Preparation and Spectroscopic Studies of Four Stereoisomers of Tris[(*S*)-1,3-butanediamine]cobalt(III) Complex

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Four stereoisomers, *mer*-Δ, *mer*-Λ, *fac*-Δ, and *fac*-Λ, of the tris[(*S*)-1,3-butanediamine]cobalt(III) complex were obtained, and their absorption and circular dichroism spectra were recorded in water in the absence or presence of sulfate ions. The shift of absorption bands and the variation of circular dichroism spectra caused by the addition of sulfate ions seem to be correlated with the conformational instability of six-membered (*S*)-1,3-butanediamine chelate rings in the complexes.

Experimental observations[1—4] indicate that the most stable conformation of the (*S*)(or (*R*))-1,3-butanediamine(*S*(or *R*)-bn) chelate ring is the chair form with an equatorially disposed methyl group. However, a six-membered chelate ring is known to be conformationally flexible and to interchange easily its conformation between two forms, the chair and the skew depending on environment. The *S*(or *R*)-bn chelate ring in the δ(or λ)-skew conformation also has the methyl group in equatorial orientation (see Fig. 2). In a previous paper,[5] we have suggested that the variation of circular dichroism spectra of some cobalt(III) complexes containing (*R*,*R*)-2,4-pentanediamine (*RR*-ptn) in various solvents is closely related with such conformational instability of the six-membered *RR*-ptn chelate ring. The most stable conformation of the *RR*-ptn chelate ring is the λ-skew form in which the two methyl groups are equatorially disposed. In order to compare the effects of a methyl group on the conformational instability of six-membered chelate rings, this paper reports the preparation of four stereoisomers of the $[Co(S\text{-bn})_3]^{3+}$ complex and their absorption and circular dichroism spectra in the absence or presence of sulfate ions. The circular dichroism spectrum of $[Co(NH_3)_4(S\text{-bn})]^{3+}$ is also recorded.

Experimental

Ligand. 1,3-Butanediamine (bn) was prepared by the method of Strack *et al.*[6] and resolved by the method of Balieu *et al.*[7] The $(+)_{589}$-isomer is known to have the *S*-configuration,[7] and its dihydrochloride salt (S-bn·2HCl) was used to prepare cobalt(III) complexes.

$[Co(NH_3)_4(S\text{-bn})](ClO_4)_3$. This complex was prepared from $[Co(H_2O)(NH_3)_5](ClO_4)_3$ and *S*-bn·2HCl by a method similar to that for the corresponding (*R*,*R*)-2,4-pentanediamine (*RR*-ptn) complex.[5]

trans-*$[CoCl_2(S\text{-bn})_2]Cl$.* An aqueous solution (50 cm^3) of *S*-bn·2HCl (4.8 g, 30 mmol) was neutralized with Na_2CO_3 (3.1 g, 30 mmol). To this solution was added a solution of $Na_3[Co(NO_2)_6]$ (6.1 g, 15 mmol) in water (40 cm^3), and the mixture was heated at 70 °C for 3 h. The resulting yellow solution was mixed with concd HCl (50 cm^3), and heated at 70 °C for 2 h with occasional stirring to give a reddish violet solution. Green crystals which formed by concentrating the solution to a small volume in a rotary evaporator were filtered off and washed with ethanol. Yield: *ca.* 30%.

*Tris(*S*-bn)cobalt(III) Complex.* A suspension of *S*-bn·2HCl (0.4 g, 2.5 mmol) and sodium methoxide (0.22 g, 4 mmol) in methanol (3 cm^3) was added to a solution of *trans*-$[CoCl_2(S\text{-bn})_2]Cl$ (0.69 g, 2 mmol) in DMSO (30 cm^3). The mixture was stirred for a day at room temperature, then diluted with 1 dm^3 of water and passed through an SP-Sephadex column (ϕ 2.7×5 cm). A small portion of the Sephadex charged with the product was loaded on the top of adsorbent layer of an SP-Sephadex column (ϕ 2.7×120 cm), and the adsorbed complexes were developed with a 0.2 M aqueous solution of sodium $(+)_{589}$-tartratoantimonate(III). The column gave three separate bands, I, II, and III in the order of elution, which were *mer*-Δ, *fac*-Δ, and a mixture of *mer*-Λ and *fac*-Λ isomers, respectively. The effluent of the band III was diluted with water and loaded again on an SP-Sephadex column, and the adsorbed band was eluted with a 0.2 M sodium sulfate solution. Two isomers, *fac*-Λ(IIIA) and *mer*-Λ(IIIB) were eluted separately from the column in this order. The formation ratio, *mer*-Δ(I) : *fac*-Δ(II) : *fac*-Λ(IIIA) : *mer*-Λ(IIIB) was 2 : 1 : 1 : 2. Each effluent was reloaded on SP-Sephadex and the isomers were isolated by the following methods.

$(-)_{546}$-mer-Δ-$[Co(S\text{-bn})_3]Cl_3\cdot3H_2O$ and $(-)_{470}$-fac-Λ-$[Co(S\text{bn})_3]Cl_3\cdot2H_2O$. The complex adsorbed on SP-Sephadex was eluted with 1.0 M HCl. The effluent was evaporated to

Table 1. Analytical data of the new complexes

Complex	C/% Found	C/% Calcd	H/% Found	H/% Calcd	N/% Found	N/% Calcd
mer-Δ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot2H_2O$	21.90	21.91	5.90	6.13	12.69	12.78
mer-Δ-$[Co(S\text{-bn})_3]Cl_3\cdot3H_2O$	29.48	29.79	8.52	8.75	17.39	17.37
fac-Δ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot2H_2O$	22.12	21.91	5.61	6.13	12.72	12.78
fac-Δ-$[Co(S\text{-bn})_3]Cl_3\cdot3.5H_2O$	29.16	29.25	8.47	8.79	17.33	17.05
fac-Λ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot H_2O$	22.87	22.53	5.82	5.99	13.23	13.14
fac-Λ-$[Co(S\text{-bn})_3]Cl_3\cdot2H_2O$	30.66	30.94	8.47	8.66	18.06	18.04
mer-Λ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot2H_2O$	21.66	21.91	5.86	6.13	12.82	12.78
mer-Λ-$[Co(S\text{-bn})_3]Cl_3\cdot2H_2O$	31.02	30.94	8.78	8.66	18.27	18.04
$[Co(NH_3)_4(S\text{-bn})](ClO_4)_3$	9.25	9.35	4.67	4.71	16.51	16.36

almost dryness in a vacuum desiccator over P_2O_5 and NaOH. Orange crystals which formed by the addition of ethanol were filtered off and washed with ethanol.

