Bull. Chem. Soc. Jpn., *55*, *1454—1459 (1982)* [Vol. 55, No. 5

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

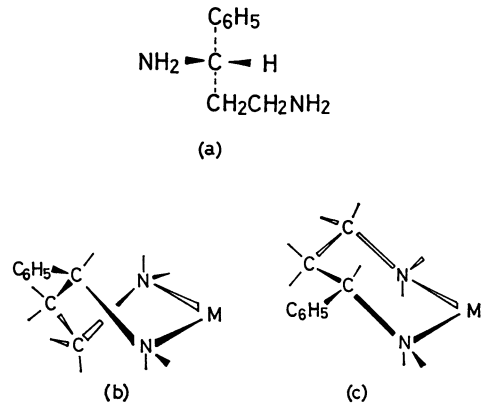
Masaaki Kojima and Junnosuke Fujita*

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received September 8, 1981)

Three, *fac-Δ*, *fac-Λ*, and *mer-Δ*, of four possible diastereomers of the [Co(*S*-phtn)$_3$]$^{3+}$ complex (*S*-phtn= (*S*)-1-phenyl-1,3-propanediamine) were obtained by two methods, a reaction between *trans*-[CoCl$_2$(*S*-phtn)$_2$]$^+$ and *S*-phtn in DMSO (dimethyl sulfoxide), and oxidation of a DMSO solution containing Co(II) ions and *S*-phtn with air in the presence of active charcoal. Neither method yielded the *mer-Λ* isomer. The absorption and circular dichroism spectra of the isomers were recorded in water in the absence and presence of Na$_2$SO$_4$, and in DMSO. The shifts of the first absorption bands caused by changing solvents and the changes of circular dichroism spectra caused by the addition of sulfate ions seem to be related with the conformational instability of the flexible six-membered chelate ring in the complexes. The tetraammine complex of *S*-phtn was also prepared.

In the previous papers, we reported that the circular dichroism (CD) spectra of some cobalt(III) complexes containing six-membered diamine chelate rings such as trimethylenediamine (tn),[1] (*R*,*R*)-2,4-pentanediamine (*RR*-ptn),[1] or (*S*)-1,3-butanediamine (*S*-bn)[2] vary remarkably with changes in counter ions and solvents. Such CD variations were accounted for by conformational interconversions of the flexible six-membered chelate rings caused by ion-pair formation. Conformational flexibility of a 1,3-diamine chelate ring would depend on the nature of substituents on the chelate ring. In order to investigate the effect of a bulky substituent on conformational stability of a chelate ring, we have prepared cobalt(III) complexes containing (*S*)-1-phenyl-1,3-propanediamine (*S*-phtn) and measured their absorption and CD spectra under various conditions. The skeletal structure of the *S*-phtn chelate ring is similar to that of the *S*-bn one, although these (*S*)-diamines form stable *skew* conformations of different chirality;[3] the former with the equatorial phenyl group is either the *chair* or the *λ-skew* form, while the latter with the same equatorial methyl group is the *chair* or *δ-skew* form (Fig. 1).



Ligand	conformation δ-skew	λ-skew	chair
S-phtn	a	e	e(a)
S-bn	e	a	e(a)
RR-ptn	aa	ee	ae
meso-ptn	ae	ae	ee(aa)
SS-dppn	aa	ee	ae

e: substituent equatorial
a: substituent axial

Fig. 1. (a) Absolute configuration of *S*-phtn, (b) *λ*-skew and (c) chair conformations of the *S*-phtn chelate ring, and relationship between conformations of 1,3-diamine chelate rings and dispositions of substituent(s).

Experimental

Ligand. 3-Phenyl-3-aminopropionic acid[4] was converted into the amide by the method of Yang and Rising.[5] The amide was reduced with LiAlH$_4$ in dry tetrahydrofuran to give 1-phenyl-1,3-propanediamine (phtn) according to a method similar to that for 2-methyl-1,4-butanediamine.[6] The rac-diamine thus obtained was resolved by the following method. To an aqueous solution (30 cm^3) of the diamine (13.5 g, 0.09 mol) was added an aqueous solution (50 cm^3) of (+)-tartaric acid (27.5 g, 0.18 mol), and the solution was allowed to stand overnight at 5 °C. White crystals thus obtained were collected, washed with ethanol–water (1:1), and recrystallized from water (50 cm^3). One careful recrystallization was sufficient to obtain the optically pure isomer. Yield: 8.3 g. To an aqueous solution (10 cm^3) of the diastereomer (8.3 g, 18 mmol) was added an aqueous solution (15 cm^3) of KCl (2.7 g, 36 mmol). Potassium hydrogen (+)-tartrate was precipitated, filtered off, and washed with cold water (10 cm^3). The combined filtrate and washing were concentrated to a small volume under reduced pressure. White needles of (*S*)-1-phenyl-1,3-propanediamine dihydrochloride were formed by the addition of ethanol and acetone, filtered, and washed with acetone. Yield: 3.7 g. $[\alpha]_D^{25}=+9.06°$ (*c* 0.0136, H$_2$O).

