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Studies of the Metal Complexes of Cyclohexane Derivatives. VIII.[1)] Preparation and Properties of Platinum(II) and Cobalt(III) Complexes Containing (1*R*,2*S*,3*S*)- or (1*S*,2*R*,3*R*)-3-Methyl-1,2-cyclohexanediamine

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(1*RS*,2*SR*,3*SR*)-3-Methyl-1,2-cyclohexanediamine (3m-chxn), a methyl derivative of *cis*-1,2-cyclohexanediamine, was prepared and optically resolved. The absolute configurations of the enantiomers obtained were assigned on the basis of the Cotton effect of the *trans*-dichlorobis(diamine) complexes, each containing active 3m-chxn. The complexes of the $[Pt(NH_3)_2L]^{2+}$, $[Pt(en)L]^{2+}$, and $[CoL_3]^{3+}$ types (en=1,2-ethanediamine, L=*R*,*S*,*S*- or *S*,*R*,*R*-3m-chxn) were also synthesized and characterized on the basis of their absorption, CD, and ^{13}C NMR spectra. It has been found that the chelate rings adopted by *R*,*S*,*S*- and *S*,*R*,*R*-3m-chxn predominantly take the δ and λ conformations respectively, because of the preferred equatorial orientation of the C_2–C_3 bond of the cyclohexane ring. The four diastereomers of $[Co(R,S,S\text{-3m-chxn})_3]^{3+}$ were chromatographically isolated and assigned to *fac*-Λ(*lel*$_3$), *mer*-Λ(*lel*$_3$), *fac*-Δ(*ob*$_3$), and *mer*-Δ(*ob*$_3$).

There have been many studies of the correlation between the conformations of the 1,2-diamine chelate ring and the steric structures of the ligands, but they have almost all been on the effects by the substituents attached to the diamine chelate ring.[2,3)] The influences on complex formation of the substituents bonded to the carbon atom outside the chelate ring have not been so widely studied. Recently we ourselves have reported the properties of the complex containing (1*R*,2*S*)-1-aminomethyl-2-methylcyclohexylamine (*R*,*S*-2m-amcha).[1)] The methyl group of this ligand, that is in the β-position to one of the donor atoms, strongly affects the conformation of the chelate ring. The conformation in which the C_1–C_2 bond of the cyclohexane ring is equatorially oriented with respect to the chelate ring is much more favorable than the other one which requires the methyl group to occupy a position over the chelate ring. In this study, we have prepared some Pt^{II} and Co^{III} complexes of (1*R*,2*S*,3*S*)- or (1*S*,2*R*,3*R*)-3-methyl-1,2-cyclohexanediamine (*R*,*S*,*S*- or *S*,*R*,*R*-3m-chxn). The methyl group is presumed to be situated in an equatorial position in the chair conformation of the cyclohexane ring. Its steric influence on the conformational preference in complex formation is considered to be similar to that of *R*,*S*-2m-amcha. Another concern of this paper is to obtain experimental data about the properties of the complexes of *cis*-1,2-cyclohexanediamine (*cis*-chxn) derivatives. Little investigatory work has been done on the Pt^{II} and Co^{III} complexes of this series of diamines compared with the *trans*-chxn derivatives.[4—6)]

Experimental

Preparation and Resolution of the Ligands. *C*-3- Methyl-4-ene-*r*-1,*c*-2-cyclohexenedicarboxylic acid was prepared according to the procedure in the literature.[7)] The reduction of the product with hydrogen in the presence of the rhodium catalyst gave the saturated dicarboxylic acid. A Schmidt reaction[8)] of the reduced diacid yielded (1*RS*,2*SR*,3*SR*)-3-methyl-1,2-cyclohexanediamine. Optical resolution was performed using (2*R*,3*R*)-di-*O*-benzoyltartaric acid. From the less soluble diastereomeric salt ($[\alpha]_D$=−76° (*c* 1.1, CH_3OH)), (+)-3m-chxn·2HCl was isolated. Found: C, 41.77; H, 8.96; N, 13.66%. Calcd for $C_7H_{18}N_2Cl_2$: C, 41.80; H, 9.02; N, 13.93%. $[\alpha]_D$=2.9° (*c* 10, H_2O). In spite of its low $[\alpha]_D$ value, it is considered to be optically pure and is assigned to (1*R*,2*S*,3*S*)-3m-chxn·2HCl on the basis of the CD spectrum of *trans*-$[CoCl_2((+)\text{-3m-chxn})_2]^+$.[9)] The decomposition of the more soluble diastereomeric salt ($[\alpha]_D$=−96° (*c* 0.43, H_2O)) gave (−)-3m-chxn·2HCl, assignable to (1*S*,2*R*,3*R*). Found: C, 41.60; H, 9.21; N, 13.76%. Calcd for $C_7H_{18}N_2Cl_2$: C, 41.80; H, 9.02; N, 13.93%. $[\alpha]_D$=−2.9° (*c* 10, H_2O).