$(+)_{546}$-mer-Λ-[Co(S-bn)$_3$]Cl$_3$·2H$_2$O. This complex was obtained in a similar way to that for the *mer-Δ* or the *fac-Λ* isomer except that methanol was used for crystallization instead of ethanol.

$(+)_{470}$-fac-Δ-[Co(S-bn)$_3$]Cl$_3$·3.5H$_2$O. This complex did not crystallize on the addition of common organic solvents to a concentrate of the effluent. Thus the orange residue obtained by evaporating the effluent in a vacuum desiccator was used for measurements.

mer-Δ-, fac-Δ-, and mer-Λ-[Co(S-bn)$_3$](ClO$_4$)$_3$·2H$_2$O and fac-Λ-[Co(S-bn)$_3$](ClO$_4$)$_3$·H$_2$O. The adsorbed complex was eluted with a 1.5 M sodium perchlorate solution and the effluent was concentrated to a small volume in a rotary evaporator. Orange crystals which formed on cooling the concentrate were filtered off and washed with ethanol.

Other complexes, *mer-* and *fac-*[Co(*meso*-ptn)$_3$]$^{3+}$ were prepared and resolved by the method reported previously.[8]

Table 1 shows the results of chemical analysis.

Measurements. Absorption and circular dichroism spectra were recorded on a Hitachi 323 spectrophotometer, and a JASCO model J-20 spectropolarimeter, respectively. PMR spectra were recorded on a JEOL C-60H spectrometer in D_2O–DCl with DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as the internal reference.

Results and Discussion

1. Tetraammine(S-bn)cobalt(III) Complex. As Fig. 1 shows, [Co(NH$_3$)$_4$(*S*-bn)](ClO$_4$)$_3$ in water exhibits extremely weak CD in the region of the d-d absorption bands. Hawkins and Lawrance[2] reported that [Co(NH$_3$)$_4$(*S*-bn)](NO$_3$)$_3$·H$_2$O shows no measurable CD in this region. In general, a tetraammine complex containing an optically active diamine chelate exhibits CD much stronger than that of the *S*-bn complex in the region of the first absorption band, and the sign of a main CD band depends on the conformational chirality of a diamine chelate ring. For example, [Co(NH$_3$)$_4$(*R*-pn)]$^{3+}$ (*R*-pn=*R*-propylenediamine) gives a positive CD band ($\Delta\varepsilon=+0.33$) at 461 nm, and the *R*-pn chelate ring is assigned to the λ-gauche conformation.[9] The main CD band of [Co(NH$_3$)$_4$(*RR*-ptn)]$^{3+}$ is rather weak ($\Delta\varepsilon=+0.10$, 490 nm), and the *RR*-ptn chelate ring is suggested to be in equilibrium between the λ-skew and the chair conformations.[5] Accordingly, the weak CD of the *S*-bn complex in water may indicate that the *S*-bn chelate ring exists predominantly in the achiral chair conformation with the equatorial methyl group as suggested by Hawkins and Lawrance.[2] Energy minimization calculation on a hypothetical complex, [CoCl$_4$(*S*-bn)]$^-$ shows that the predominant conformer of the *S*-bn chelate ring is the same chair form.[10]

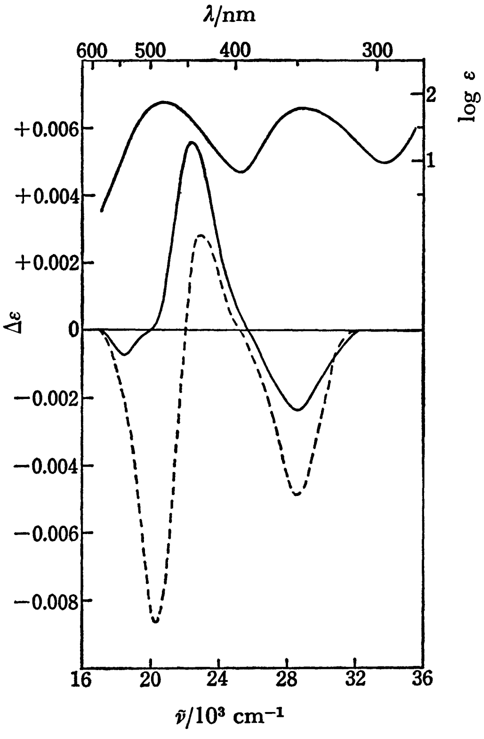
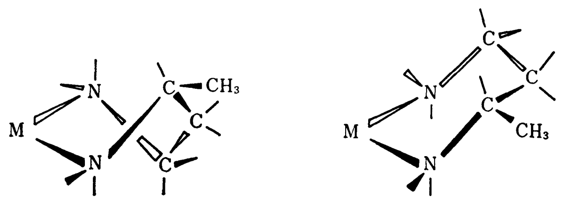


Fig. 1. Absorption and CD spectra of [Co(NH$_3$)$_4$(*S*-bn)](ClO$_4$)$_3$ in water (——) and CD spectrum in 0.2 M Na$_2$SO$_4$ (------).



