. 2. Two multiplet peaks around 1.4 and 1.7 ppm are attributable to the axial and equatorial methylene protons in the cyclohexane ring, respectively, although they were overlapped by one another. The signal around 2.1 ppm was assigned to the methin proton bonded axially to C_2 carbon of the cyclohexane ring, because an equatorial methin proton signal is expected to appear at a lower field. The two doublets (3.36 and 3.61 ppm) regarded as an AB pattern were assigned to the methylene protons of the aminomethyl

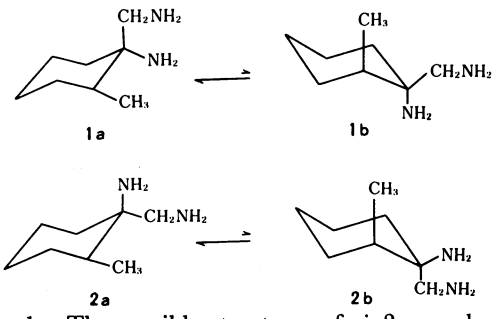

Chart 1. The possible structures of *cis*-2m-amcha (**1a**, **1b**) and *trans*-2m-amcha (**2a**, **2b**).

TABLE 2. ^{13}C-NMR AND ^{1}H-NMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS($J_{^{195}Pt-^{13}C}$ and $J_{^{195}Pt-^{1}H}$)[b]

Complex	^{13}C resonance				^{1}H resonance	
	Cyclohexane ring			CH_2NH_2	CH_2NH_2	
	C_1	C_2	C_6		H_{eq}	H_{ax}
R,S-2m-amcha·2HCl	59.86	39.42	32.06	40.96	3.61[c]	3.36[c]
$[Pt(NH_3)_2(R,S\text{-2m-amcha})]^{2+}$	66.90[d]	37.91 (31.74)	32.11[d]	50.34 (12.20)	2.80[e] (56)	2.70[e,f]
$[Pt(bpy)(R,S\text{-2m-amcha})]^{2+}$	67.54[d]	39.18 (34.18)	34.01[d]	47.61[d]	3.06[g] (62)	2.91[f,g]

a) In ppm. b) In Hz. c) $J_{H-H}=-15$ Hz. d) Platinum satellite were not clearly observed. e) $J_{H-H}=-13$ Hz. f) One of platinum satellite peak was observed, but other was overlapping with H resonance. g) $J_{H-H}=-13$ Hz.

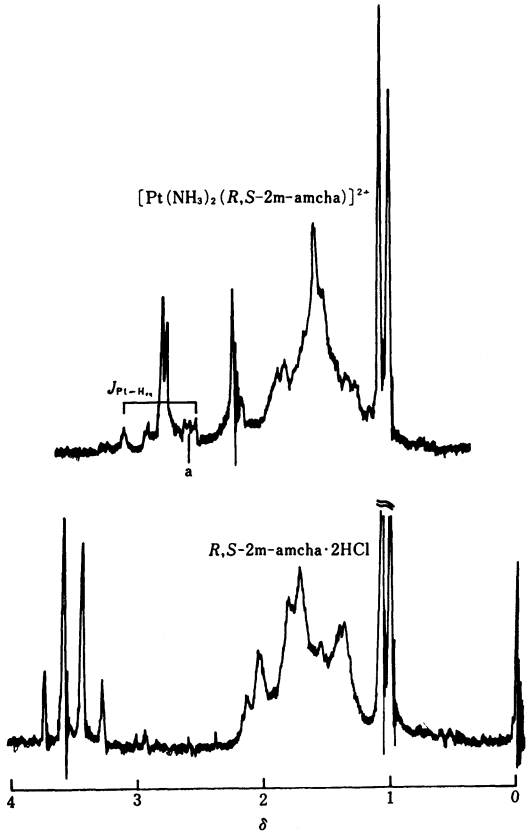

Fig. 2. ^{1}H-NMR spectra of *R,S*-2m-amcha·2HCl and $[Pt(NH_3)_2(R,S\text{-2m-amcha})]^{2+}$.
a: One of platinum satellite peaks based on the Pt–H_{ax} coupling.