The absolute configuration of the diamine was determined by preparing (−)-3-phenyl-3-aminopropionic acid of the known absolute configuration (*S*). *N*-Formyl-3-phenyl-3-aminopropionic acid was prepared by the method of Fischer *et al.*,[7] and the diastereomer with quinidine was prepared by the method of Cohen *et al.*[4] (−)-3-Phenyl-3-aminopropionic acid derived from the more soluble diastereomer is known to have the (*S*) configuration.[8] Since the (*S*)-diamine dihydrochloride obtained from the (*S*)-(−)-amino acid by the same method as that for the racemate was dextrorotatory, (+)-phtn·2HCl was determined to have the (*S*) configuration.

trans-[*CoCl*$_2$(S-*phtn*)$_2$]*Cl*·*H*$_2$*O*. A methanol solution (30 cm^3) containing sodium methoxide (1.89 g, 35 mmol) and *S*-phtn·2HCl (4.0 g, 18 mmol) was stirred for about 1 h, and then filtered to remove sodium chloride precipitated. The filtrate was added to a methanol solution (170 cm^3) of $CoCl_2 \cdot 6H_2O$ (2.0 g, 8.5 mmol). The solution was aerated for 2.5 h at room temperature and then mixed with concd HCl (10 cm^3). Green crystals were obtained by concentrating the solution to a small volume under reduced pressure, filtered, and washed with a small amount of water. Yield: 0.7 g. The second crop was obtained by the addition of water to the filtrate. Yield: 1.1 g. The complex was recrystallized from methanol. Found: C, 44.45; H, 5.92; N, 11.60%. Calcd for $C_{18}H_{30}N_4Cl_3OCo$=*trans*-[$CoCl_2$(*S*-phtn)$_2$]Cl·H_2O: C, 44.69; H, 6.25; N, 11.58%.

[*Co*(S-*phtn*)$_3$]$^{3+}$. *Method 1*: To a dimethyl sulfoxide (DMSO) solution (40 cm^3) of *trans*-[$CoCl_2$(*S*-phtn)$_2$]Cl·H_2O (0.097 g, 2 mmol) was added a suspension of *S*-phtn·2HCl (0.53 g, 2.4 mmol) and sodium methoxide (0.23 g, 4.2 mmol) in methanol (2 cm^3). The mixture was stirred for 2.5 h at 70 °C, diluted with 1 dm^3 of water, and acidified (pH 2) with hydrochloric acid. The solution was passed through an SP-Sephadex column (ϕ2.7×5 cm). A small portion of the Sephadex charged with the product was placed on the top of the adsorbent layer of an SP-Sephadex column (ϕ2.7×120 cm), and the adsorbed complexes were eluted with a 0.5 M Na_2SO_4 (1 M=1 mol/dm^3) solution adjusted to pH 2 with hydrochloric acid. The column showed four bands, I(pink, very small amount), II(orange, very small amount), IIIA(orange-red, large amount), and IIIB(red, small amount) from bottom to top of the column. Bands IIIA and IIIB were eluted much slower than bands I and II. The effluent of band IIIA was diluted with 10^{-2} M HCl and loaded again on an SP-Sephadex column. The adsorbed band was eluted with a 0.25 M sodium (+)-tartratoantimonate(III) solution. The column showed two bands, *mer-Δ*(IIIA-1) and *fac-Δ*(IIIA-2) in the order of elution. Band IIIB was the *fac-Λ* isomer. The formation ratio, *mer-Δ*(IIIA-1) :*fac-Δ*(IIIA-2):*fac-Λ*(IIIB) was 8:5:1. No indication of the presence of the *mer-Λ* isomer was observed.

Method 2: To a stirred suspension of *S*-phtn·2HCl (2.0 g, 9.0 mmol) and sodium methoxide (0.92 g, 17 mmol) in methanol (8.5 cm^3) were added a DMSO solution (35 cm^3) of $Co(NO_3)_2 \cdot 6H_2O$ (0.73 g, 2.5 mmol), and active charcoal (0.5 g). The mixture was aerated for 4 h at room temperature, and filtered. The filtrate was diluted with 10^{-2} M HCl and passed through an SP-Sephadex column. The product adsorbed on SP-Sephadex was chromatographed by the same method as that for Method 1. Only two isomers, *mer-Δ* and *fac-Δ* were yielded, their formation ratio being 1.0:1.4.

mer-Δ[*Co*(S-*phtn*)$_3$](*ClO*$_4$)$_3$·6*H*$_2$*O*, fac-Δ-[*Co*(S-*phtn*)$_3$](*ClO*$_4$)$_3$·2*H*$_2$*O*, *and* fac-Λ-[*Co*(S-*phtn*)$_3$](*ClO*$_4$)$_3$·4*H*$_2$*O*. Each eluate of the isomers was diluted with 10^{-2} M HCl and passed through an SP-Sephadex column (ϕ1.5×3 cm). After the column had been washed with 10^{-2} M HCl (*ca.* 100 cm^3), the adsorbed complex was eluted with a 1.5 M $NaClO_4$ ethanol–water (1:1) solution. The eluate was acidified (pH 2) with $HClO_4$ and concentrated to a small volume in a vacuum desiccator over P_2O_5 to yield orange-red crystals. They were filtered, washed with a small amount of water, and recrystallized from 10^{-2} M $HClO_4$. *mer-Δ* isomer, Found: C, 35.35; H, 6.18; N, 8.80%. Calcd for $C_{27}H_{54}N_6Cl_3O_{18}Co$=[Co(*S*-phtn)$_3$]($ClO_4$)$_3$·6$H_2O$: C, 35.40; H, 5.94; N, 9.17%. *fac-Δ* isomer, Found: C, 38.20; H, 5.28; N, 9.98%. Calcd for $C_{27}H_{46}N_6Cl_3O_{14}Co$=[Co(*S*-phtn)$_3$]($ClO_4$)$_3$·2$H_2O$: C, 38.42; H, 5.49; N, 9.96%. *fac-Λ* isomer, Found: C, 37.09; H, 5.75; N, 9.33%. Calcd for $C_{27}H_{50}N_6Cl_3O_{16}Co$=[Co(*S*-phtn)$_3$]($ClO_4$)$_3$·4$H_2O$: C, 36.85; H, 5.73; N, 9.54%.

