Preparation and Structural Studies of Tris[(1*R*,2*R*)- or (1*R*,2*S*)-2-(Aminomethyl)cyclohexylamine]cobalt(III) Complexes

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New cobalt(III) complexes containing (1*R*,2*R*)- or (1*R*,2*S*)-2-(aminomethyl)cyclohexylamine(=amcha) have been synthesized and separated into diastereoisomers. $[Co(1R,2R\text{-amcha})_3]^{3+}$ gives two diastereoisomers, structures of which were deduced to be *mer*-Δ and *fac*-Δ based upon their ^{13}C-NMR and CD spectra. $[Co(1R,2S\text{-amcha})_3]^{3+}$ gives three diastereoisomers, structures of which were determined to be *mer*-Λ, *mer*-Δ, and *fac*-Λ. The conformations of the six-membered chelate rings were investigated in the absence or presence of sulfate ions.

The structural study of antitumor Pt(II) complexes of 2-(aminomethyl)cyclohexylamine(=amcha) isomers showed that the chelate ring of (1*R*,2*R*)-amcha is interconvertible between the two chair forms through a λ-skew form, and that of (1*R*,2*S*)-amcha exists in the fixed-chair form, as shown in Fig. 1.[1,2] Since tris(amcha)Co(III) complexes have an octahedral structure, they are expected to form crowded structures rather than square planar Pt(II) complexes. Therefore, the influence of steric interactions among the adjacent ligands is considered to contribute greatly to the conformation of the ligands. In order to investigate the conformation of the six-membered chelate rings of tris(amcha)Co(III) complexes, the authors prepared and separated them into diastereoisomers.

In this paper, the authors will discuss the structures of Co(III) complexes of amcha isomers and the conformations of the chelate rings, based upon their electronic absorption, circular dichroism, and ^{13}C-NMR spectra. This information should be useful in understanding antitumor Pt(IV) complexes of amcha isomers, which are now under investigation.

Experimental

Ligand. A synthesis of *cis*- and *trans*-2-(aminomethyl)cyclohexylamine: These ligands were synthesized from corresponding 1,2-cyclohexanedicarboxylic acids according to a method reported by Armarego *et al.*[3] Resolution of *cis*- and *trans*-amcha was achieved to give (1*R*,2*R*)- and (1*R*,2*S*)-amcha, respectively, according to a method described in the literature.[1]

Preparation of Tris[(1R,2R)- or (1R,2S)-amcha]cobalt(III) Complexes. *trans*-$[CoCl_2(1R,2R\text{- or }1R,2S\text{-amcha})_2]Cl$. To an aqueous solution (15 cm³) containing 2.42 g of $Na_3[Co(NO_2)_6]$ was added an aqueous suspension (20 cm³) of (1*R*,2*R*)- or (1*R*,2*S*)-amcha (1.5 g). The mixture was heated for 4 h at 70 °C with continuous agitation. To the resultant orange solution were added 25 cm³ of conc HCl and stirred for 2 h at 70 °C. Deposited green crystals were collected, washed with ethanol and dried *in vacuo*. Yield: 1.5 g for $[CoCl_2(1R,2R\text{-amcha})_2]Cl$ and 2.3 g for $[CoCl_2(1R,2S\text{-amcha})_2]Cl \cdot 1.5\ H_2O$.

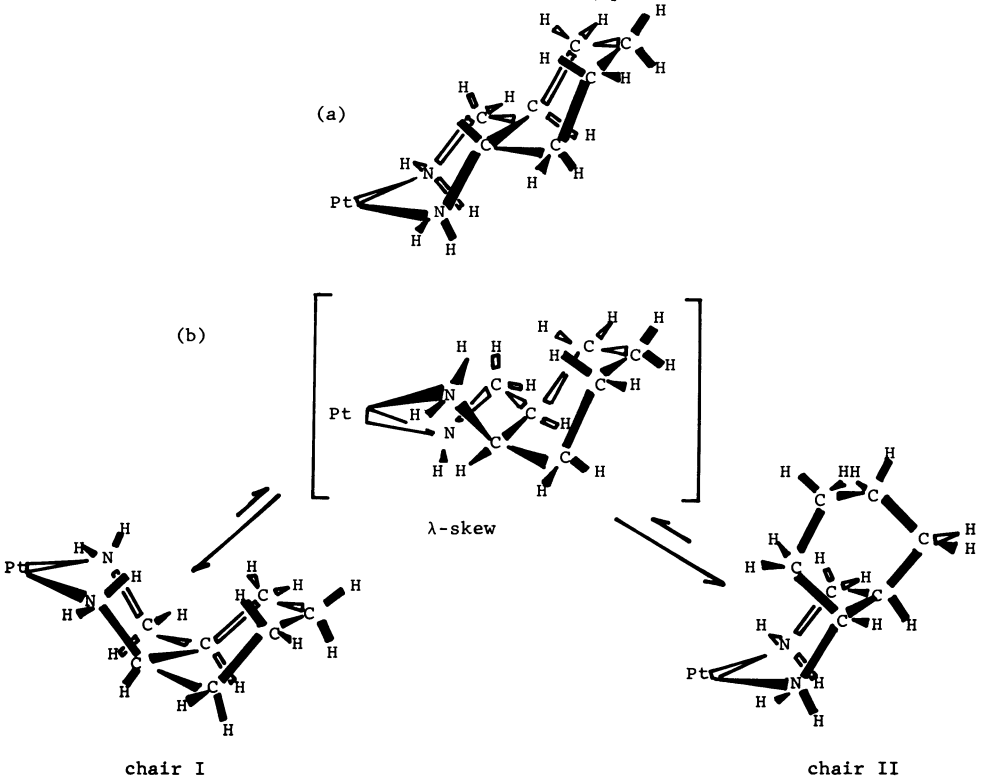

Fig. 1. Conformations of Pt(II) complexes of amcha isomers.
(a) 1*R*,2*S*-amcha, (b) 1*R*,2*R*-amcha.