δ-skew chair

Fig. 2. Possible conformations of six-membered *S*-bn chelate.

The CD spectrum of [Co(NH$_3$)$_4$(*S*-bn)]$^{3+}$ in water changes remarkably on the addition of Na$_2$SO$_4$, as shown in Fig. 1. The sign of the main CD band in the region of the first absorption band is reversed, and the spectral pattern is almost mirror image of that of [Co(NH$_3$)$_4$(*RR*-ptn)]$^{3+}$ in which the *RR*-ptn chelate ring will be in equilibrium between the λ-skew and the chair conformations as stated previously. Thus, it is suggested that the δ-skew conformation of the *S*-bn chelate ring is stabilized by the addition of Na$_2$SO$_4$. Both the chair and the δ-skew conformations have the equatorially disposed methyl group, as shown in Fig. 2. However, the strength of the CD bands is still very weak in the presence of Na$_2$SO$_4$. The *S*-bn chelate ring will also exist predominantly in the chair conformation in this solution.

2. Tris(S-bn)cobalt(III) Complexes. a) Characterization of the Isomers: The tris(*S*-bn)cobalt(III) complex exists in four stereoisomers, *mer-Δ*, *mer-Λ*, *fac-Δ*, and *fac-Λ* (Fig. 3). As Fig. 4 shows, the PMR spectra of the isomers, II and IIIA show only one kind of doublet signal due to the methyl protons, while those of the isomers, I and IIIB give signals indicating the presence of nonequivalent methyl groups. From symmetry argument (*fac*(C$_3$), *mer*(C$_1$)), therefore, the isomers, I, II, IIIA, and IIIB can be assigned to *mer*, *fac*, *fac*, and *mer* configurations, respectively.

Figures 5—8 show the CD spectra of all the isomers in water and in 0.2 M Na$_2$SO$_4$ solutions. In the region of

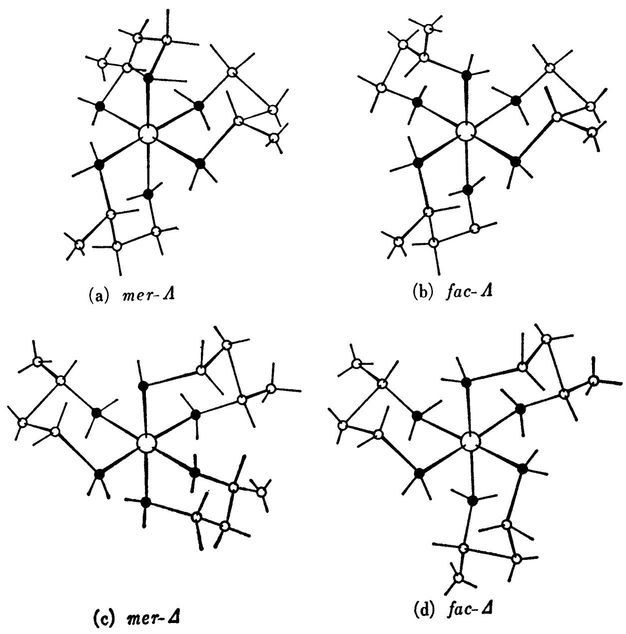


Fig. 3. Schematic structure of tris(*S*-bn)cobalt(III) ions in the chair$_3$ conformer.

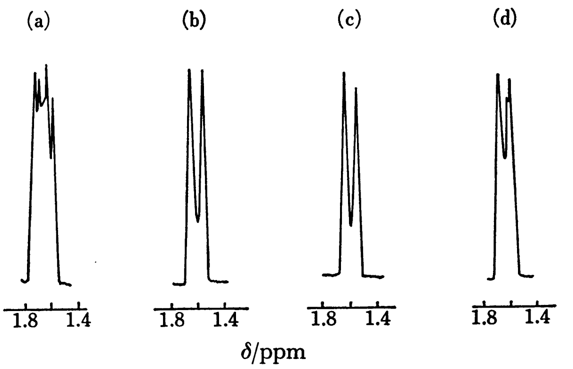


Fig. 4. PMR spectra of the isomers, (a) I(*mer*-Δ), (b) II(*fac*-Δ), (c) IIIA(*fac*-Λ), and (d) IIIB(*mer*-Λ).

the first absorption band, the main CD bands of the isomers, I(*mer*) and II(*fac*) in water have negative sign, while those of the isomers, IIIA(*fac*) and IIIB(*mer*) positive sign. Thus, the former two and the latter two are suggested to have the Δ and Λ configurations, respectively. In the charge transfer region, the isomers, I(*mer*) and II(*fac*) exhibit three CD bands with positive, negative, and positive signs from longer to shorter wavelengths. This pattern coincides with that of Δ-$[Co(tn)_3]^{3+}$ (tn = trimethylenediamine), whose absolute configuration has been determined by X-ray work[11] (Fig. 9). The other isomers, IIIA(*fac*) and IIIB(*mer*) show the same CD pattern in this region, but the signs are reversed. These results lead to the conclusion that the isomers, I, II, IIIA, and IIIB are *mer*-Δ, *fac*-Δ, *fac*-Λ, and *mer*-Λ configurations, respectively. The effect of sulfate ions on the CD spectra will be described later.