[*Co*(*NH*$_3$)$_4$(S-*phtn*)](*ClO*$_4$)$_3$·*H*$_2$*O*. A methanol solution (5 cm^3) of *S*-phtn (0.57 g, 5 mmol) was prepared by the same method as that described for *trans*-[$CoCl_2$(*S*-phtn)$_2$]Cl·H_2O. This was added to a DMSO solution (40 cm^3) of [$Co(NH_3)_5(H_2O)$](ClO_4)$_3$ (2.3 g, 5 mmol). The solution was stirred for 3 d at room temperature. The resulting red solution was diluted with 10^{-2} M HCl and passed through an SP-Sephadex column (ϕ2.7×5 cm). The product adsorbed was chromatographed by a method similar to that for [Co(*S*-phtn)$_3$]$^{3+}$ with 0.2 M Na_2SO_4 adjusted to pH 2 with hydrochloric acid. Six bands were eluted in the order of orange-red ([$Co(NH_3)_5(H_2O)$]$^{3+}$), yellow-orange ([$Co(NH_3)_6$]$^{3+}$), purple ([$Co(NH_3)_5$(DMSO)]$^{3+}$), orange ([$Co(NH_3)_4$(*S*-phtn)]$^{3+}$), orange (probably [$Co(NH_3)_5$(*S*-Hphtn)]$^{4+}$),[9] and pink (small amount, not characterized) bands. The eluate of the fourth band was diluted with 10^{-2} M HCl and passed through an SP-Sephadex column (ϕ1.5×3 cm). The adsorbed complex was eluted with 1.5 M $HClO_4$, and the eluate was concentrated to a small volume in a vacuum desiccator over P_2O_5 to yield orange needles, which were filtered and washed with ethanol. Found: C, 18.12; H, 5.07; N, 14.03%. Calcd for $C_9H_{23}N_6Cl_3O_{13}Co$=[$Co(NH_3)_4$(*S*-phtn)](ClO_4)$_3$·H_2O: C, 18.18; H, 4.75; N, 14.13%.

Attempts to Equilibrate [*Co*(S-*phtn*)$_3$]$^{3+}$. The *mer-Δ*-[Co(*S*-phtn)$_3$](ClO_4)$_3$·6H_2O (0.3 g) isomer was refluxed in water (50 cm^3) in the presence of active charcoal (0.1 g) for 3—8 h. The equilibrium process was accompanied by decomposition of the complex to reduce Co(III) to Co(II). A similar experiment was carried out in DMSO, but neither equilibration nor decomposition of the complex occured.

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-20 spectropolarimeter, respectively. Optical rotations at 589 nm were measured with a JASCO DIP-4 polarimeter at 25 °C. ^{13}C NMR spectra were obtained in DMSO solutions with a JEOL FX-60 spectrometer using dioxane as an external reference.

Results and Discussion

[*Co*(*NH*$_3$)$_4$(S-*phtn*)]$^{3+}$. Figure 2 compares CD spectra of the tetraammine complexes of *S*-phtn, *S*-bn, and *RR*-ptn in aqueous solutions. The CD pattern of the *S*-phtn complex is enantiomeric to that of the *S*-bn complex in the first absorption band region. Since the *S*-phtn and *S*-bn chelate rings will be stabilized with the equatorially disposed substituent in the *chair* and/or the *λ-skew*, and in the *chair* and/or the *δ-skew* conformations, respectively (Fig. 1), it is possible to attribute these CD patterns to the presence of *skew* conformers of the diamines. However, the signs of main CD bands of the complexes are opposite to those reported for the vicinal effect of many chiral, *gauche* and *skew* conformers of diamine chelates; a *λ*(*δ*)-conformer gives the positive (negative) vicinal effect in the first absorption band region. Therefore, it appears that the *S*-phtn and *S*-bn chelates in the tetraammine complexes have the achiral *chair* conformation, and that the weak CD peaks are those related essentially to the vicinal effect of the chiral