Table 1. Elemental analyses of cobalt(III) complexes of 2-(aminomethyl)cyclohexylamine

Complex	H (%)		C (%)		N (%)	
	Found	Calcd	Found	Calcd	Found	Calcd
trans-[$CoCl_2$(1*R*,2*R*-amcha)$_2$]Cl	7.92	7.66	39.69	39.86	13.17	13.29
trans-[$CoCl_2$(1*R*,2*S*-amcha)$_2$]Cl 1.5H_2O	7.57	7.74	38.93	39.03	13.43	13.01
mer-Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO_4)$_3$	6.26	6.53	33.91	33.98	10.98	11.32
fac-Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO_4)$_3$	6.22	6.53	33.87	33.98	11.14	11.32
mer-Λ-[Co(1*R*,2*S*-amcha)$_3$](ClO_4)$_3$ $HClO_4$·7H_2O	6.65	6.57	25.95	26.03	8.73	8.67
mer-Δ-[Co(1*R*,2*S*-amcha)$_3$](ClO_4)$_3$ $HClO_4$·2H_2O	6.29	6.09	28.95	28.70	9.67	9.57
fac-Λ-[Co(1*R*,2*S*-amcha)$_3$](ClO_4)$_3$ $HClO_4$·7H_2O	6.35	6.57	25.76	26.03	8.69	8.67

Tris(amcha)cobalt(III) Complexes. To a DMSO solution (20 cm^3) of *trans*-[$CoCl_2$(1*R*,2*R*-amcha)$_2$]Cl (or *trans*-[$CoCl_2$-(1*R*,2*S*-amcha)$_2$]Cl)(1.0 g) was added a methanol solution (5 cm^3) of (1*R*,2*R*)- (or 1*R*,2*S*-)amcha (0.3 g). The mixture was stirred overnight at 60 °C. A reddish-orange solution was diluted with 3 dm^3 of water and was adsorbed on SP-Sephadex C-25. These adsorbed complexes were separated by the following procedures.

*a) Separation of Tris(1*R*,2*R*-amcha)Co(III) Complexes.* The complexes adsorbed on the resin were placed on a column (3.0 IDX120 cm) of SP-Sephadex C-25 and were developed with 0.2 mol dm^{-3} sodium(+)$_{589}$-tartratoantimonate-(III). The complexes were separated into two bands, $F_{C\text{-}1}$ and $F_{C\text{-}2}$, in the order of eluation. The fractions were diluted with water as many as ten times, followed by adsorption in an SP-Sephadex column.

mer-*Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO_4)$_3$.* The $F_{C\text{-}1}$ fraction loaded in an SP-Sephadex column was washed with a large volume of 0.005 mol dm^{-3} $HClO_4$ solution and was then eluated with a 0.5 mol dm^{-3} $HClO_4$ solution. The eluate was concentrated in a desiccator *in vacuo* over P_4O_{10} and NaOH. Deposited orange crystals were collected and dried in a desiccator over P_4O_{10} and NaOH. Yield: 20 mg

fac-*Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO_4)$_3$.* This complex was obtained from the $F_{C\text{-}2}$ fraction by the same procedure as that for the *mer*-Δ isomer. Yield: 50 mg.

*b) Separation of Tris(1*R*,2*S*-amcha)Co(III) Complexes.* The adsorbed band of tris(1*R*,2*S*-amcha)Co(III) complexes was placed on an SP-Sephadex column and was developed with 0.2 mol dm^{-3} sodium(+)$_{589}$-tartratoantimonate(III). The band split into two bands, $F_{T\text{-}1}$ and $F_{T\text{-}2}$, in the order of eluation. The $F_{T\text{-}1}$ fraction was diluted with water as many as ten times and was loaded on an SP-Sephadex column (2.0 IDX110 cm) and rechromatographed with 0.2 mol dm^{-3} Na_2SO_4. The band split into two bands, $F_{T\text{-}1\text{-}1}$ and $F_{T\text{-}1\text{-}2}$.

mer-*Λ and* mer-*Δ-[Co(1*R*,2*S*-amcha)$_3$](ClO_4)$_3$·nH_2O.* The *mer*-Λ *and mer*-Δ complexes were obtained from the $F_{T\text{-}1\text{-}1}$ and $F_{T\text{-}1\text{-}2}$ fractions, respectively, by a similar procedure to that of *mer*-Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO_4)$_3$. Yield: 30 mg for *mer*-Λ and 50 mg for *mer*-Δ.

fac-*Λ-[Co(1*R*,2*S*-amcha)$_3$](ClO_4)$_3$·2H_2O.* The complex was obtained from the $F_{T\text{-}2}$ fraction by a similar procedure to that indicated above. Yield: 140 mg.

The results of elemental analyses of the Co(III) complexes, thus obtained, are shown in Table 1.