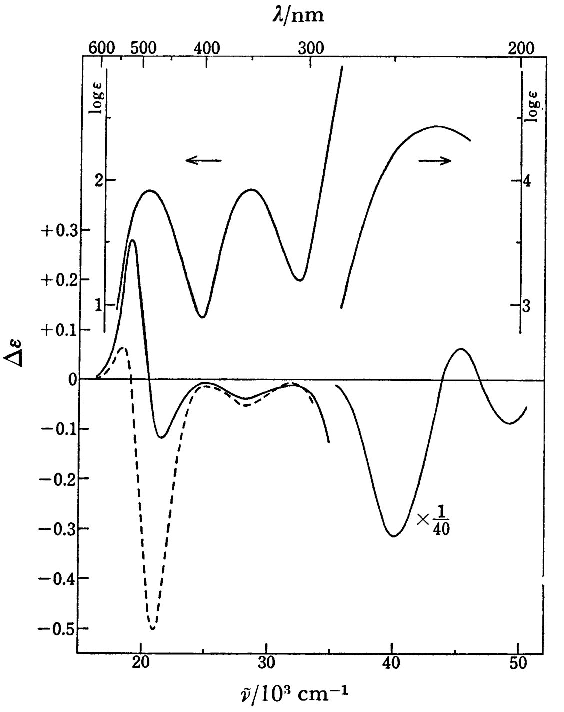


Fig. 5. Absorption and CD spectra of IIIA: *fac*-Λ-[Co(*S*-bn)$_3$](ClO$_4$)$_3$·H$_2$O; 3.06×10^{-3} M in visible region and 1.88×10^{-4} M in UV region in water (——), and 3.06×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

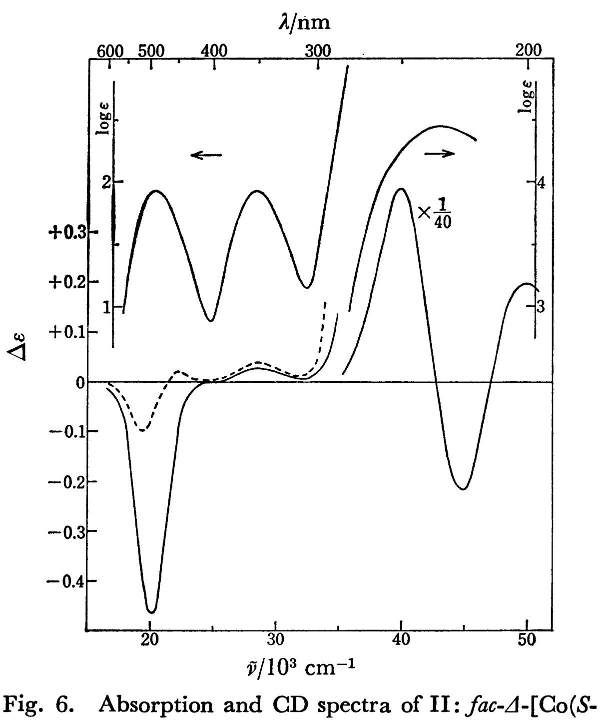


Fig. 6. Absorption and CD spectra of II: *fac*-Δ-[Co(*S*-bn)$_3$](ClO$_4$)$_3$·2H$_2$O; 4.02×10^{-3} M in visible region and 1.90×10^{-4} M in UV region in water (——), and 4.02×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

b) Absorption Spectra: Table 2 shows that the maxima of the first absorption bands of the four isomers are in the range of 489.5 (20430) to 491 nm (20370 cm^{-1}). For a complex of six-membered 1,3-diamine, maximum position of the first absorption band seems to depend on the conformation of the diamine; a diamine complex in the skew conformation gives the first absorp-

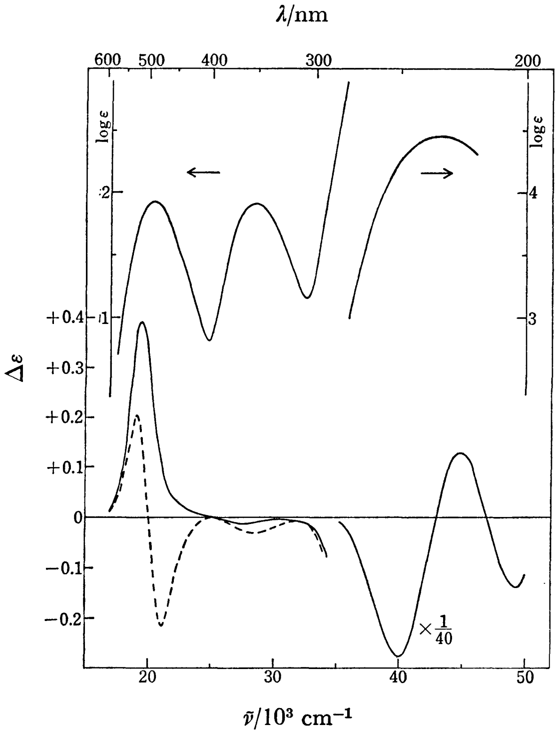


Fig. 7. Absorption and CD spectra of IIIB: *mer*-Λ-[Co(S-bn)$_3$](ClO$_4$)$_3$·2H$_2$O; 3.08×10^{-3} M in visible region and 1.23×10^{-4} M in UV region in water (——), and 3.08×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

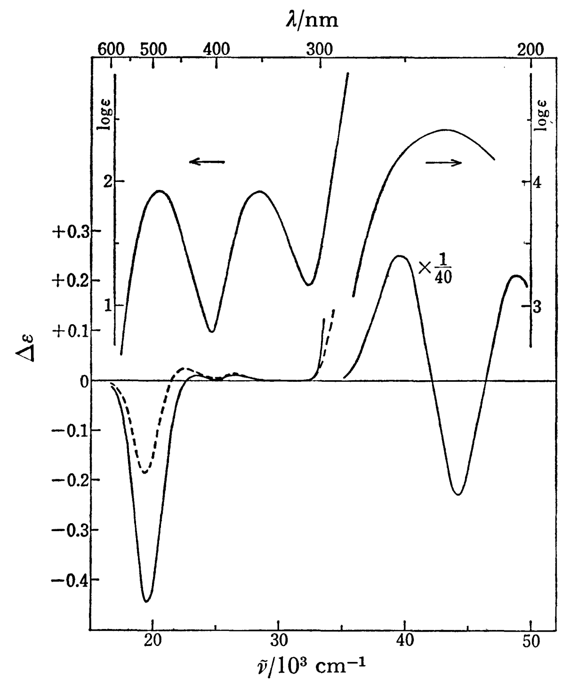


Fig. 8. Absorption and CD spectra of I: *mer*-Δ-[Co(S-bn)$_3$](ClO$_4$)$_3$·2H$_2$O; 2.82×10^{-3} M in visible region and 1.13×10^{-4} M in UV region in water (——), and 2.82×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