Table 1. Absorption and CD spectral data

Complex	Absorption $\tilde{\nu}_{max}$/cm^{-1}(log ε)	CD $\tilde{\nu}$/cm^{-1}($\Delta\varepsilon$)	Concentration C/mol dm^{-3}
$[Co(NH_3)_4(S\text{-phtn})](ClO_4)_3\cdot H_2O$	20830(1.89)	18620(+0.0052) 21980(−0.027)	7.17×10^{-3}
$mer\text{-}\Delta\text{-}[Co(S\text{-phtn})_3](ClO_4)_3\cdot 6H_2O$	20200(2.04) 28000(2.34)^{sh}	19920(−0.698) 27800(+0.070)	2.51×10^{-3}
	35200(4.09) 43100(4.46)	35000(−1.9) 41300(+9.7) 45500(−1.9) 48500(+13.5)	1.00×10^{-4}
$fac\text{-}\Delta\text{-}[Co(S\text{-phtn})_3](ClO_4)_3\cdot 2H_2O$	20320(2.04)	18800(−0.226) 21000(+0.311)	2.79×10^{-3}
	28000(2.35)^{sh}		
	35200(4.0)^{sh} 43500(4.44)	35700(−5.3) 41000(+5.5) 46100(−12) 48100(+4.5)	1.12×10^{-4}
$fac\text{-}\Lambda\text{-}[Co(S\text{-phtn})_3](ClO_4)_3\cdot 4H_2O$	20040(2.05) 28000(2.4)^{sh}	19880(+1.39) 27800(−0.07)	2.63×10^{-3}
	35200(4.0)^{sh}		
	42700(4.45)	40000(−12) 45100(+7.7) 46900(+11)	1.05×10^{-4}

sh: Shoulder.

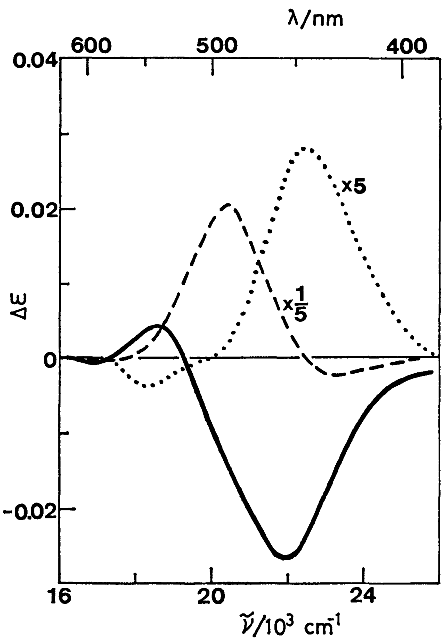


Fig. 2. CD spectra of $[Co(NH_3)_4(1,3\text{-diamine})]^{3+}$ in water. 1,3-Diamine: S-phtn (——), RR-ptn (----), and S-bn (······).

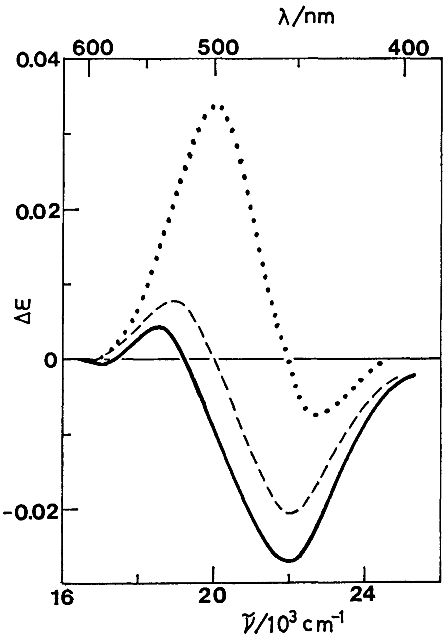


Fig. 3. CD spectra of $[Co(NH_3)_4(S\text{-phtn})]^{3+}$ in water (——), in 0.2 M Na_2SO_4 (----), and in DMSO–H_2O (1:1) (······).

carbon atom. The CD strength of the S-phtn complex is about six times as large as that of the S-bn complex (Table 1). The CD of a tetraammine complex with a bulky phenyl-substituted diamine chelate seems to be larger than that of the corresponding methyl-substituted complex. For example, $[Co(NH_3)_4(R\text{-pen})]^{3+}$ (R-pen=(R)-1-phenyl-1,2-ethanediamine, $\Delta\varepsilon=+0.465$, 21600 cm^{-1})10) and $[Co(NH_3)_4(R\text{-pn})]^{3+}$ (R-pn=(R)-1,2-propanediamine, $\Delta\varepsilon=+0.326$, 21690 cm^{-1});10) $[Co(NH_3)_4(SS\text{-dpen})]^{3+}$ (SS-dpen=(S,S)-1,2-diphenyl-1,2-ethanediamine, $\Delta\varepsilon=-0.75$, 21370 cm^{-1})11) and $[Co(NH_3)_4(SS\text{-}2,3\text{-bn})]^{3+}$ (SS-2,3-bn =(S,S)-2,3-butanediamine, $\Delta\varepsilon=-0.35$, 21740 cm^{-1}).10)

The S-phtn complex increases the CD strength of the positive component and decreases complementarily that of the negative one in 0.2 M Na_2SO_4 and in DMSO–H_2O (1:1) (Fig. 3). The CD pattern in the latter solvent quite resembles that of $[Co(NH_3)_4(RR\text{-ptn})]^{3+}$ in water. The stable conformer of the RR-ptn chelate ring will be the λ-*skew* form in which the