Measurements. Absorption and circular dichroism spectra were measured with a Hitachi 557 spectrophotometer and a JASCO J-40 spectropolarimeter. FT ^{13}C-NMR spectra were obtained with a JEOL JNM-FX-100 spectrometer.

Results and Discussion

^{13}C-NMR Spectra. There are two geometrical isomers, *i.e.*, *mer* and *fac*, for tris(1*R*,2*R*-amcha)Co-(III) complexes. The $F_{C\text{-}1}$ and $F_{C\text{-}2}$ fractions separated through an SP-Sephadex column exhibited ^{13}C-NMR spectra (Fig. 2). The ^{13}C-NMR spectrum of the $F_{C\text{-}2}$ fraction showed 7 singlet resonance lines, indicating the *fac*-isomer, where the three coordinated amcha are chemically equivalent. The $F_{C\text{-}1}$ fraction showed a similar ^{13}C-NMR pattern to that of the *fac*-isomer, except that each resonance peak was composed of a doublet or triplet, indicating a lower symmetric *mer*-isomer with unequivalent ligands. Assignments of the resonance lines were tentatively made based on the assignments for [Pt(en)(1*R*,2*R*-amcha)]Cl_2.

Tris(1*R*,2*S*-amcha)Co(III) complexes were separated into three fractions, *i.e.*, $F_{T\text{-}1\text{-}1}$, $F_{T\text{-}1\text{-}2}$, and $F_{T\text{-}2}$, typical two ^{13}C-NMR spectra of which are illustrated in Fig. 2. The $F_{T\text{-}2}$ fraction exhibited 7 singlet resonance lines in the ^{13}C-NMR spectrum and was assigned to the symmetric *fac*-isomer. The $F_{T\text{-}1\text{-}1}$ and $F_{T\text{-}1\text{-}2}$ fractions showed a similar ^{13}C-NMR spectral pattern to that of $F_{T\text{-}2}$, except that each resonance peak was composed of a doublet or triplet, suggesting the *mer* configuration. The assignments of the resonance lines for these Co(III) complexes were made as shown in Fig. 2, based upon the assignments of [Pt(en)(1*R*,2*S*-amcha)]Cl_2.[1]

Absorption Spectra. The absorption maxima of the first absorption bands of Co(III) complexes containing 1,3-diamines were reported to shift depending upon the configurations of the complexes. For example, the tris(meso-ptn)Co(III) complex was reported to have *fac*- and *mer*-isomers with a chair conformation. The interaction among the ligands was larger in the *mer*-isomer than the *fac*-isomer and the absorption maximum of the former shifted 2 nm toward a longer-wavelength region compared to that of the latter.[4]

*a) Tris(1*R*,2*R*-amcha)Co(III) Complexes.* Comparing the absorption maxima of the *fac*- and *mer*-isomers of tris(1*R*,2*R*-amcha)Co(III), the maximum of the *fac*-isomer was at 489 nm and that of the *mer*-isomer

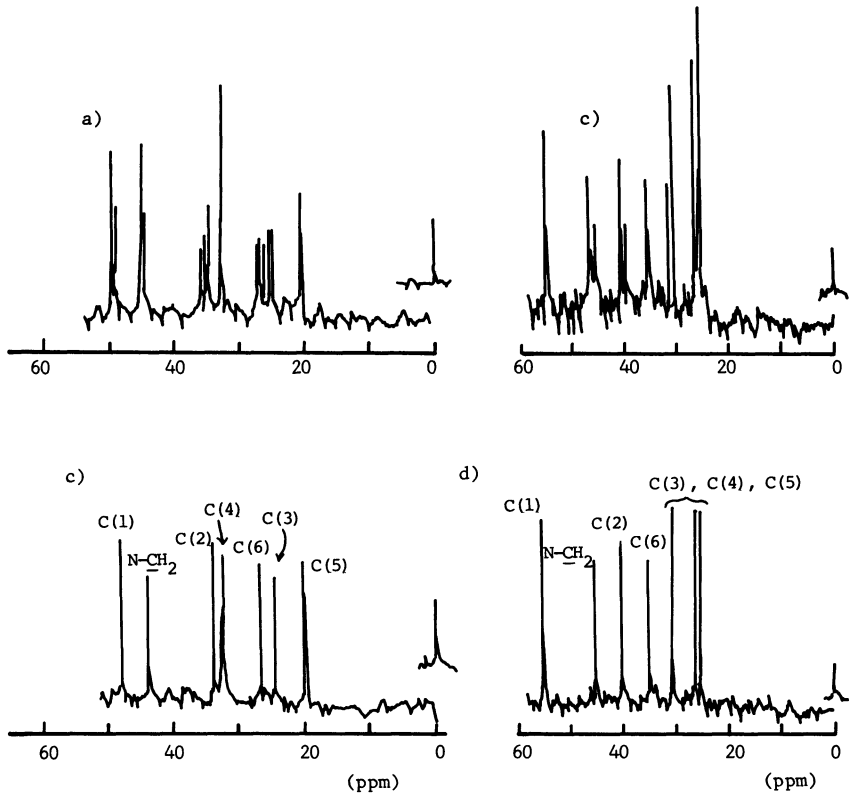

Fig. 2. ^{13}C-NMR spectra of tris(amcha)cobalt(III) complexes.
(a): F_{C-1}; *mer*-Δ-[Co(1*R*,2*R*-amcha)$_3$]$^{3+}$, (b): F_{C-2}; *fac*-Δ-[Co(1*R*,2*R*-amcha)$_3$]$^{3+}$, (c): F_{T-1-2}; *mer*-Δ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$, (d): F_{T-2}; *fac*-Λ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$.