Preparation of Complexes. *$[Pt(NH_3)_2L]Cl_2$ and $[Pt(en)L]Cl_2$ (en=1,2-ethanediamine, L=*R,S,S- *or* S,R,R-*3m-chxn)*: $[Pt(NH_3)_2L]Cl_2$ and $[Pt(en)L]Cl_2$ were prepared by the reaction of $[PtCl_2L]$ with an aqueous ammonia and an en solution respectively in a manner similar to the procedure in the literature.[10,11)] Found: $[Pt(NH_3)_2(R,S,S,\text{-3m-chxn})]Cl_2$, C, 19.26; H, 5.01; N, 12.71%, $[Pt(NH_3)_2(S,R,R\text{-3m-chxn})]Cl_2$, C, 19.02; H, 5.08; N, 12.65%. Calcd for $[Pt(NH_3)_2L]Cl_2 \cdot 0.5H_2O = C_7H_{22}N_4Cl_2Pt \cdot 0.5H_2O$: C, 19.23; H, 5.30; N, 12.81%. Found: $[Pt(en)(R,S,S\text{-3m-chxn})]Cl_2$, C, 23.41; H, 5.23; N, 12.41%, $[Pt(en)(S,R,R\text{-3m-chxn})]Cl_2$, C, 23.62; H, 5.30; N, 12.45%. Calcd for $[Pt(en)L]Cl_2 = C_9H_{24}N_4Cl_2Pt$: C, 23.79; H, 5.32; N, 12.33%.

trans-*$[CoCl_2L_2]ClO_4$*: An attempt to synthesize these complexes from $CoCl_2 \cdot 6H_2O$ and the respective active diamine by the usual air oxidation was unsuccessful. Therefore, they were prepared by a method similar to that used for *trans*-$[CoCl_2(trans\text{-chxn})_2]^+$, using $[CoCO_3(NH_3)_4]NO_3 \cdot 0.5H_2O$ as the starting material.[12)] The resulting product seemed to be a mixture of *cis*- and *trans*-dichlorobis (diamine) complexes. The expected complexes were obtained by refluxing a methanol solution of a mixture by a method described in the literature.[13)] Found: *trans*-$[CoCl_2(R,S,S\text{-3m-chxn})_2]ClO_4$, C, 34.01; H, 6.71; N, 11.13%, *trans*-$[CoCl_2(S,R,R\text{-3m-chxn})_2]ClO_4$, C, 34.39; H, 6.66; N, 11.31%. Calcd for $[CoCl_2L_2]ClO_4 \cdot 0.5H_2O = C_{14}H_{32}N_4O_4Cl_3Co \cdot 0.5H_2O$: C, 33.99; H, 6.72; N, 11.32%.

*Four Isomers of $[Co($*R,S,S*$\text{-3m-chxn})_3]Cl_3$*: These complexes were synthesized in a manner similar to that described previously.[1] The resulting product prepared from *trans*-$[CoCl_2py_4]Cl$ (1.3 mmol) and *R,S,S*-3m-chxn (6.5 mmol), was adsorbed on SP-Sephadex C-25. This resin was loaded on the top of an SP-Sephadex C-25 column (2.7 cm×95 cm) and eluted with a 0.2 mol/dm³ Na_2SO_4 solution. The four bands which appeared, were named B′-1, B′-2, B-3, and B-4 in the order of elution. The B′-1 and B′-2 bands overlapped each other and contained only a small amount of the complexes. After six chromatographic runs, the combined fractions of B′-1 and B′-2 were evaporated to afford an orange solid. This solid was then chromatographed again using an SP-Sephadex C-25 column (2.7 cm×95 cm) with a 0.15 mol/dm³ Na_3PO_4 solution. Two bands well-separated appeared, they were called B-1 and B-2 in the order of elution. The B-1, B-2, B-3, and B-4 complexes were obtained as chlorides by a procedure similar to that described in a previous report.[1] Yields: B-1; *ca.* 30 mg, B-2; *ca.* 60 mg, B-3; *ca.* 1300 mg, B-4; *ca.* 1600 mg. They were dissolved in a small amount of water and recrystallized by adding a 6 mol/dm³ hydrochloric acid solution. The B-1, B-2, B-3, and B-4 complexes were obtained as red orange needles, a red orange crystalline powder, an orange crystalline powder, and orange needles respectively. Found: B-1, C, 42.56; H, 8.36; N, 14.11%, B-2, C, 42.28; H, 8.25; N, 14.13%. Calcd for $[CoL_3]Cl_3\cdot0.5H_2O\cdot HCl=C_{21}H_{48}N_6Cl_3Co\cdot0.5H_2O\cdot HCl$: C, 42.36; H, 8.46; N, 14.11%. Found: B-3, C, 41.13; H, 9.11; N, 13.86%. Calcd for $[CoL_3]Cl_3\cdot3.5H_2O=C_{21}H_{48}N_6Cl_3Co\cdot3.5H_2O$: C, 41.15; H, 9.04; N, 13.71%. Found: B-4, C, 41.88; H, 9.00; N, 14.17%. Calcd for $[CoL_3]Cl_3\cdot3H_2O=C_{21}H_{48}N_6Cl_3Co\cdot3H_2O$: C, 41.76; H, 9.01; N, 13.91%.