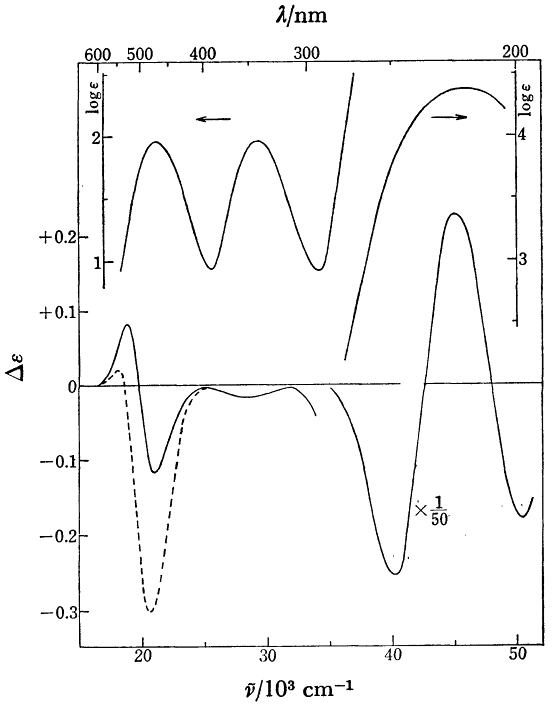


Fig. 9. Absorption and CD spectra of Λ-[Co(tn)$_3$](ClO$_4$)$_3$; 5.68×10^{-3} M in visible region and 2.27×10^{-4} M in UV region in water (——), and 5.68×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

tion band at a shorter wavelength than that in the chair conformation. For example, Δ-[Co(RR-ptn)$_3$]$^{3+}$ of which the most stable conformation is the λ-skew form exhibits the first absorption band at 482 nm (20750 cm^{-1}), while those of *fac*-[Co(*meso*-ptn)$_3$]$^{3+}$ and [Co(tn)$_3$]$^{3+}$ in which the chelate ligands take predominantly the chair conformation are at 491 (20370) and 490 nm (20410 cm^{-1}), respectively. Therefore, it is suggested that the S-bn chelate rings in all the [Co(S-bn)$_3$]$^{3+}$ isomers are intrinsically the most stable in the chair conformation.

The first absorption band of the *fac*-Λ isomer (489.5 nm, 20430 cm^{-1}) is a little at a shorter wavelength than that of the *fac*-Δ isomer (490.5 nm, 20390 cm^{-1}). It is observed that for a pair of diastereomers, the d-d absorption bands of the one involving more steric interactions lie at longer wavelengths than those of the other.[12] In contrast to such observations, molecular models show that the structure of the *fac*-Λ isomer (489.5 nm) seems to be a little more crowded than that of the *fac*-Δ isomer (490.5 nm), because the three methyl groups of the former in the chair conformation are disposed so as to concentrate around the C$_3$ axis of the complex ion (Fig. 3). The observed difference in the peak positions between the two *fac* isomers may be related with conformational instability of the chelate rings in solution. As stated previously, the δ-skew conformation of a S-bn chelate ring also has the equatorially disposed methyl group. When the S-bn chelate ring forms the δ-skew conformation, the *fac*-Λ isomer results in the $lel_3(\Lambda(\delta\delta\delta))$ structure, while the *fac*-Δ isomer the $ob_3(\Delta(\delta\delta\delta))$ one. Since the ob_3 conformer has been calculated by conformational analysis to have a substantially higher energy,[13] the chelate rings in only the *fac*-Λ isomer could interchange between the chair and the δ-skew conformations, and the complex would be in equilibrium between these two conformers.

TABLE 2. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption	CD		Concentration
	log ε ($\tilde{\nu}_{max}$/cm^{-1})	$\Delta\varepsilon$	($\tilde{\nu}$/cm^{-1})	C/M
mer-Δ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot 2H_2O$	1.92 (20370)	−0.446	(19530)	2.82×10^{-3}
		+0.012	(23310)	
	1.92 (28400)	+0.011	(26670)	
	4.41 (42900)	+10	(39500)	1.13×10^{-4}
		−9.3	(44100)	
		+8.3	(48800)	
mer-Δ-$[Co(S\text{-bn})_3]Cl_3\cdot 3H_2O$	1.92 (20370)	−0.411	(21530)	4.18×10^{-3}
		+0.014	(23260)	
	1.92 (28400)	+0.014	(26300)	
	4.42 (42900)	+10	(39500)	1.67×10^{-4}
		−8.9	(44600)	
		+8.7	(49800)	
fac-Δ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot 2H_2O$	1.93 (20390)	−0.461	(19900)	4.02×10^{-3}
	1.93 (28400)	+0.040	(28600)	
	4.45 (43000)	+12	(39700)	1.90×10^{-4}
		−7.6	(44800)	
		+6.1	(50000)	
fac-Δ-$[Co(S\text{-bn})_3]Cl_3\cdot 3.5H_2O$	1.93 (20390)	−0.374	(19840)	3.51×10^{-3}
	1.93 (28400)	+0.021	(28500)	
	4.46 (43000)	+12	(39700)	1.82×10^{-4}
		−7.4	(44800)	
		+6.4	(50000)	
fac-Λ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot 2H_2O$	1.93 (20430)	+0.266	(19080)	3.06×10^{-3}
		−0.105	(21510)	
	1.94 (28400)	−0.037	(28300)	
	4.43 (43100)	−12	(40200)	1.88×10^{-4}
		+1.6	(45200)	
		−4.1	(49300)	
fac-Λ-$[Co(S\text{-bn})_3]Cl_3\cdot 2H_2O$	1.93 (20430)	+0.216	(19050)	4.18×10^{-3}
		−0.220	(21280)	
	1.92 (28400)	−0.040	(28600)	
	4.41 (43100)	−12	(40200)	1.68×10^{-4}
		+1.8	(45200)	
		−3.9	(49300)	
mer-Λ-$[Co(S\text{-bn})_3](ClO_4)_3\cdot 2H_2O$	1.92 (20430)	+0.394	(19380)	3.08×10^{-3}
	1.91 (28410)	−0.013	(27800)	
	4.45 (43100)	−11	(39800)	1.23×10^{-4}
		+5.0	(44600)	
		−5.5	(49500)	
mer-Λ-$[Co(S\text{-bn})_3]Cl_3\cdot 2H_2O$	1.92 (20430)	+0.361	(19340)	4.45×10^{-3}
	1.91 (28410)	−0.011	(28200)	
	4.45 (43100)	−11	(40000)	1.71×10
		+4.2	(44600)	
		−5.9	(49500)	
$[Co(NH_3)_4(S\text{-bn})](ClO_4)_3$	1.83 (20860)	−0.00071	(18520)	1.76×10^{-2}
		+0.0056	(22520)	
	1.78 (29200)	−0.0024	(28400)	
	4.35 (48300)	not detected		