Table 2. Numerical data of absorption(AB) and cicular dichroism(CD)

Complex	AB λ_{max}/nm (log ε/mol^{-1} dm^3 cm^{-1})	CD λ_{max}/nm (Δε/mol^{-1} dm^3 cm^{-1})
mer-Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO$_4$)$_3$	495.0 (1.97)	517.0 (−0.853)
		530.0 (−0.365)[a]
		475.0 (+0.436)[a]
fac-Δ-[Co(1*R*,2*R*-amcha)$_3$](ClO$_4$)$_3$	489.0 (2.09)	521.0 (−0.666)
		458.5 (+0.089)
		535.0 (−0.239)[a]
		478.0 (+0.749)[a]
mer-Λ-[Co(1*R*,2*S*-amcha)$_3$](ClO$_4$)$_3$ HClO$_4$·7H$_2$O	485.0 (1.97)	505.0 (+0.749)
		505.0 (+0.632)[a]
mer-Δ-[Co(1*R*,2*S*-amcha)$_3$](ClO$_4$)$_3$ HClO$_4$·2H$_2$O	485.0 (2.01)	505.0 (−0.890)
		507.0 (−0.721)[a]
fac-Λ-[Co(1*R*,2*S*-amcha)$_3$](ClO$_4$)$_3$ HClO$_4$·7H$_2$O	485.0 (1.97)	495.0 (+1.025)
		497.0 (+0.437)[a]

a) CD data in 0.2 mol dm^{-3} Na_2SO_4 solutions.

at 495 nm. This shift can be explained by the fact that the *mer*-isomer is stereostructurally more crowded than the *fac*-isomer.

b) Tris(1R,2S-amcha)Co(III) Complexes. All three isomers showed absorption maxima at 485 nm, indicating little interaction among the ligands. The fact that the absorption maximum observed for *fac*-[Co(1*R*,2*S*-amcha)$_3$] shifted 4 nm towaed a longer-wavelength region compared to that of the corresponding *fac*-[Co(1*R*,2*R*-amcha)$_3$] may be explained by a more crowed structure of the former than of the latter.

Circular Dichroism Spectra. In tris(diamine)Co(III) complexes with five-membered chelate rings, there exists a good correlation between the signs of the CD bands corresponding to the E component of the first absorption bands and the configurations. However, in tris(diamine)Co(III) complexes with six-membered chelate rings, the correlation between the signs of the CD bands and the configurations has not been well established. A typical example was found for [Co(tn)$_3$]$^{3+}$.[5-9] However, in the case of tris(*S*-bn)(bn=1,3-butanediamine) complexes, the correlation was well maintain-