Measurements: A JASCO J-40 spectropolarimeter and a Shimadzu UV-210-A spectrometer were used to measure the CD and absorption spectra respectively. The optical rotation at 589 nm were measured with a JASCO DIP-4 polarimeter. The ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 spectrometer, with D_2O as a solvent. The chemical shifts were measured with dioxane (δ 67.70 ppm) as the internal reference.

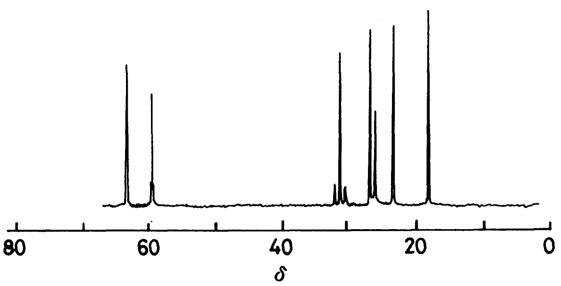

Fig. 1. ^{13}C NMR spectrum of $[Pt(NH_3)_2(S,R,R\text{-3m-chxn})]^{2+}$.

Results and Discussion

Conformation of the Chelate Ring of the Pt^II Complexes. A representative ^{13}C NMR spectrum of the Pt^{II} complexes prepared in this study is shown in Fig. 1, while the numerical data are given in Table 1. The peak at around 32 ppm was assigned to the C_3 carbon by the aid of the off-resonance proton-decoupling technique. The signal at around 27 ppm is attributable to the resonance of the C_6 carbon, because it is expected to appear in a lower field than those of the C_4 and C_5 carbons. In the *R,S,S*- or *S,R,R*-3m-chxn Pt^{II} complexes, the C_3 carbon exhibited $^3J_{Pt-C}$ values of 37—38 Hz. They were smaller than that of $[Pt(bpy)(trans\text{-chxn})]^{2+}$ (52 Hz)(bpy=2,2′-bipyridine),[5] whose chelate ring takes a rigid conformation, and also smaller than the two-folded $^3J_{Pt-C}$ values of $[Pt(NH_3)_2(cis\text{-chxn})]^{2+}$ and $[Pt(en)(cis\text{-chxn})]^{2+}$[14] (25—26 Hz)(Table 1). In the *cis*-chxn complex, the two λ and δ conformations are feasibly interconvertible, with a simultaneous inversion of the cyclohexane ring. The $^3J_{Pt-C_3}$ values for the present complexes were found to be almost identical with those of $[Pt(bpy)(pn)]^{2+}$ (38 Hz)(pn=1,2-propanediamine)[5] and $[Pt(bpy)(2m\text{-amcha})]^{2+}$ (34 Hz).[1] On the other hand, no satellite peaks due to the coupling with ^{195}Pt and the C_6 carbon were observed.

The *R,S,S*- and *S,R,R*-3m-chxn ligands are assumed to have the same configuration as that of the *c*-3-methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid used for the preparation.[7] The possible conformations of *S,R,R*-3m-chxn are shown in Fig. 2. The cyclohexane ring of the ligand is presumed to exist predominantly

TABLE 1. ^{13}C NMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] FOR *R,S,S*- OR *S,R,R*-3m-chxn Pt^{II} COMPLEXES

Complex	^{13}C Resonance								
	C_2	C_1	C_3	C_6	$\overbrace{C_4, C_5}$		CH_3	en	
$[Pt(NH_3)_2(R,S,S\text{-3m-chxn})]Cl_2$	63.56	59.80 (9)	31.68 (37.8)	27.10	26.37	23.64	18.43		
$[Pt(NH_3)_2(S,R,R\text{-3m-chxn})]Cl_2$	63.56	59.80 (10)	31.69 (37.8)	27.10	26.42	23.64	18.34		
$[Pt(en)(R,S,S\text{-3m-chxn})]Cl_2$	63.07	59.32 (12)	31.73 (36.6)	27.10	26.42	23.64	18.43	48.01	47.86
$[Pt(en)(S,R,R\text{-3m-chxn})]Cl_2$	63.07	59.32 (12)	31.73 (36.6)	27.05	26.42	23.64	18.43	48.01	47.86
$[Pt(NH_3)_2(cis\text{-chxn})]Cl_2$[14]	58.78[c]		27.01[d] (25.7)		21.40[e]				
$[Pt(en)(cis\text{-chxn})]Cl_2$[14]	58.07[c] (8)		27.03[d] (25.0)		21.40[e]			47.94	

a) Carbon chemical shifts in ppm from external TMS measured *vs.* internal dioxane. b) Coupling constants ($J_{^{195}Pt-C}$) are found in parentheses in Hz. c) Assignable to C_1 and C_2 carbon. d) Assignable to C_3 and C_6 carbon. e) Assignable to C_4 and C_5 carbon.