The formation of the skew conformer causes shift in the first absorption band to a shorter wavelength as stated previously. The fact that the first absorption band of the more crowded *fac*-Λ isomer is at a shorter wavelength than that of the less crowded *fac*-Δ isomer may be accounted for by such a conformational equilibrium of the *S*-bn chelate ring.

In the presence of Na_2SO_4 (0.5 M), the first absorption band of the *fac*-Λ isomer shifts a little, but more than 1 nm to a shorter wavelength. The *fac*-Δ isomer also shows such a band shift toward a shorter wavelength under the same condition, but the magnitude of shift is very small (less than 0.5 nm). In the presence of sulfate ions, the *lel*$_3$($\Lambda(\delta\delta\delta)$) conformer may be stabilized by ion-pair formation between the complex cation and the sulfate ion, and the first absorption band shifts further to a shorter wavelength owing to the increasing amount of the δ-skew conformer. For a tris-diamine

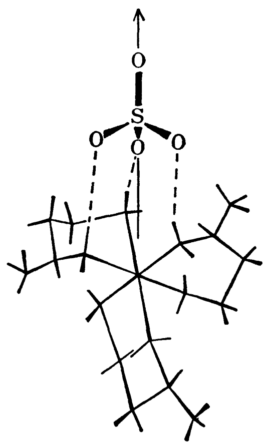


Fig. 10. A proposed structure of the ion-pair between *fac*-*Δ*(chair$_2$δ(*ob*))-[Co(*S*-bn)$_3$]$^{3+}$ and SO$_4^{2-}$.

complex, the *lel*$_3$ conformer is known to have the most effective structure in forming an ion-pair through hydrogen bonding between the amino protons and the sulfate ion.[5] The [Co(tn)$_3$]$^{3+}$ complex of which the conformational behavior is expected to resemble that of the *fac*-*Λ* isomer also shows a similar shift (*ca.* 1 nm) in the first absorption band on the addition of sulfate ions. The *fac*-*Δ* isomer could not form the *lel*$_3$(*Δ*(λλλ)) conformer without difficulty, because the λ-skew conformation has the axial methyl group. However, the first absorption band of this isomer also shifts a little to a shorter wavelength in the presence of sulfate ions. If it is assumed that such a shift is caused by the formation of a certain conformer involving the δ-skew form stabilized by an ion-pair with the sulfate ion, the most probable conformer will be of *fac*-*Δ*(chair$_2$δ(*ob*)) form as shown in Fig. 10. This conformer has a set of three N–H bonds provided by two *S*-bn chelate ligands, one being in the chair and the other in the δ-skew conformation. These N–H bonds are parallel to an axis as shown in Fig. 10, and the complex may form an ion-pair in a similar way with the oxoanions such as sulfate ion through hydrogen bonding. The increase in the amount of the *fac*-*Δ*(chair$_2$δ(*ob*)) conformer in the presence of sulfate ions may cause shift similarly to a shorter wavelength in the first absorption band of the *fac*-*Δ* isomer.

The first absorption bands of the *mer*-*Δ* (491 nm, 20370 cm^{-1}) and the *mer*-*Λ* (489.5 nm, 20430 cm^{-1}) isomers are at nearly the same wavelengths as those of the corresponding *fac* isomers, respectively (Table 2). If all of the *S*-bn chelate rings adopt the chair conformation, these *mer* isomers will be more crowded and strained than the *fac* isomers, since the two chelate rings in each *mer* isomer approach very close to each other. For [Co(*meso*-ptn)$_3$]$^{3+}$ in which the *meso*-ptn chelate rings are expected to be very stable in the chair conformation, the first absorption band of the more crowded *mer* isomer is at longer wavelengths by 2 nm than that of the less crowded *fac* isomer.[8] The fact that both *Δ*- and *Λ*-isomers of the *mer*-[Co(*S*-bn)$_3$]$^{3+}$ complex exhibit the first absorption bands at nearly the same wavelengths as those of the *fac* isomers may indicate that one of the two close *S*-bn chelate ligands in each *mer* isomer prefers to take the δ-skew conformation to reduce interactions between the ligands. The chair$_2$δ conformer will give the first absorption band at a shorter wavelength than that expected for the chair$_3$ conformer. The difference in the absorption maxima of the two *mer* isomers may be interpreted by the difference in the structures of the isomers. In the *mer*-*Λ* isomer, two methyl groups on the two close *S*-bn chelate rings are disposed away from each other (*exo* form), while those in the *mer*-*Δ* isomer come near to each other (*endo* form) (Fig. 3). The *endo*-*mer*-*Δ* isomer should be more crowded, and gives the first absorption band (491 nm) at a longer wavelength compared with that of the other *exo*- *mer*-*Λ* isomer (489.5 nm). Furthermore, the latter isomer can also form the *lel*$_3$(*Λ*(δδδ)) conformer, the first absorption band of which will be at a shorter wavelength than those of the other conformers involving the chair conformation.