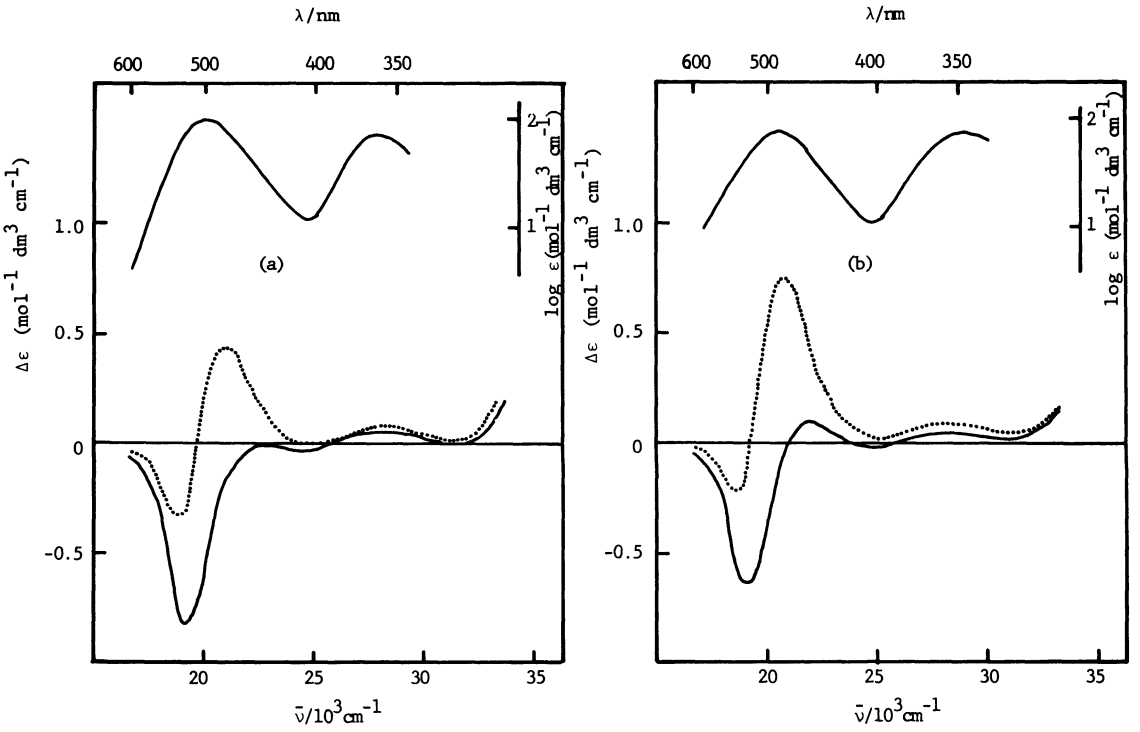

Fig. 3. Absorption and CD spectra of tris(1*R*,2*R*-amcha)cobalt(III) complexes.
(a): *mer*-Δ-[Co(1*R*,2*R*-amcha)$_3$]$^{3+}$, CD spectra of 3.4×10^{-3} mol dm^{-3} in water (——) and 1.7×10^{-3} mol dm^{-3} in 0.2 mol dm^{-3} Na_2SO_4 (·····), (b): *fac*-Δ-[Co(1*R*,2*R*-amcha)$_3$]$^{3+}$, CD spectra of 2.7×10^{-3} mol dm^{-3} in water (——) and 1.7×10^{-3} mol dm^{-3} in 0.2 mol dm^{-3} Na_2SO_4 (·····).

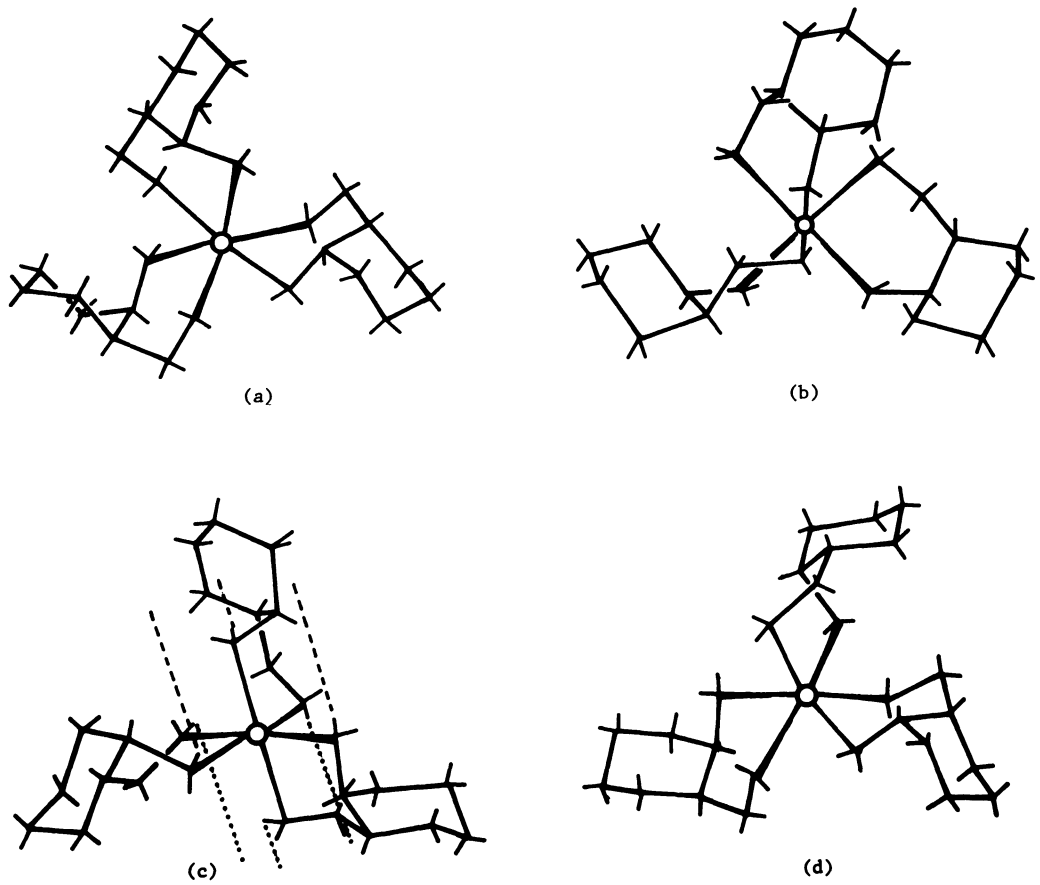

Fig. 4. Schematic structures of *fac*-Δ-[Co(1*R*,2*R*-amcha)$_3$]$^{3+}$.
(a): (chair I)$_3$, (b): (chair II)$_3$, (c): (λ-skew)$_3$, (d): (chair I)$_2$ (λ-skew).

ed, giving positive CD bands for *mer*-Λ and *fac*-Λ isomers and negative ones for the *mer*-Δ and *fac*-Δ isomers.[10]

The CD spectral behavior of tris(1*R*,2*R*- or 1*R*,2*S*-amcha) Co(III) complexes resembles that of tris(*S*-bn)Co(III) complexes, and the configurations of the former were elucidated based on the correlations found in the latter ones.

*a) Tris(1*R*,2*R*-amcha)Co(III) Complexes.* As shown in Fig. 3, both *mer*- and *fac*-isomers of tris(1*R*,2*R*-amcha)Co(III) complexes showed negative CD bands at 517 and 521 nm with $\Delta\varepsilon$ values of −0.853 and −0.666 in the first absorption region, respectively. Their configurations were deduced to be Δ. The *fac*-Δ isomer also showed a small positive CD band at 458 nm ($\Delta\varepsilon$=+0.089). In a 0.2 mol dm^{-3} sodium sulfate solution, the CD band of the *mer*-Δ isomer split into two bands, giving negative and positive bands at 530 and 475 nm with $\Delta\varepsilon$ values of −0.365 and +0.436, respectively. The increment of the positive band was also observed for the *fac*-Δ isomer (Fig. 3(b)). The occurrence of the positive CD bands can be explained by taking account of the λ-gauche conformation due to a hydrogen bond formation between sulfate ions and the amino protons. This was confirmed by the molecular model speculations.