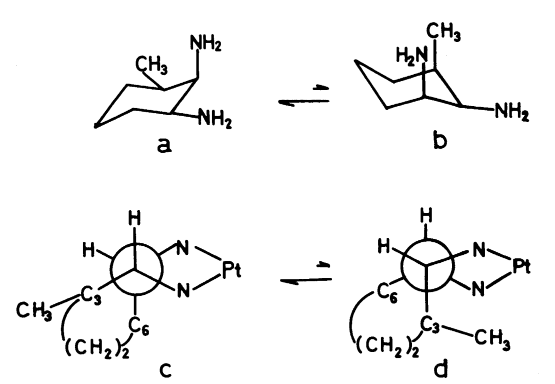

Fig. 2. Conformations of the S,R,R-3m-chxn and the chelate rings of the S,R,R-3m-chxn complex.
a, b: The conformational pair of S,R,R-3m-chxn, c, d: λ and δ conformations of S,R,R-3m-chxn complex.

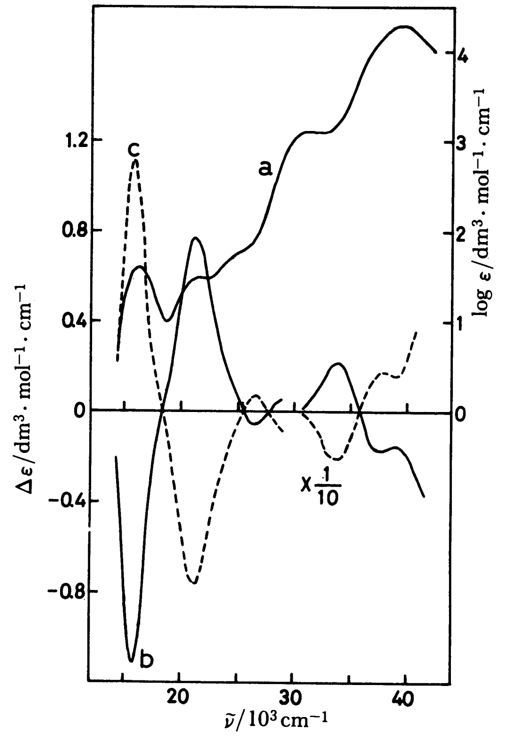

Fig. 3. Electronic (a) and CD (b, c) spectra.
—: *trans*-[CoCl$_2$(R,S,S-3m-chxn)$_2$]$^+$, --: *trans*-[CoCl$_2$(S,R,R-3m-chxn)$_2$]$^+$.

in the conformation shown in Fig. 2, a, because the preference for the diequatorial-axial conformation (a) over the diaxial-equatorial conformation (b) seems very reasonable. The λ and δ conformations of the S,R,R-3m-chxn complex are also shown in Fig. 2. If the cyclohexane is assumed to take the more stable conformation (Fig. 2, a), then the chelate ring is seen necessarily to exist in the λ conformation (c). The δ conformation (d), in which the cyclohexane ring is assumed to adopt an unstable conformation (b), is disadvantageous. In addition, the steric hindrance caused by the methyl group located above the chelate ring may destabilize the δ conformation. This unfavorable steric effect attributable to the methyl group seemed to be similar to that of the higher-energy conformer of the R,S-2m-amcha complex.[1] The empirical result that no $^3J_{\mathrm{Pt-C_6}}$ was detected indicates that the distribution of the less favorable conformer in the $\lambda \rightleftharpoons \delta$ equilibrium is very small. The smaller ^3J values for the present complexes should be ascribed to the unsymmetrical structure distorted from the idealized gauche form illustrated in Fig. 2, as has been described by Yano *et al.*[15] Therefore, it is concluded that the chelate ring of S,R,R-3m-chxn complexes