On the addition of sulfate ions, the first absorption bands of both the *mer*-*Δ* and -*Λ* isomers shift to a shorter wavelength, the latter (*ca.* 1 nm) showing larger shift than the former (*ca.* 0.5 nm). These band shifts may be caused by a mechanism similar to that described for the *fac* isomers. The *mer*-*Λ* isomer can form the *lel*$_3$(*Λ*(δδδ)) conformer suitable for ion-pair formation with the sulfate ion. On the other hand, the *mer*-*Δ* isomer in the *Δ*(chair$_2$δ(*ob*)) conformation can provide a set of three N–H bonds in a similar manner to that of the *fac*-*Δ* isomer in the same conformation. These conformers will be stabilized by ion-pair formation with sulfate ions, and give the first absorption bands at shorter wavelengths than those in the absence of sulfate ions.

c) Circular Dichroism Spectra. The CD patterns of all the isomers of [Co(*S*-bn)$_3$]$^{3+}$ in water satisfy the known relationship between the absolute configuration and the CD sign, if our assignments were correct. However, the additive law for the configurational and the vicinal effects does not hold for the present diastereomeric isomers. For example, the CD spectra of the *fac*-*Δ* and -*Λ* isomers are not mirror image of each other, although the CD spectrum of [Co(NH$_3$)$_4$(*S*-bn)]$^{3+}$ shows that the vicinal effect of the *S*-bn chelate ligand is negligible. This result also indicates that the complexes are in equilibrium among some conformers and that the conformational equilibrium of one complex is different from those of the other complexes. In a previous paper,[5] we have reported that the CD spectra of conformationally flexible complexes such as *Δ*-[Co(*RR*-ptn)$_3$]$^{3+}$ or *Δ*(or *Λ*)-[Co(tn)$_3$]$^{3+}$ are remarkably affected by the vicinal effect of chelate rings in a certain conformation stabilized by ion-pair formation between a complex ion and its counter ion. The *fac*-*Λ*-[Co(*S*-bn)$_3$]$^{3+}$ isomer seems to be the case. In the region of the first absorption band, the CD spectrum of the complex chloride in water shows a clear dependence on the concentration, as shown in Fig. 11. The complex perchlorate exhibits no such dependence in the concentration range of 3.25×10^{-2} to 3.15×10^{-4} M. In the presence of sulfate ions, the negative CD component at a shorter wavelength is considerably enhanced (Fig. 5). Such features quite resemble those observed for *Λ*-[Co(tn)$_3$]$^{3+}$, indicating that the CD variation is brought about by the vicinal effect of the δ-skew conformer of the *S*-bn chelate ring

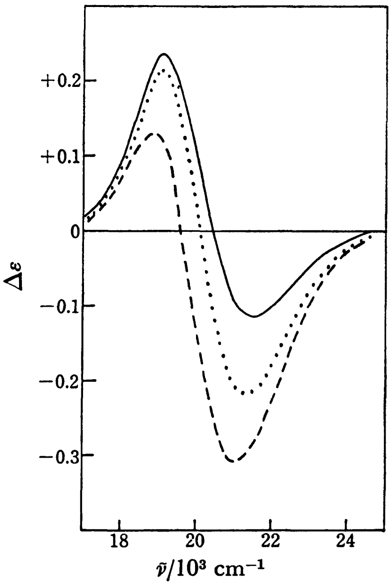


Fig. 11. Dependence of CD of *fac*-Λ-[Co(*S*-bn)$_3$]Cl$_3$·2H$_2$O on its concentration in water: 4.21×10^{-4} M (——), 4.18×10^{-3} M (······), and 4.17×10^{-2} M (-----).

stabilized by ion-pair formation. The vicinal effect of the δ-skew conformation is known to exhibit negative CD in this region. Therefore, it can be concluded that the *fac*-*Λ* isomer is conformationally flexible and is in equilibrium between the chair$_3$ and the *lel*$_3$(*Λ*(δδδ)) conformers. This conclusion coincides with that obtained from the study of absorption spectra.

In contrast to the *fac*-*Λ* isomer, the other three complex chlorides show little dependence on the concentration, the CD patterns in the region of the first absorption band remaining unchanged; *fac*-*Δ* = −0.37 (3.54×10^{-4} M)—−0.30 (3.66×10^{-2} M): *mer*-*Λ*=0.38 (3.13×10^{-4} M)—0.34 (3.12×10^{-2} M): *mer*-*Δ* = −0.42 (4.00×10^{-4} M)—−0.39 (2.72×10^{-2} M). Since the ability of these isomers to form ion-pairs with chloride ions will not differ greatly from that of the *fac*-*Λ* isomer, the result indicates that these isomers are not stabilized in particular conformers by ion-pair formation with chloride ions. The isomers may be less conformationally flexible than the *fac*-*Λ* isomer as claimed in the previous discussion. In the presence of sulfate ions, however, these three isomers change the CD patterns remarkably (Figs. 6—8). Of these CD changes, that of the *mer*-*Λ* isomer is similar to the CD change of the *fac*-*Λ* isomer. Each of these *Λ* isomers in the presence of sulfate ions gives a strong negative CD band at the expense of the positive CD band. As stated previously, the *mer*-*Λ* isomer could also form the *lel*$_3$(*Λ*(δδδ)) conformer. The oxoanions such as sulfate ion may induce the conformational change of rather crowded, rigid chelate rings by forming strong hydrogen bonds with the amino protons of the complex. Thus, the *mer*-*Λ* isomer in the presence of sulfate ions may be stabilized in the *lel*$_3$(*Λ*(δδδ)) conformer.