As shown in Fig. 1, 1*R*,2*R*-amcha has the possibility to assume chair conformations, one of which has an axial amino group and an equatorial aminomethyl group (chair I). The other has a reverse orientation-(chair II). As to the *fac*-Δ isomer, a (chair I)$_3$ conformer is advantageous over a (chair II)$_3$ conformer, which has a large steric hindrance than the former. However, an interconversion between the chair conformers is possible. Therefore, the small positive CD band in H_2O which was observed for the *fac*-Δ isomer may suggest the existence of a (chair I)$_2$ (λ-skew) conformer. The molecular models of (chair I)$_3$, (chair II)$_3$, and (λ-skew)$_3$ conformers indicate that a (λ-skew)$_3$ conformer can be stabilized by ion-pairs between sulfate ions and amino protons. That is, in the presence of sulfate ions, the (λ-skew)$_3$ form is more stable than other forms.

Concerning the *mer*-Δ isomer, the (chair I)$_3$ conformer is the most stable form and the (chair II)$_3$ conformer was not considered due to its steric hindrances. The other possible structure is a (chair I)$_2$ (chair II) conformer. Thus, an equilibrium between (cahir I)$_3$ and (chair I)$_2$ (chair II) is probable, but the frequency of the interconversion, which can take place through the λ-skew, is low compared to that between (chair I)$_3$ and (chair II)$_3$ for the *fac*-Δ isomer. The model of a *mer*-Δ(λλλ) conformer indicates that two ion-pairs are also possible similar to the *fac*-Δ isomer, giving an enhanced intensity of the positive CD band in the presence of sulfate ions.

*b) Tris(1*R*,2*S*-amcha)Co(III) Complexes.* CD spectra of the mer isomers exhibited a positive and a negative CD band at 505 nm in H_2O for $F_{T\text{-}1\text{-}1}$ and $F_{T\text{-}1\text{-}2}$ fractions, respectively. The *fac*-isomer showed positive CD band at 505 nm. From these CD data, the configurations of $F_{T\text{-}1\text{-}1}$ and $F_{T\text{-}1\text{-}2}$, and $F_{T\text{-}2}$ complexes were deduced to be *mer*-Λ, *mer*-Δ, and *fac*-Λ, respectively. Their CD spectra are illustrated in Fig. 5.

In the presence of sulfate ions, the *fac*-Λ isomer exhibited a significant decrease in $\Delta\varepsilon$ (from +1.02 to +0.43). On the other hand, both the *mer*-Λ and *mer*-Δ isomers showed only a little decrease in $\Delta\varepsilon$ in 0.2 mol dm^{-3} sodium sulfate solutions. These CD spectra are also illustrated in Fig. 5. The CD spectral behavior of tris(1*R*,2*S*-amcha)Co(III) complexes suggested different conformations to those of the tris(1*R*,2*R*-amcha)-Co(III) complexes. The differences may arise due to the fact that the conformations of 1*R*,2*S*-amcha were restricted to the chair and λ-skew forms, as shown in [Pt(en)(1*R*,2*S*-amcha)]$^{2+}$.

From the molecular models of the tris(1*R*,2*S*-amcha) Co(III) complexes the following conclusions were obtained concerning the stereostructures of the three isomers. For the *fac*-Λ isomer, (chair)$_3$ and (λ-skew)$_3$ conformers are stable and in the former ion-pairs can be formed between sulfate ions and amino protons, while in the latter ion-pair formation is not possible due to its (ob)$_3$-type structure. That is, in H_2O the *fac*-Λ isomer exists as a (Λ-skew)$_3$ conformer, which changes conformations and the (chair)$_3$ conformer becomes stable in a 0.2 mol dm^{-3} sodium sulfate solution by ion-pair formation. This explains the observed decrease in $\Delta\varepsilon$.

For the *mer*-Λ isomer, a (λ-skew)$_3$ conformer is more stable than (chair)$_3$, in which steric hindrance exists between ligand A and B as shown in Fig.7. The presence of sulfate ions brought about a slight decrease in $\Delta\varepsilon$ (from +0.749 to +0.632), suggesting a partial conformational change among the three ligands. Among the three possibe (λ-skew)$_2$(chair) conformers, the one involving ligand C in a chair conformation stabilized with less steric hindrance and was able to form ion-pairs. Another conformer, containing ligand B in a chair conformation, was also stable but it could not form the ion-pairs. The other conformer containing ligand A in chair was less stable than the other two conformers due to its steric hindrance. The molecular models indicate that *mer*-Λ isomer exists as a (λ-skew)$_3$ conformer in H_2O and in the presence of sulfate ions a (λ-skew)$_2$ (chair) conformer with ligand C in a chair conformation is stabilized by the ion-pair formation with a slight decrease in $\Delta\varepsilon$.