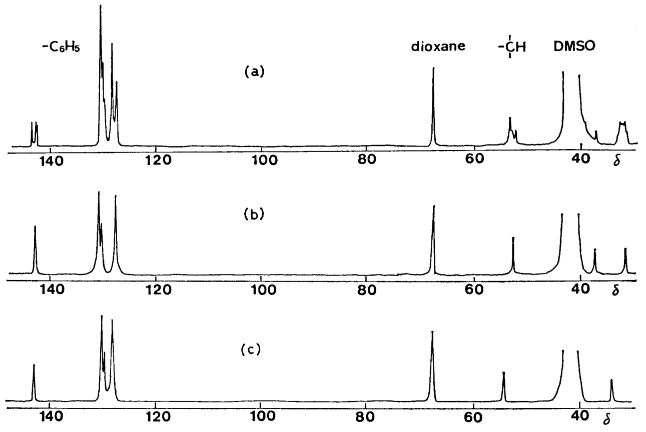


Fig. 4. ^{13}C NMR spectra of the three isomers of [Co(*S*-phtn)$_3$]$^{3+}$ in DMSO; (a) IIIA-1 (*mer*-*Δ*), (b) IIIA-2 (*fac*-*Δ*), and (c) IIIB (*fac*-*Λ*).

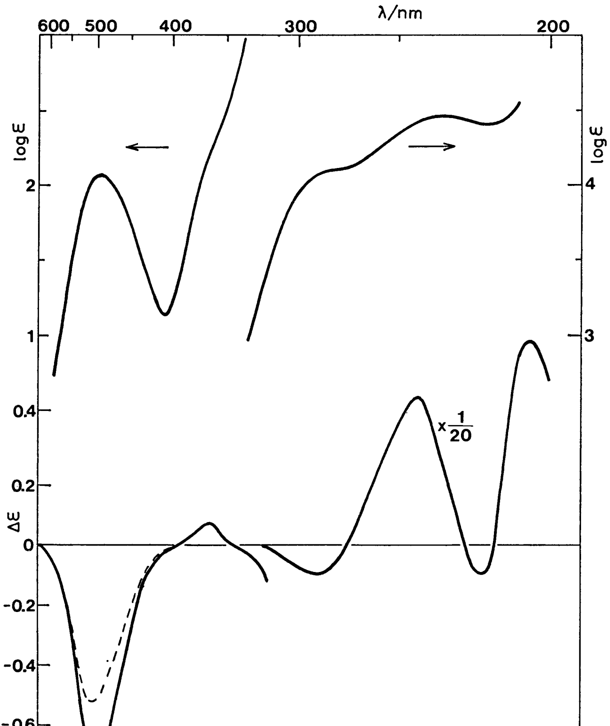


Fig. 5. Absorption and CD spectra of *mer*-*Δ*-[Co(*S*-phtn)$_3$]$^{3+}$ (IIIA-1) in water (——) and in 0.2 M Na$_2$SO$_4$ (----).

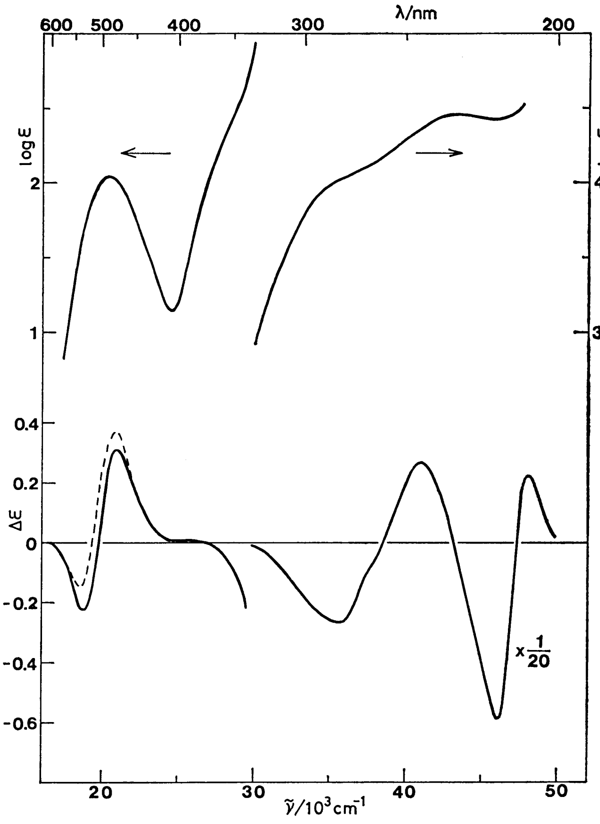


Fig. 6. Absorption and CD spectra of *fac*-*Δ*-[Co(*S*-phtn)$_3$]$^{3+}$ (IIIA-2) in water (——) and in 0.05 M Na$_2$SO$_4$ (----) (The complex is hardly soluble in 0.2 M Na$_2$SO$_4$.).