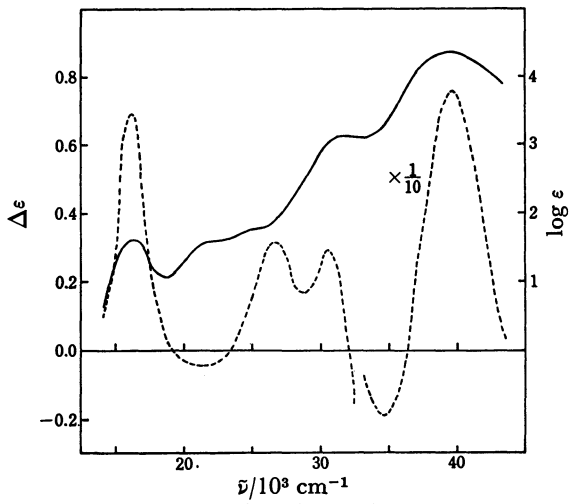

Fig. 3. Electronic (—) and CD (----) spectra of *trans*-$[CoCl_2(R,S\text{-2m-amcha})_2]^{+}$.

group. This spectral pattern suggests that *trans*-2m-amcha has the rigid structure shown in Chart 1, **2a**.

Resolution of the racemic *trans*-diamine was accomplished by recrystallization of its less soluble (2*R*,3*R*)-di-*O*-benzoyltartrate. The absolute configuration of (−)-*trans*-2m-amcha was assigned to (1*R*,2*S*) as described below.

Conformation of the Chelate Ring of the Pt(II) Complexes. In $[Pt(NH_3)_2(R,S\text{-2m-amcha})]^{2+}$ and $[Pt(bpy)(R,S\text{-2m-amcha})]^{2+}$, the equatorial proton of the aminomethyl group showed the $^{3}J_{Pt-H}$ values of 56 and 62 Hz, respectively, while the C_2 carbon of the cyclohexane ring exhibited $^{3}J_{Pt-C}$ 31.7 and 34.2 Hz, respectively (Table 2). These values were somewhat smaller than those of $[Pt(NH_3)_2(pn\text{-}d_1)]^{2+}$ [14] and $[Pt(bpy)(pn)]^{2+}$ [9] (pn-d_1= 1,2-propane-2-*d*-diamine). They were fairly small compared to those of $[Pt(NH_3)_2(R,R\text{-bn})]^{2+}$ [15] and $[Pt(bpy)(chxn)]^{2+}$ [9] having a strongly prefered conformation (*R,R*-bn=*R,R*-2,3-butanediamine, chxn=*trans*-1,2-cyclohexanediamine). We observed that the $^{3}J_{Pt-C}$ value for $[Pt(NH_3)_2(amcha)]^{2+}$ whose chelate ring is considered to interconvert between two conformations was 22.6 Hz (amcha=1-aminomethylcyclohexylamine).[16] This value is also relatively lower than that of $[Pt(bpy)(ms\text{-bn})]^{2+}$ with two conformational forms by rapid ring inversion (*ms*-bn=*meso*-2,3-butanediamine).[9] Erickson *et al.* estimated the relative contribution for the λ conformer of $[Pt(bpy)(pn)]^{2+}$ to be 72%.[9] On the other hand, Yano *et al.* reported that the $^{3}J_{Pt-C}$ values of unsymmetrical diamine complexes are smaller than those of symmetrical ones.[14] As shown in Chart 2 (b), the methyl group of 2m-amcha locates above the chelate ring, if the complex adopts a conformation with axial C_1–C_2 bond. The conformational preference of

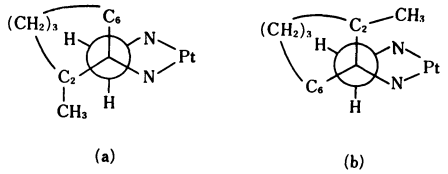

Chart 2. The chelate ring viewed down on C_1–CH_2NH_2 bond.
(a): λ conformaiton of *R,S*-2m-amcha complex, (b): λ conformaiton of *S,R*-2m-amcha complex.