TABLE 2. ELECTRONIC AND CD SPECTRAL DATA OF Co$^{\mathrm{III}}$ COMPLEXES

Complex	Electronic		CD	
	$\tilde{\nu}$/10^{3}cm^{-1}	(log ε)	$\tilde{\nu}$/10^{3}cm^{-1}	(Δε)
trans-[CoCl$_2$(R,S,S-3m-chxn)$_2$]$^+$	16.2	(1.60)	15.8	(−1.12)
	21.6	(1.49)	21.2	(+0.78)
	25.3	(1.79)	26.5	(−0.06)
	31.3	(3.12)	33.9	(+2.24)
	39.2	(4.29)	37.7	(−1.8)
trans-[CoCl$_2$(S,R,R-3m-chxn)$_2$]$^+$	16.2	(1.60)	15.8	(+1.11)
	21.6	(1.50)	21.2	(−0.76)
	25.3	(1.79)	26.5	(+0.07)
	31.3	(3.10)	33.9	(−2.19)
	39.2	(4.26)	37.7	(+1.8)
fac-Λ(*lel*$_3$)-[Co(R,S,S-3m-chxn)$_3$]$^{3+}$	20.8	(1.99)	19.8	(+3.03)
			23.0	(−0.07)
	28.7	(1.98)	27.5	(+0.35)
	45.5	(4.27)	42.3	(−33.8)
mer-Λ(*lel*$_3$)-[Co(R,S,S-3m-chxn)$_3$]$^{3+}$	20.8	(2.02)	19.8	(+3.20)
	28.7	(2.01)	27.1	(+0.28)
	45.5	(4.26)	42.2	(−34.0)
fac-Δ(*ob*$_3$)-[Co(R,S,S-3m-chxn)$_3$]$^{3+}$	20.5	(2.17)	20.4	(−5.96)
	28.3	(2.19)	28.2	(+0.50)
	45.5	(4.31)	44.6	(+18.4)
mer-Δ(*ob*$_3$)-[Co(R,S,S-3m-chxn)$_3$]$^{3+}$	20.6	(2.14)	20.5	(−5.13)
	28.5	(2.14)	28.2	(+0.42)
	45.5	(4.30)	44.2	(+18.1)

preferrentially adopts the λ conformation, with the C_2–C_3 bond equatorially oriented.

Absolute Configulation of the Ligands. It has been established that the CD spectra of the *trans*-[$CoCl_2$(1,2-diamine)$_2$]$^+$ complexes, were 1,2-diamine=C-substituted optically active 1,2-diamine, were mainly due to the conformational effect.[16–18] In order to assign the configurations of the resolved (+)- and (−)-3m-chxn ligands, we synthesized the two enantiomers, *trans*-[$CoCl_2$((+)-3m-chxn)$_2$]$^+$ and *trans*-[$CoCl_2$((−)-3m-chxn)$_2$]$^+$. The electronic and CD spectra are shown in Fig. 3, while the numerical results are given in Table 2. The CD signs of *trans*-[$CoCl_2$((−)-3m-chxn)$_2$]$^+$ were observed to be positive in the I_a (16200 cm^{-1}) region and negative in the I_b (21600cm^{-1})

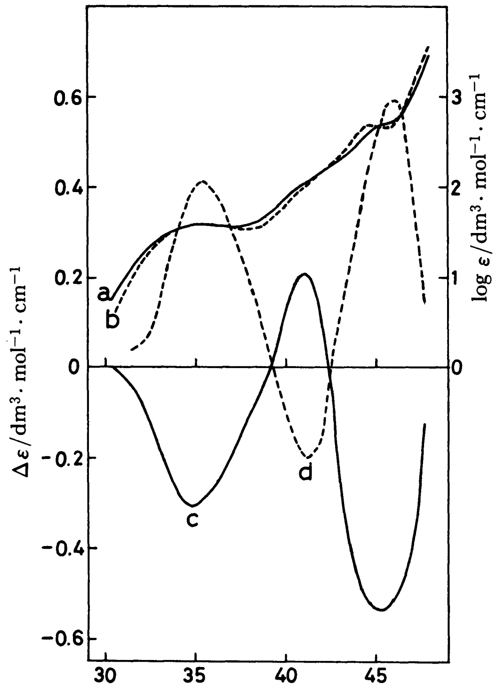

Fig. 4. Electronic (a, b) and CD (c, d) spectra.
—: [$Pt(NH_3)_2$(*R,S,S*-3m-chxn)]$^{2+}$, --: [Pt(en)(*S,R,R*-3m-chxn)]$^{2+}$.