two methyl groups are disposed equatorially.1) Thus the *S*-phtn complex is suggested to involve the *λ*-*skew* conformer stabilized under the conditions given. When the *S*-phtn chelate ring adopts the *λ*-*skew* form, the complex ion has a set of three N–H bonds suitable for hydrogen bonds with a sulfate or a perchlorate ion, the N–H bonds being provided by two ammonia molecules and the *S*-phtn chelate.1) The N–H bonds of the diamine in the *chair* form are not directed properly for such hydrogen bonding. A perchlorate ion could form an ion-pair with the complex ion in DMSO–H$_2$O (1:1).1)

*[Co(*S*-phtn)$_3$]$^{3+}$. Characterization and Formation Ratio of the Isomers*: The [Co(*S*-phtn)$_3$]$^{3+}$ complex can have four diastereomers, *mer*-*Δ*, *mer*-*Λ*, *fac*-*Δ*, and *fac*-*Λ*. ^{13}C NMR spectroscopy was used to distinguish between the *mer* and *fac* isomers (Fig. 4). The spectra of isomers IIIA-2 and IIIB give one and four resonances for the methine and the phenyl carbons, respectively, while that of isomer IIIA-1 shows complicated signals, indicating the presence of nonequivalent methine and phenyl groups. From symmetry argument (*fac*(C_3), *mer*(C_1)), isomers IIIA-1, IIIA-2, and IIIB can be assigned to the *mer*, *fac*, and *fac* configurations, respectively. Figures 5—7 show CD spectra of the three isomers in aqueous solutions in the absence and presence of sulfate ions. On the basis of the CD patterns in the first absorption band region, isomers IIIA-1, IIIA-2, and IIIB can be assigned to the *Δ*, *Δ*, and *Λ* configurations, respectively. For a cobalt(III) complex containing 1,3-diamine chelates, the CD pattern in this region often depends greatly on conditions measured, so that the use of the sign of the lowest energy CD band appearing in the Co(III)–diamine charge-transfer region has been recommended for assigning the absolute configuration;12) the *Λ*-[Co(diamine)$_3$]$^{3+}$ complex shows a negative CD band at the lowest energy in this region. All the isomers give such a band at *ca.* 40000 cm^{-1}. The negative CD bands at *ca.* 35000 cm^{-1} of isomers IIIA-1 and

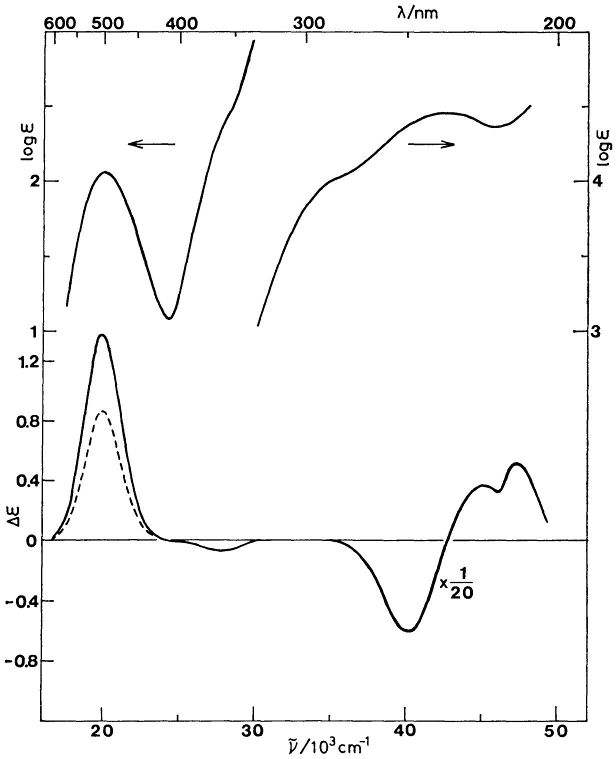


Fig. 7. Absorption and CD spectra of *fac*-Λ-$[Co(S\text{-phtn})_3]^{3+}$ (IIIB) in water (——) and in 0.2 M Na_2SO_4 (----).

IIIA-2 should correspond to transitions of the phenyl group. Thus two isomers IIIA-1 and IIIA-2, and isomer IIIB which show a positive and negative CD band, respectively, at *ca.* 40000 cm^{-1} are assigned to Δ and Λ configurations, respectively. This assignment agrees with that based on the CD pattern in the first absorption band region. Thus it is concluded that isomers IIIA-1, IIIA-2, and IIIB are the *mer*-Δ, *fac*-Δ, and *fac*-Λ configurations, respectively.