The molecular models of the last isomer, *mer*-Δ indicate that it can also exist as a (λ-skew)$_3$ or (λ-skew)$_2$ (chair) conformer, in the latter of which ligand A or B in the chair conformation. Its CD spectral behavior in H_2O and a 0.2 mol dm^{-3} sodium sulfate solution seems to indicate that a partial conformational change from chair to λ-skew takes place with a decreased absolute $\Delta\varepsilon$ in the latter solution. That is, the *mer*-Δ isomer exists in a (λ-skew)$_2$(chair) form in H_2O and a (λ-skew)$_3$ form in the presence of sulfate ions. How-

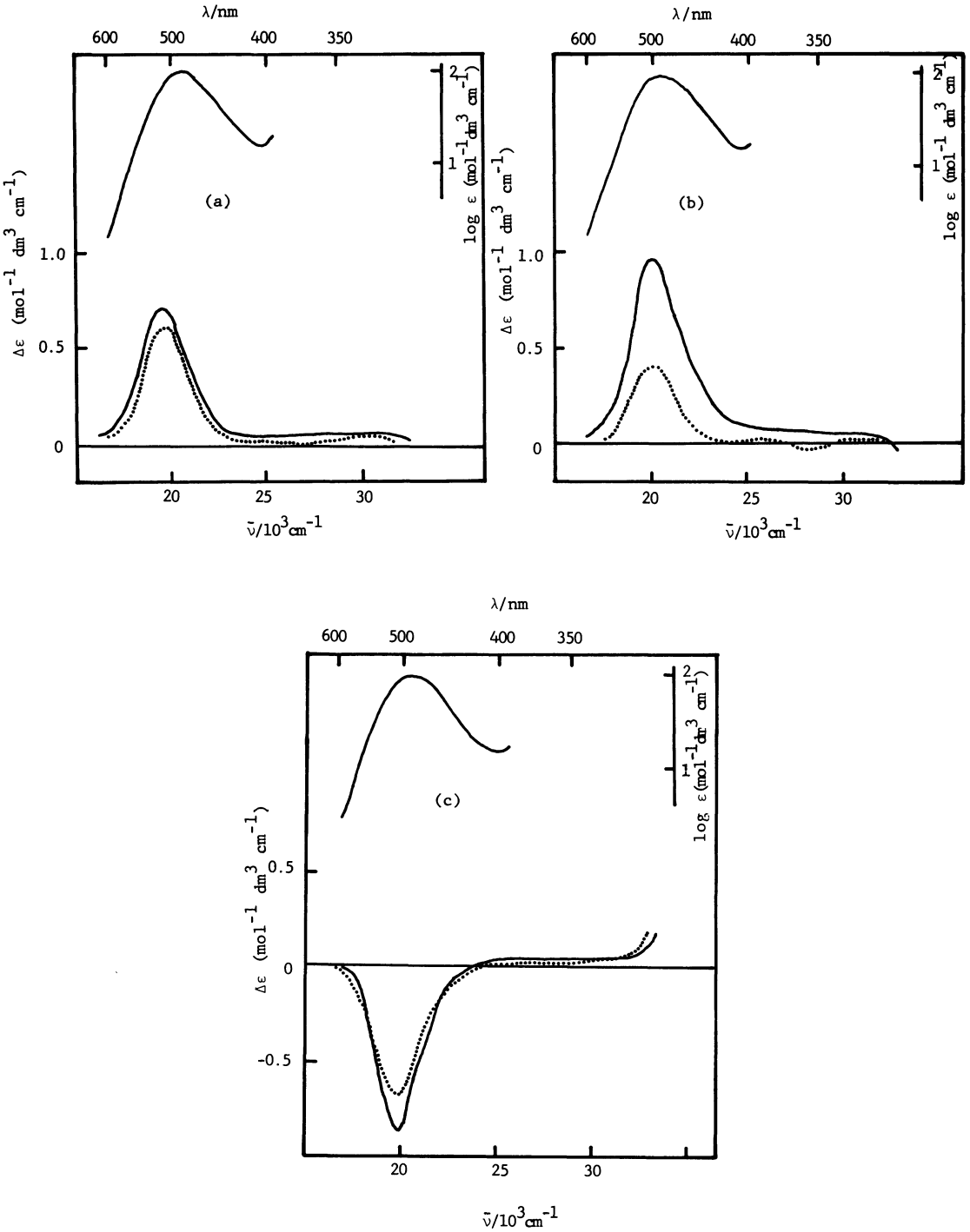

Fig. 5. Absorption and CD spectra of tris(1*R*,2*S*-smcha)cobalt(III) complexes.
(a): *mer*-Λ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$, CD spectra of 5.19×10^{-3} mol dm^{-3} in water (——) and 0.2 mol dm^{-3} Na_2SO_4 (·····), (b): *fac*-Λ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$, CD spectra of 5.16×10^{-3} mol dm^{-3} in water (——) and 0.2 mol dm^{-3} Na_2SO_4 (·····), (c): *mer*-Δ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$, CD spectra of 5.73×10^{-3} mol dm^{-3} in water (——) and 0.2 mol dm^{-3} Na_2SO_4 (·····).

ever, this explanation is in conflict with the Δε value of −0.89 in H_2O for the *mer*-Δ isomer, because the combination of a Δ configuration and λ conformations would be expected to give a somewhat smaller absolute Δε than the value of +0.749 observed for the *mer*-Λ isomer with (λ-skew)$_3$ conformations. Therefore, the conformation of *mer*-Δ was not possible to determine with the present CD spectral data.