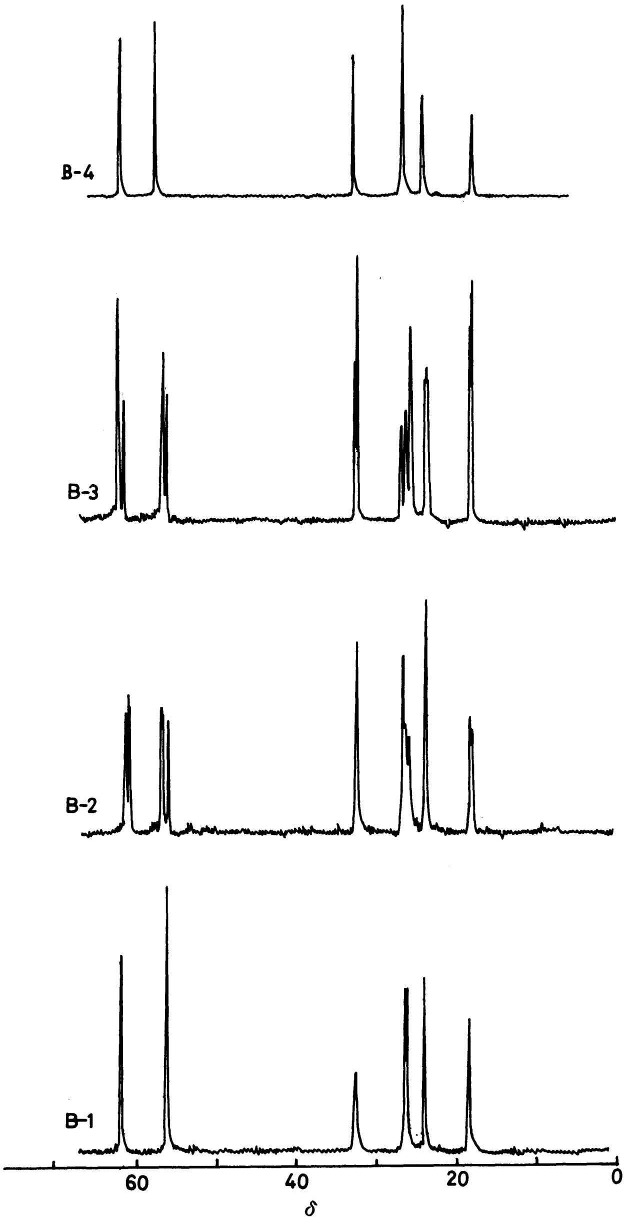

Fig. 5. ^{13}C NMR spectra of the B-1, B-2, B-3, and B-4 isomers of [Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$.

TABLE 3. ELECTRONIC AND CD SPECTRAL DATA OF Pt^{II} COMPLEXES

Complex	Electronic		CD	
	$\tilde{\nu}/10^3$cm^{-1}	(log ε)	$\tilde{\nu}/10^3$cm^{-1}	($\Delta\varepsilon$)
[$Pt(NH_3)_2$(*R,S,S*-3m-chxn)]$^{2+}$	35.4	(1.59)	34.9	(−0.31)
	41 sh[a]	(2.0)	41.0	(+0.21)
	45.0	(2.66)	45.1	(−0.54)
[$Pt(NH_3)_2$(*S,R,R*-3m-chxn)]$^{2+}$	35.4	(1.58)	34.9	(+0.30)
	41 sh	(2.0)	41.0	(−0.23)
	45.0	(2.65)	45.1	(+0.53)
[Pt(en)(*R,S,S*-3m-chxn)]$^{2+}$	35.5	(1.59)	35.4	(−0.40)
	41 sh	(2.0)	41.2	(+0.18)
	44.6	(2.66)	46.1	(−0.54)
[Pt(en)(*S,R,R*-3m-chxn)]$^{2+}$	35.5	(1.60)	35.4	(+0.41)
	41 sh	(2.0)	41.2	(−0.20)
	44.6	(2.68)	46.1	(+0.59)

a) Shoulder.

region. Accordingly, this complex was supposed to have the λ conformation, like the *trans*-[$CoCl_2$(*R*-pn)$_2$]$^+$ complex.[17,18] Since the λ conformation is much more favorable for the *S,R,R*-3m-chxn complex than for the *R,S,S*-3m-chxn complex (Fig. 2), the configuration of the (−)-diamine is identified as (1*S*,2*R*,3*R*). The other (+)-ligand is naturally deduced to have the (1*R*,2*S*,3*S*) configuration.

The CD Spectra of the Pt^{II} Complexes. The present complexes have two asymmetric carbons, with the *S,R*- or *R,S*- configuration,in their chelate ring, in contrast to the well-studied complexes, which have one *R(S)* or two *R,R(S,S)* chiral carbon(s) in the diamine ring. The electronic and CD spectra of [Pt(NH_3)$_2$(*R,S,S*-3m-chxn)]$^{2+}$ and [Pt(en)(*S,R,R*-3m-chxn)]$^{2+}$ are shown in Fig. 4. The three main bands (Table 3) observed at around 3500, 4100, and 4500 cm^{-1} were tentatively assigned to the $^1A_{1g}\rightarrow{}^3E_g$, $^1A_{1g}\rightarrow{}^1A_{2g}$, and $^1A_{1g}\rightarrow{}^1E_g$ transitions respectively.[4,19,20] According to the assignment by Nakayama *et al.*, however, the last band possibly includes a weak band due to the $^1A_{1g}\rightarrow{}^1B_{1g}$ transition.[21] The Cotton effects of the $^1A_{1g}\rightarrow{}^3E_g$ and $^1A_{1g}\rightarrow{}^1E_g$ transitions of the C-substituted diamine complexes with the *R*-configuration and the λ conformation have been known to be positive. Both the signs and the CD strengths of the ^1E_g and ^3E_g bands in [Pt(NH_3)$_2$(*S,R,R*-3m-chxn)]$^{2+}$ and [Pt(en)(*S,R,R,*-3m-chxn)]$^{2+}$ were similar to those in *R*-pn analogs.[4] These results indicate that, in the above transitions, the contribution to the Cotton effects imposed by the asymmetric α-carbons is small. On the basis of the signs of these bands, two series of Pt^{II} complexes, both containing *S,R,R*- and *R,S,S*-3m-chxn, were found to have λ and δ conformations respectively, as concluded from the CD spectra of the *trans*-[$CoCl_2L_2$]$^+$ complexes.