The $[Co(S\text{-phtn})_3]^{3+}$ complex was prepared by two methods. Method 1 is a substitution reaction between *trans*-$[CoCl_2(S\text{-phtn})_2]^+$ and *S*-phtn in DMSO, and Method 2 oxidation of a DMSO solution containing Co(II) ions and *S*-phtn with air in the presence of active charcoal (Experimental). The formation ratios of the isomers, *mer*-Δ:*fac*-Δ:*mer*-Λ:*fac*-Λ, by Methods 1 and 2 were 8:5:0:1, and 1.0:1.4:0:0, respectively. Neither method yielded the *mer*-Λ isomer. A molecular model indicates that this isomer involves two phenyl groups situated very close to each other regardless of the conformation of the chelate rings. Although attempts to equilibrate the isomers were unsuccessful, the ratio obtained by Method 2 might be close to that at equilibrium, since the method was carried out in the presence of active charcoal. No Λ isomers were formed by Method 2. The *S*-phtn chelate ring can take the λ-*skew* conformation. When the diamines are in this conformation, the Δ- and Λ-$[Co(S\text{-phtn})_3]^{3+}$ isomers form the lel_3 and ob_3 structures, respectively.[13] For $[Co(tn)_3]^{3+}$, the ob_3 isomer has been calculated by conformational analysis to have a substantially higher energy than the lel_3 and $chair_3$ isomers.[14] No formation of the Λ isomers might be related to the unstable structure of the ob_3 isomer. The formation ratio of the isomers, *mer*-Δ, *fac*-Δ, *mer*-Λ, and *fac*-Λ, in the corresponding $[Co(S\text{-bn})_3]^{3+}$ complex was obtained as 1:2:1:14 by a method similar to Method 2 in this study. The *S*-bn complex gives all of the four possible isomers, although it also yields the Λ isomers to a greater extent than the Δ isomers. Since the chiralities of the *S*-bn and *S*-phtn chelates in the *skew* form are opposite to each other, the structure of Λ(Δ)-$[Co(S\text{-bn})_3]^{3+}$ corresponds to that of Δ(Λ)-$[Co(S\text{-phtn})_3]^{3+}$. The Λ-$[Co(S\text{-bn})_3]^{3+}$ complex favors greatly the *fac* isomer over the *mer* one, while the Δ-$[Co(S\text{-phtn})_3]^{3+}$ complex gives nearly the same amount of the *mer* and *fac* isomers. The stabilities of these isomers depend largely on the size of the substituent on the 1,3-diamine chelate ligand.

Absorption Spectra: The maximum positions of the first absorption bands of the $[Co(S\text{-phtn})_3]^{3+}$ isomers differ considerably from each other (Table), in contrast to the case of $[Co(S\text{-bn})_3]^{3+}$ in which the absorption maxima are in a small range of 20430 to 20370 cm^{-1}.[2] In a previous paper,[2] we reported that a $[Co(1,3\text{-diamine})_3]^{3+}$ complex in the *skew* conformation gives the first absorption band at higher energy than that of the complex in the *chair* conformation. The fairly large energy difference in the absorption maixma among the isomers of $[Co(S\text{-phtn})_3]^{3+}$ seems to be related with the difference in the conformation of chelate rings among the isomers.

When the *S*-phtn chelate ring adopts the λ-*skew* conformation, the *fac*-Λ and the *fac*-Δ isomers form the ob_3 and the lel_3 structures, respectively. Since the ob_3 structure should be less stable than the $chair_3$ one,[14] the *fac*-Λ isomer would be stabilized in the $chair_3$ form. On the other hand, the chelate rings in the *fac*-Δ isomer would be able to interchange between the chair and the λ-*skew* (*lel*) conformations, since the stability difference between the $chair_3$ and the lel_3 forms would be small.[14] The fact that the *fac*-Δ isomer gives the first absorption maximum (20230 cm^{-1}) at fairly higher energy than does the *fac*-Λ isomer (20040 cm^{-1}) indicates that the predominant conformation in the *fac*-Δ isomer is the λ-*skew* form. This isomer shows the blue shift in the first absorption band in DMSO (20410 cm^{-1}). The shift can be interpreted as the result of stabilization of the $lel_3(\Delta(\lambda\text{-}skew_3))$ conformer in this solvent by ion-pair formation between the complex ion and the counter ion (*vide infra*). No solvent effect was observed for the *fac*-Λ isomer, suggesting the stability of the $chair_3$ structure.

The *mer*-Δ isomer shows the first absorption maximum at 20200 cm^{-1} in water. The two *S*-phtn chelate rings in the *mer*(C_1) configuration approach very close to each other, when they adopt the *chair* conformation. As suggested for the *mer* isomers of $[Co(S\text{-bn})_3]^{3+}$,[2] the close approach of two chelate rings can be avoided when one of these rings takes the λ-*skew* conformation. Thus the stable structure of the *mer*-Δ isomer would be the $(chair)_2(\lambda\text{-}skew)$ form in water. In fact, the first absorption maximum of the isomer is between those of the *fac*-Δ and *fac*-Λ isomers, in which the predominant conformers of *S*-

phtn have been assigned to the *λ-skew* and *chair* forms, respectively. The first absorption band of the *mer-Δ* isomer shows a small red shift in DMSO (20140 cm^{-1}), but the reverse shift in DMSO–H_2O (1:1) (20280 cm^{-1}). Although the reason for this is not clear, the complex might be stabilized in the *lel*$_3$-(*λ-skew*)$_3$ structure in the latter solvent. In the case of the *fac-Δ* isomer, the band shifts monotonously depending upon the ratio of DMSO to water.

Circular Dichroism Spectra: The study of absorption spectra suggested that the predominant conformer in one isomer differs from that in another. Such conformational flexibility of the *S*-phtn chelate ring is also reflected on the CD spectra. For example, the additive law[16] for the configurational and the vicinal (conformational) effects does not hold for the diastereomeric pair, *fac-Δ*- and *fac-Λ*-$[Co(S\text{-phtn})_3]^{3+}$. The lack of such additivity has also been found for the *RR*-ptn and *S*-bn complexes, and ascribed to the conformational flexibility of the six-membered chelate rings.