Table 3. Electronic and CD spectral data

Complex	Electronic		CD	
	$\tilde{\nu}/10^3$ cm^{-1}	(log ε)	$\tilde{\nu}/10^3$ cm^{-1}	($\Delta\varepsilon$)
trans-[$CoCl_2$(*R*,*S*-2m-amcha)$_2$]$^+$	16.3	(1.61)	16.2	(+0.69)
	22.2	(1.59)	21.6	(−0.05)
	25.0	(1.78)	26.7	(+0.31)
	31.6	(3.14)	30.6	(+0.30)
			34.6	(−1.90)
	39.4	(4.38)	39.7	(+7.60)
fac-Λ(lel_3)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$	20.8	(2.11)	20.1	(−3.54)
			23.4	(+0.06)
	28.7	(2.10)	27.6	(−0.15)
			30 sh	(−0.11)
	46.7	(4.28)	42.6	(+23.9)
mer-Λ(lel_3)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$	20.8	(2.09)	19.9	(−3.48)
			23.1	(+0.13)
	29.0	(2.07)	27.4	(−0.20)
			29—31 sh	(−0.11)
	46.7	(4.28)	42.4	(+24.2)
mer-Λ(ob_3)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$	20.9	(2.09)	20.6	(+4.47)
	29.0	(2.07)	28.4	(−0.13)
			31.0	(+0.06)
	46.7	(4.28)	41.7	(−11.3)
fac-Λ(ob_3)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$	21.1	(2.04)	20.6	(+3.91)
	29.0	(2.03)	26.7	(+0.09)
			28.9	(−0.09)
			31.3	(+0.04)
	46.3	(4.26)	41.7	(−14.7)

sh: Shoulder.

2m-amcha complex is considered to be strong owing to the steric hindrance by this methyl group. Therefore, the smaller $^3J_{Pt-C}$ values for the present complexes are probably due to the unsymmetrical conformation, as claimed by Yano *et al.*,[14] rather than relative population for the $\lambda \rightleftarrows \delta$ equilibrium.

Absolute Configuration of the Ligand. It has been recognized that the conformation of a chelate ring can be assigned on the basis of the signs of the Cotton effect of *trans*-[$CoCl_2$(1,2-diamine)$_2$]$^+$ complexes in the first absorption region.[17,18] To decide the configuration (1*R*,2*S*) or (1*S*,2*R*) of (−)-*trans*-2m-amcha, we prepared *trans*-[$CoCl_2$((−)-2m-amcha)$_2$]$^+$ and examined its electronic and CD spectra. The absorption spectrum of this complex was quite similar to those of *trans*-[$CoCl_2$(*R*-pn)$_2$]$^+$[17,18] and *trans*-[$CoCl_2$(*R*-chxn)$_2$]$^+$ [18,19] (Fig. 3 and Table 3). The CD sign of the (−)-2m-amcha complex was positive in the I_a (16200 cm^{-1}) and negative in the I_b (21600 cm^{-1}) regions similar to those of the *R*-pn and *R*-chxn complexes with a λ conformation. In addition, the CD spectral pattern of the (−)-2m-amcha complex in the charge-transfer region resembled those of the corresponding *R*-pn and *R*-chxn complexes, although the intensity of the CD peak was weaker for the present complex. These results indicate that the (−)-2m-amcha complex has a λ conformation. Chart 2 illustrates the λ conformation of (1*R*,2*S*)-2m-amcha and (1*S*,2*R*)-2m-amcha chelate rings. Assuming the (1*S*,2*R*)-configuration of the ligand, the considerably larger steric hindrance between the hydrogen attached

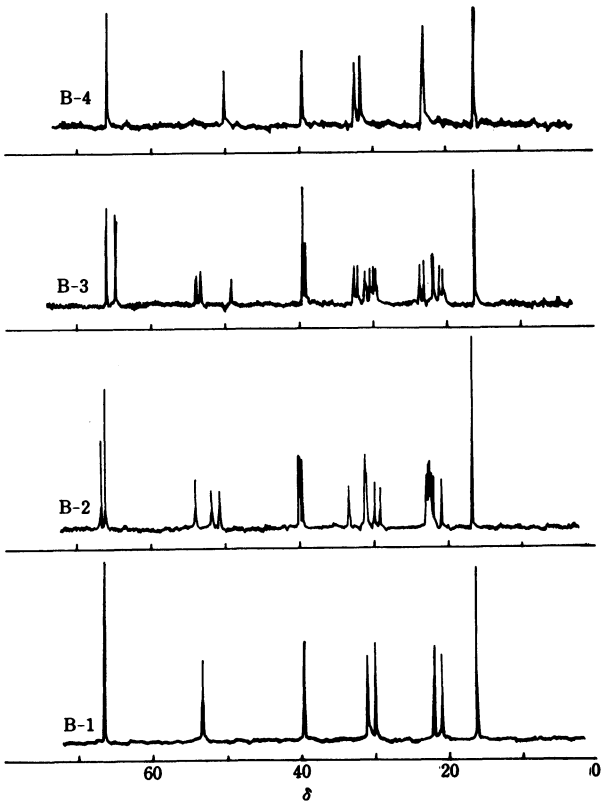

Fig. 4. ^{13}C-NMR spectra of the B-1, B-2, B-3, and B-4 isomers of [Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$.