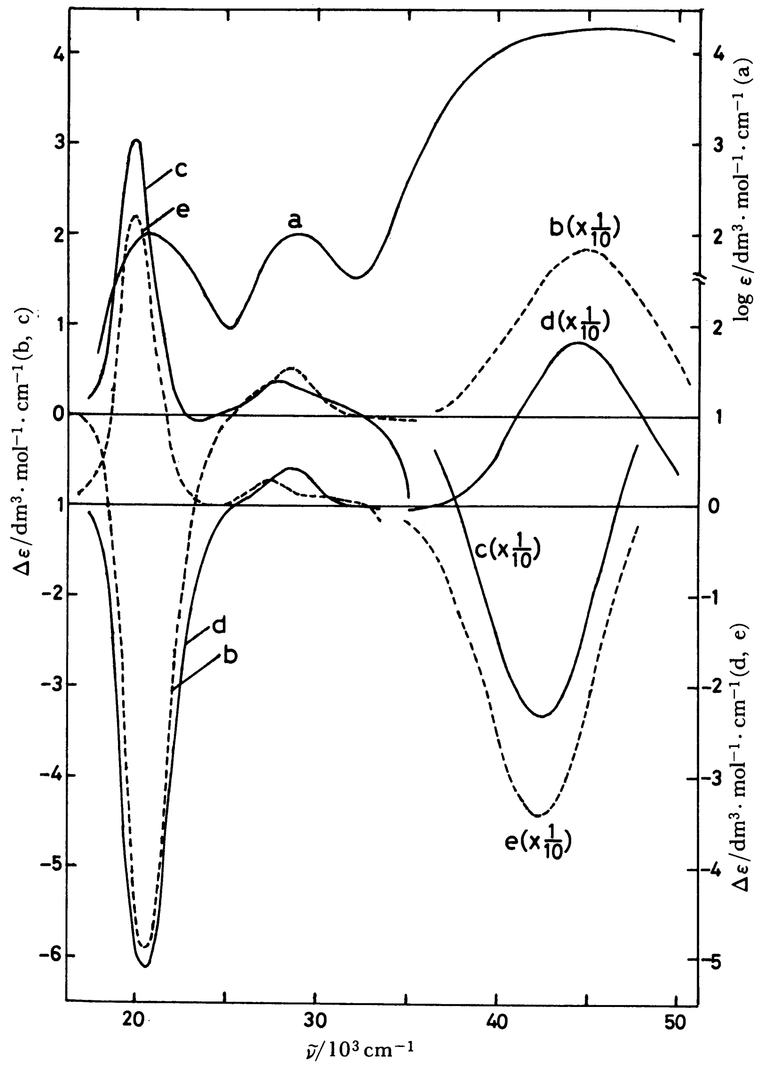

Fig. 6. Electronic spectrum of B-4 (a) and CD spectra of B-1, B-2, B-3, and B-4 (b, d, e, c).
a: *fac*-Λ(*lel*$_3$)-[Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$ (B-4), b: *fac*-Δ(*ob*$_3$)-[Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$ (B-1), c: *fac*-Λ(*lel*$_3$)-[Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$ (B-4), d: *mer*-Δ(*ob*$_3$)-[Co-(*R,S,S*-3m-chxn)$_3$]$^{3+}$ (B-2), e: *mer*-Λ(*lel*$_3$)-[Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$ (B-3).

*The Isomers of [Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$.* The [Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$ is expected to contain four isomers. The complexes named B-3 and B-4 were isolated by SP-Sephadex C-25 chromatography, using a Na_2SO_4 solution as an eluent. The isomers named B-1 and B-2, obtained in much lower yields, were not separated from each other with the same eluent.

Figure 5 shows their ^{13}C NMR spectra. Since seven and six signals were observed for the B-1 and B-4 complexes respectively, both complexes were assigned to the *fac*-isomers (C_3-symmetry). Both the B-2 and B-3 complexes were assignable to the *mer*-isomers (C_1-symmetry) because of the inequality of each carbon in their spectra. The resonances for the methine carbon of the *lel* chelate ring in the analogous diamine complexes have been reported to appear in a lower field than those of the *ob* chelate ring.[22,23] The C_1 and C_2 signals of the B-3 isomer appeared at a slightly lower field than those of the B-2 isomer. Similar downfield shifts at the corresponding methine carbons of the B-4 complex were observed compared to the B-3 complex. From these results, in combination with the relative yield, the B-1, B-2, B-3, and B-4 complexes can be assigned to *fac*-(*ob*$_3$), *mer*-(*ob*$_3$), *mer*-(*lel*$_3$), and *fac*-(*lel*$_3$) respectively.