The CD pattern of *fac-Δ*-$[Co(S\text{-phtn})_3]^{3+}$ in water is very similar to that of *Δ*-$[Co(RR\text{-ptn})_3]^{3+}$ in 0.1 M Na_2SO_4. The latter has been considered to be stabilized in the *lel*$_3$(*Δ*(*λ-skew*)$_3$) form in the presence of sulfate ions.[1] Thus it is suggested that the stable structure of the *fac-Δ* isomer in water is the *λ-skew*$_3$-(*lel*$_3$) form. This suggestion agrees with that obtained from absorption studies. The corresponding *S*-bn complex, *fac-Λ*-$[Co(S\text{-bn})_3]^{3+}$, on the other hand, is stabilized in the *chair*$_3$ structure in water.[2] On addition of sulfate ions, *fac-Δ*-$[Co(S\text{-phtn})_3]^{3+}$ diminishes the CD strength of the negative component, and complementarily enhances that of the positive component. Such a change is known to be caused by an increase in the amount of the *lel*$_3$(*Δ*(*λ-skew*)$_3$) conformer due to ion-association between the complex ion and a sulfate ion; the *lel*$_3$ form is the most effective structure in forming an ion-pair through hydrogen bonding between the amino protons and a sulfate ion, and the increase in the positive CD component is caused by the increasing amount of the *λ*-conformer, since the vicinal effect of a *λ*-conformer is positive.[16] The *lel*$_3$ conformer of the *fac-Δ* isomer would be stabilized more in the presence of sulfate ions.

The *fac-Λ* isomer shows only one positive CD band in the first absorption band region, and the CD strength diminishes considerably on addition of sulfate ions. Both of these characteristics have been observed for *fac-Λ*-$[Co(RS\text{-ptn})_3]^{3+}$ (*RS*-ptn=(*R*,*S*)-2,4-pentanediamine), in which the *RS*-ptn chelate ring should be stabilized in the *chair* conformation with the two equatorial methyl groups. Thus the stable structure of *fac-Λ*-$[Co(S\text{-phtn})_3]^{3+}$ would be the *chair*$_3$ form as suggested from absorption studies.

The CD changes caused by the addition of sulfate ions for *fac-Δ*- and *fac-Λ*-$[Co(S\text{-phtn})_3]^{3+}$ correspond to those for *fac-Λ*- and *fac-Δ*-$[Co(S\text{-bn})_3]^{3+}$, respectively. On the other hand, the effect of sulfate ions on the CD of *mer-Δ*-$[Co(S\text{-phtn})_3]^{3+}$ differs significantly from that of *mer-Λ*-$[Co(S\text{-bn})_3]^{3+}$. By the addition of sulfate ions, the *S*-bn complex shows a fairly strong negative CD band with the decrease in strength of the positive CD band, suggesting the stabilization of the *lel*$_3$ form due to ion-pair formation with a sulfate ion.[2] However, the *S*-phtn complex diminishes only the strength of the negative CD band and shows no indication of appearance of a positive CD band. Thus no stabilization to the *lel*$_3$ form seems to occur in the *mer-Δ*-$[Co(S\text{-phtn})_3]^{3+}$ isomer. This might be related with the difficulty in forming an ion-pair with a sulfate ion. In the *mer-Δ* isomer, the bulky phenyl groups are disposed on either side of the pseudo-C_3 axis of the complex ion, and would hinder a sulfate ion from approaching the complex ion along the axis. Thus the complex will not be stabilized in the *lel*$_3$ form in the presence of sulfate ions.

Each of the three isomers of $[Co(S\text{-phtn})_3]^{3+}$ exhibits a characteristic CD change by the addition of sulfate ions, and all the CD changes can be interpreted on the basis of those of the corresponding *S*-bn complexes taking the steric effect of the bulky phenyl group into consideration.

This work was partly supported by a Grant-in-Aid for Scientific Research No. 243013 from the Ministry of Education, Science and Culture.

References

1) M. Kojima, M. Fujita, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 898 (1977).

2) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 3237 (1977).

3) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

4) S. G. Cohen and S. Y. Weinstein, *J. Am. Chem. Soc.*, **86**, 725 (1964).

5) P. S. Yang and M. M. Rising, *J. Am. Chem. Soc.*, **53**, 3183 (1931).

6) M. Kojima, K. Morita, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 2947 (1981).

7) E. Fischer, H. Scheibler, and R. Groh, *Chem. Ber.*, **43**, 2020 (1910).

8) B. Sjöberg, B. Hansson, and R. Dahlbom, *Acta Chem. Scand.*, **16**, 1057 (1962).

9) H. Ogino, *Bull. Chem. Soc. Jpn.*, **50**, 2459 (1977).

10) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **54**, 2691 (1981).

11) S. Arakawa, K. Kashiwabara, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **50**, 2331 (1977).

12) M. Kojima and J. Fujita, *Chem. Lett.*, **1976**, 429.

13) J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

14) S. R. Niketic and F. Woldbye, *Acta Chem. Scand.*, **27**, 621 (1973).

15) S. Arakawa, K. Kashiwabara, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **50**, 2108 (1977).

16) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).