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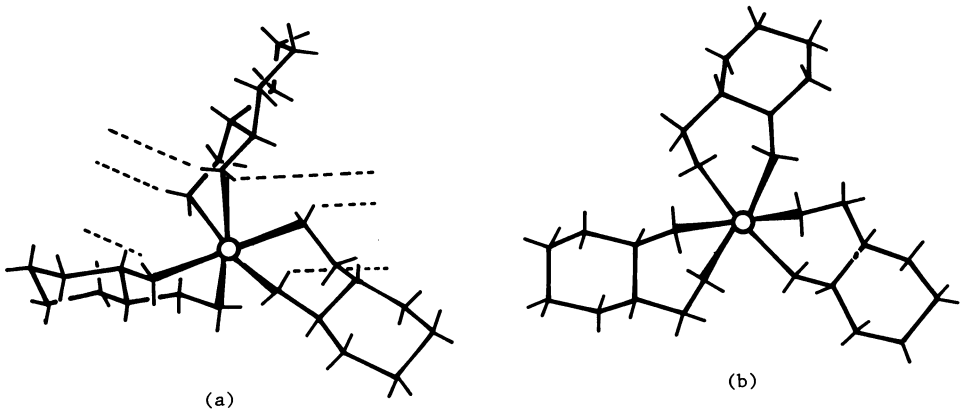

Fig. 6. Schematic structures of *fac*-Δ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$.
(a): (chair)$_3$, (b): (λ-skew)$_3$.

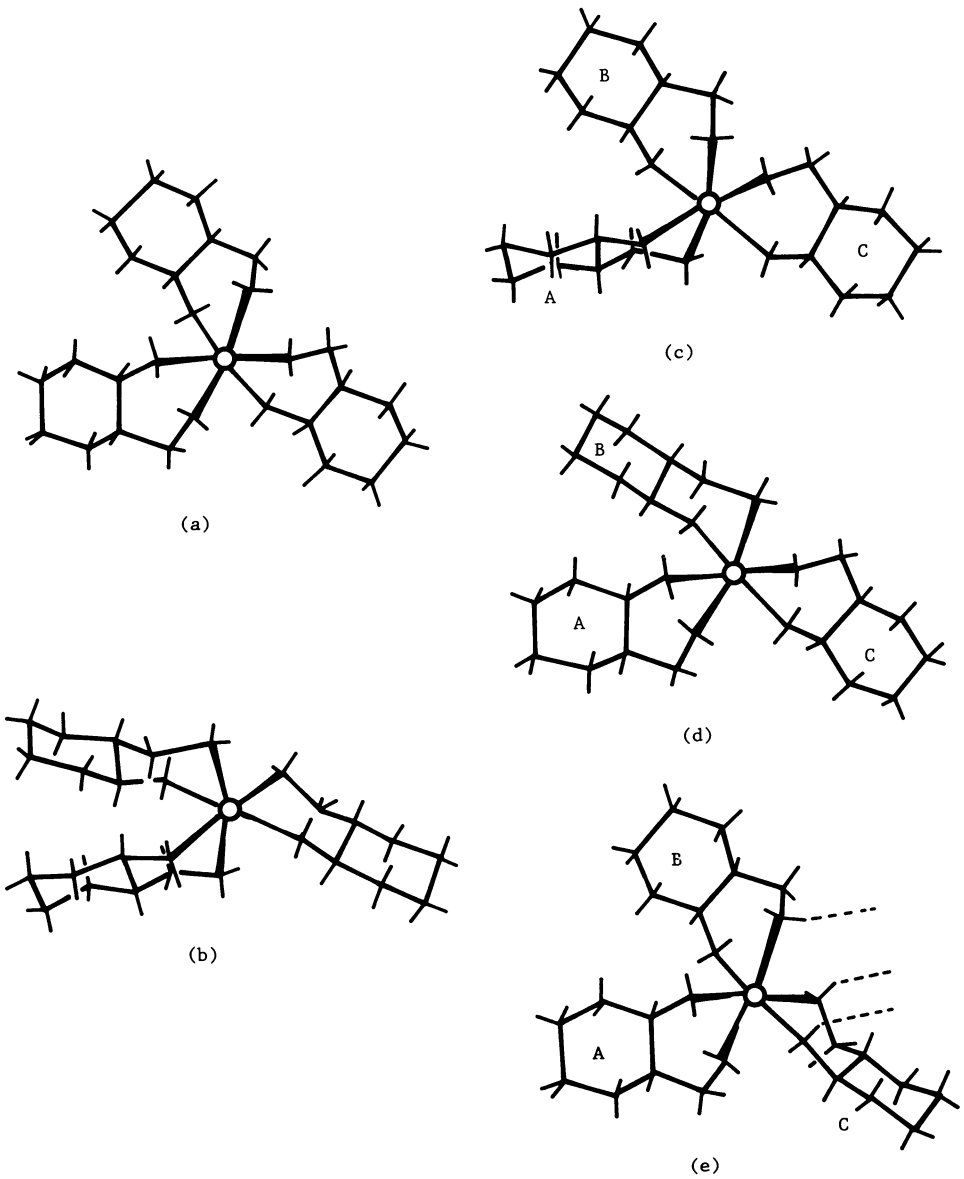

Fig. 7. Schematic structures of *mer*-Λ-[Co(1*R*,2*S*-amcha)$_3$]$^{3+}$.
(a): (λ-skew)$_3$, (b): (chair)$_3$, (c): (λ-skew)$_2$ (chair A), (d): (λ-skew)$_2$ (chair B), (e): (λ-skew)$_2$ (chair C).

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