Sakakibara *et al.*[24] reported that the relative rate of the elution of [CoN$_6$]$^{3+}$-type-complex isomers was influenced by both the interaction between SP-Sephadex and the complex cation and that between the complex cation and the eluent anions, and presented an empirical rule for the elution order of the above type of complexes. However, the present *lel*$_3$ complexes did not follow this rule, being eluted extraordinarily slowly with a Na_3PO_4 solution. This may be caused by the considerably stronger interactions between the complex and SP-Sephadex resulting from the bulky ligand.

The absorption and CD spectra of these complexes are shown in Fig. 6, while the spectral data are summarized in Table 2. The CD spectra of the B-3 and B-4 complexes showed a positive peak in the first-absorption-band region, while those of the B-1 and B-2 complexes showed a very strong negative peak in the same region. Applying the empirical rule on the relationship between the absolute configuration of the tris diamine complex and the CD sign of the first absotption band[25,26] to these complexes, it is concluded that the B-1 and B-2 complexes have the *Δ* configuration, while the B-3 and B-4 have the *Λ* configuration. Since the chelate ring of the *R,S,S*-3m-chxn is restricted to the *δ* conformation, we have assigned the B-1, B-2, B-3, and B-4 complexes to *fac*-*Δ*(*ob*$_3$), *mer*-*Δ*(*ob*$_3$), *mer*-*Λ*(*lel*$_3$), and *fac*-*Λ*(*lel*$_3$) respectively.

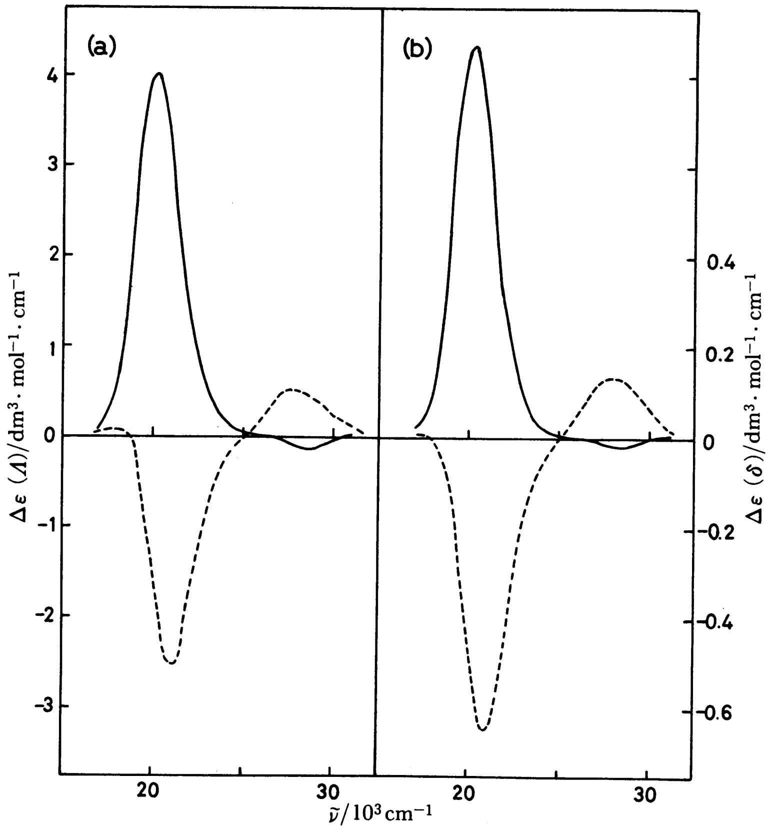

Fig. 7. Configurational effect of CD (*Δ ε* (*Λ*)) (—) and vicinal effect of CD (*Δ ε* (*δ*)) (--) of [Co(*R,S,S*-3m-chxn)$_3$]$^{3+}$.
a—: Calculated *Δ ε* (*Λ*)=1/2{*mer*-*Λ*(*lel*$_3$)−*mer*-*Δ*(*ob*$_3$)}, --: Calculated *Δ ε* (*δ*)=1/6{*mer*-*Λ*(*lel*$_3$)+*mer*-*Δ*(*ob*$_3$)}, b—: Calculated *Δ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

As is shown in Fig. 7, the configurational and vicinal CD curves derived from the *fac*-isomers resembled the respective curves from the *mer*-isomers. The CD strengths of the vicinal effect of the *tris*(*R*,*S*,*S*-3m-chxn) complexes were very similar to those of $[Co(R\text{-pn})_3]^{3+}$,[26–29] and $[Co(R\text{-chxn})_3]^{3+}$.[29] The *R*,*S*,*S*-3m-chxn complexes, as well as other related complexes involving cyclohexane rings in their structure, such as $[Co(R\text{-chxn})_3]^{3+}$,[29] $[Co(cis\text{-chxn})_3]^{3+}$,[30,31] and $[Co(R,S\text{-2m-amcha})_3]^{3+}$,[1] showed quite a large configurational effect.

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