On the other hand, both *mer*- and *fac*-isomers of the *Δ* configuration in the presence of sulfate ions diminish considerably the strength of the main CD bands, but show no marked increase in the CD bands with the reversed sign as observed in the *Λ*-isomers (Figs. 6 and 8). According to the previous discussion, the decrease in the negative CD strength indicates the formation of chelate rings with the λ-skew conformation. However, this indication seems to be unlikely, since the λ-skew conformer has the axial methyl group. A similar CD variation is seen in the spectra of *mer*- and *fac*-*Λ*(or *Δ*)-[Co(*meso*-ptn)$_3$]$^{3+}$ on the addition of sulfate ions, as shown in Figs. 12 and 13. The conformation of the *meso*-

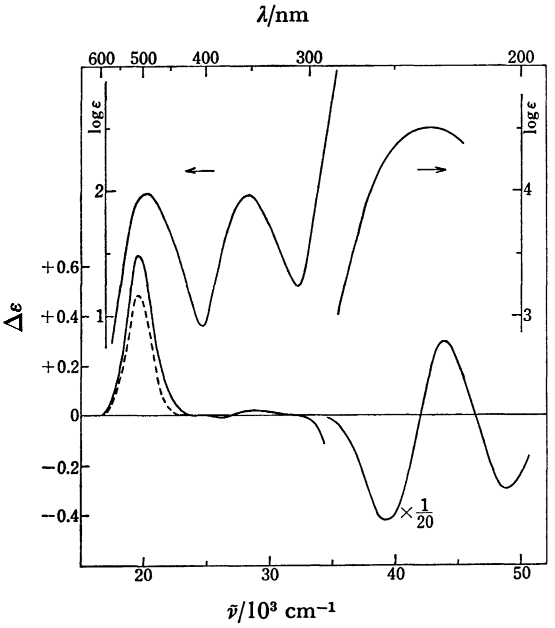


Fig. 12. Absorption and CD spectra of *mer*-Λ-[Co(*meso*-ptn)$_3$](ClO$_4$)$_3$·2H$_2$O; 2.89×10^{-3} M in visible region and 1.16×10^{-4} M in UV region in water (——), and 2.89×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

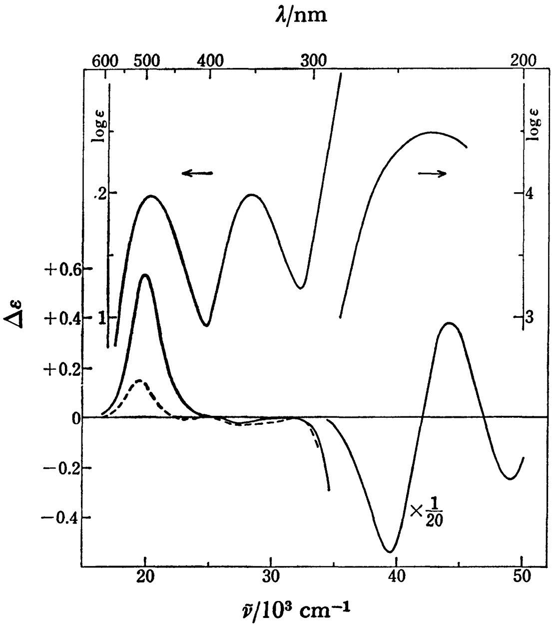


Fig. 13. Absorption and CD spectra of *fac*-Λ-[Co(*meso*-ptn)$_3$](ClO$_4$)$_3$·2H$_2$O; 3.11×10^{-3} M in visible region and 3.46×10^{-4} M in UV region in water (——), and 3.11×10^{-3} M in 0.2 M Na$_2$SO$_4$ (------).

ptn chelate ring is expected to be very stable in the chair form. The CD patterns of these S-bn and *meso*-ptn complexes in the presence of sulfate ions somewhat differ from those of the Λ isomers of S-bn and tn complexes in the same condition. In the latter two Λ isomers, the enhancement of one CD component seems to be accompanied with the diminution of the other CD component, and the total strength of the two CD components does not seem to change greatly. On the other hand, the former S-bn and *meso*-ptn complexes diminish the total CD strength. Such a difference in the CD variations can not be explained at present, but may also be related with the conformational instability of chelate rings in the complexes. The complexes, *mer*-Δ, *fac*-Δ-$[\mathrm{Co}(S\text{-bn})_3]^{3+}$, *mer*-$\Lambda$-, and *fac*-$\Lambda$-$[\mathrm{Co}(meso\text{-ptn})_3]^{3+}$ which diminish the total CD strength in the presence of sulfate ions will have more crowded, rigid structures compared with those of *fac*-Λ-$[\mathrm{Co}(S\text{-bn})_3]^{3+}$ and Λ-$[\mathrm{Co(tn)}_3]^{3+}$. For these crowded complexes, the CD variation of the more crowded *mer*-Λ-$[\mathrm{Co}(meso\text{-ptn})_3]^{3+}$ is smaller than that of the corresponding less crowded *fac*-Λ isomer. A similar relation is seen between the *mer*-Δ and the *fac*-Δ isomers. The crowded, rigid $\Lambda(ob_3)$-$[\mathrm{Co}(RR\text{-ptn})_3]^{3+}$ complex shows little variation in the CD spectra in various solvents.[5] These observations strongly suggest that the CD variations observed for both Δ-$[\mathrm{Co}(S\text{-bn})_3]^{3+}$ and $[\mathrm{Co}(meso\text{-ptn})_3]^{3+}$ are also closely related to the conformational instability of the six-membered chelate rings.

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