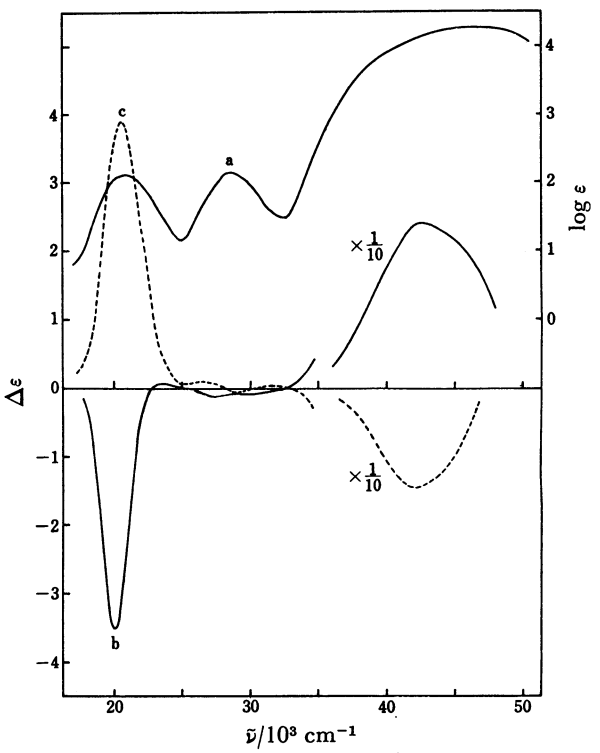

Fig. 5. Electronic (a) and CD (b, c) spectra.
—: *fac*-Λ(*lel*$_3$)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$ (B-1),
---: *fac*-Λ (*ob*$_3$)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$ (B-4).

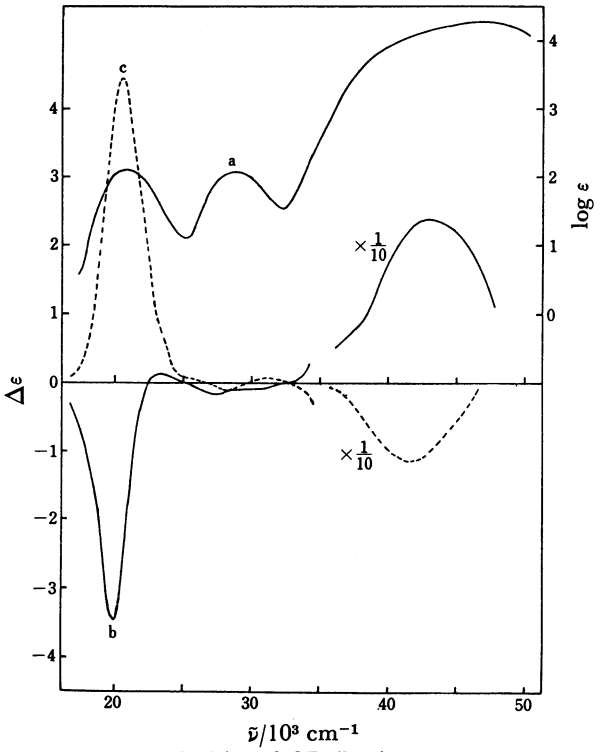

Fig. 6. Electronic (a) and CD (b, c) spectra.
—: *mer*-Δ(*lel*$_3$)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$ (B-2),
---: *mer*-Λ(*ob*$_3$)-[Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$ (B-3).

to the nitrogen of the aminomethyl group and the hydrogen of the methyl group would be explained. Therefore the absolute configuration of the (—)-2m-amcha has been deduced to be (1*R*,2*S*).

The Isomers of [*Co*(R,S-*2m-amcha*)$_3$]$^{3+}$. Four isomers named B-1, B-2, B-3, and B-4 were isolated by an SP-Sephadex C-25 chromatography (Fig. 1). The relative ratio, B-1 : B-2 : B-3 : B-4 was approximately 1 : 6 : 1.5 : 0.3. Figure 4 shows their ^{13}C-NMR spectra. Eight and seven signals were observed for the B-1 and B-4 complex, respectively. Therefore, both complexes were assigned to *fac*-isomers (C_3 symmetry). The B-2 and B-3 complexes were assigned to *mer*-isomers (C_1 symmetry) because nonequivalences for each carbon chemical shift were observed. The same assignments were also obtained from ^{1}H-NMR spectra. The B-1 and B-4 isomers showed one doublet in the methyl region, whereas complicated signals appeared for the B-2 and B-3 isomers. The resonances for methin carbons in the *lel* ring of [Co(*R*-pn)$_3$]$^{3+}$ [20] and [Co(en)$_x$-(*R*,*R*-bn)$_y$]$^{3+}$ [21] were shown to be downfield compared with those in the *ob* ring. Almost all of the signals in ^{13}C-NMR spectrum for the B-1 complex were observed in a region downfield to those of the corresponding B-4 complex. Similar downfiled shifts were also observed in the spectrum of the B-2 isomer compared with the B-3 isomer. This spectral behavior, together with relative formation ratio, suggests that the B-1, B-2, B-3, and B-4 are *fac*-(*lel*$_3$), *mer*-(*lel*$_3$), *mer*-(*ob*$_3$), and *fac*-(*ob*$_3$), respectively.

The electronic and CD spectra of these isomers are shown in Figs. 5 and 6. The numerical data are listed

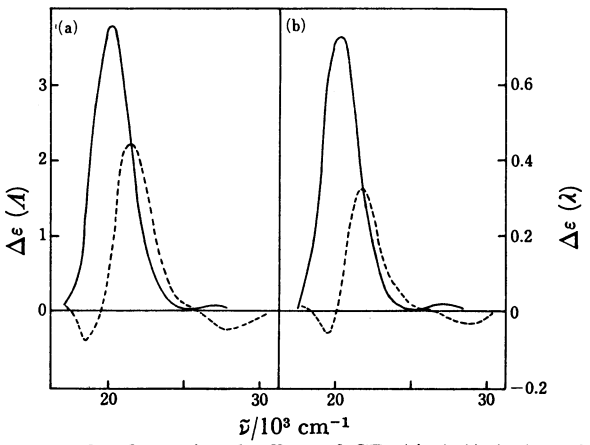

Fig. 7. Configurational effect of CD (Δε(Λ)) (—) and vicinal effect of CD (Δε(λ)) (---) of [Co(*R*,*S*-2m-amcha)$_3$]$^{3+}$.
(a) —: Calculated Δε(Λ)=1/2{*mer*-Λ(*ob*$_3$)—*mer*-Δ(*lel*$_3$)}, ---: calculated Δε(λ)=1/6{*mer*-Λ(*ob*$_3$)+*mer*-Δ(*lel*$_3$}. (b) —: Calculated Δε(Λ)=1/2{*fac*-Λ(*ob*$_3$)—*fac*-Δ(*lel*$_3$)}, : --- calculated Δε(λ)=1/6{*fac*-Λ(*ob*$_3$)+*fac*-Δ(*lel*$_3$)}.

in Table 3. The electronic spectral patterns of the four complexes closely resembled each other. In the CD spectra, the B-1 and B-2 isomers showed a negative band in the first absorption region and the B-3 and B-4 isomers a strong positive band in the same region. Accordingly, the former B-1 and B-2 isomers can be assigned to Δ configuration and the latter two isomers to Λ configuration, respectively. These assignments

were also supported by the CD signs and the relative intensities of the ultraviolet band, refering to the published reports.[4,22] It is known that the CD spectra of the *fac* and *mer* isomers of tris complexes having the same configuration are almost identical.[23-25] It was clearly observed that the CD spectrum of B-1(*fac*) isomer closely resembled that of B-2(*mer*) isomer. Therefore, these isomers have the same configuration. Similarly, B-3(*mer*) and B-4(*fac*) isomers have also the same configuration because they showed a similar CD patterns. In conclusion, we have assigned B-1, B-2, B-3, and B-4 isomers to *fac*-$\Lambda(lel_3)$, *mer*-$\Lambda(lel_3)$, *mer*-$\Lambda(ob_3)$, and *fac*-$\Lambda(ob_3)$, respectively.

Figure 7 shows the configurational and the vicinal CD curves derived from each pair ((B-2 and B-3) and (B-1 and B-4)). The calculated vicinal and configurational CD curves derived from the *fac* isomers were essentially equal to those from the *mer* isomers, respectively. This results suggest that the above assignments for the isomers were reasonable.

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