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Isomers of Tris[(*R*)-1-phenyl-1,2-ethanediamine]- and Tris[(*S*)-3,3-dimethyl-1,2-butanediamine]cobalt(III), and the Related Complexes

Masaaki Kojima and Junnosuke Fujita*

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

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The [Co{(*R*)-1-phenyl-1,2-ethanediamine}$_3$]$^{3+}$ complex yielded all of the four possible isomers, *mer-Δ(lel₃)*, *mer-Λ(ob₃)*, *fac-Δ(lel₃)*, and *fac-Λ(ob₃)*, while the [Co{(*S*)-3,3-dimethyl-1,2-butanediamine}$_3$]$^{3+}$ complex gave only two isomers of *mer-Λ(lel₃)* and *fac-Λ(lel₃)*. Two isomers, *Λ(lel₃)* and *Δ(ob₃)* of the [Co{(*S,S*)-2,3-butanediamine}$_3$]$^{3+}$ complex were obtained. The formation ratios of these tris(1,2-diamine)cobalt(III) complexes were compared with those of the analogous complexes and discussed. The tetraammine complexes of all those diamines were also prepared. Absorption and circular dichroism spectra of all the complexes were recorded.

Recently Bernth and Larsen[1] isolated three out of four possible isomers of [Co(*R*-pen)$_3$]$^{3+}$ (*R*-pen=(*R*)-1-phenyl-1,2-ethanediamine), and reported their circular dichroism (CD) spectra. This paper deals with the isolation and CD spectra of all the isomers. The CD spectrum of one isomer (*mer-Λ(ob₃)*) reported by Bernth and Larsen differs markedly from that obtained in this study. The present paper also reports the preparation and CD spectra of two isomers of [Co(*S*-dmbn)$_3$]$^{3+}$ (*S*-dmbn=(*S*)-3,3-dimethyl-1,2-butanediamine), two isomers of [Co(*SS*-2,3-bn)$_3$]$^{3+}$ (*SS*-2,3-bn=(*S,S*)-2,3-butanediamine), and the tetraammine complexes of those diamines. The *R*-pen and *S*-dmbn ligands have a bulky substituent on the carbon atom, and the *SS*-2,3-bn the methyl group on each carbon atom.

Experimental

Ligands. 1-Phenyl-1,2-ethanediamine (pen) was obtained by reducing 2-amino-2-phenylethaneamide which was derived from 2-amino-2-phenylacetic acid (Tokyo Kasei Co.), with $LiAlH_4$ according to the known method,[2] and resolved with (+)-tartaric acid to give *R*-pen by the method of Reihlen *et al.*[3] Optically active *R*-pen was also derived from (−)-(*R*)-2-amino-2-phenylacetic acid (Aldrich Chem. Co.) by the same method. However, the product was not optically pure so that the procedure of resolution given above was necessary.

(+)-(*S*)-3,3-Dimethyl-1,2-butanediamine (*S*-dmbn) was obtained by the method of Hawkins and Peachey.[4] The dihydrochloride salt (*S*-dmbn·2HCl) was used to prepare cobalt(III) complexes.

2,3-Butanediamine (2,3-bn) was prepared by the method of Bailar *et al.*[5] and separated into the *meso* and *racemic* isomers by the method of Billo and Vitiello.[6] The (+)-*SS*-2,3-bn isomer was obtained from the racemate by the method of Dickey *et al.*[7]

mer-Δ- *and* fac-Δ-*[Co(*R-*pen)₃]Cl₃·2.5H₂O,* mer-Λ-*[Co(*R-*pen)₃]Cl₃·3H₂O, and* fac-Λ-*[Co(*R-*pen)₃]Cl₃·4H₂O.* A mixture of [Co(NH$_3$)$_5$(H$_2$O)](ClO$_4$)$_3$ (0.5 g, 1.1 mmol), *R*-pen (0.68 g, 5 mmol), and active charcoal (0.2 g) in 30 cm^3 of water was heated at 60 °C for 5 h, and filtered. The filtrate was diluted with 1 dm^3 of water and passed through an SP-Sephadex column (ϕ2.7×3 cm). The Sephadex charged with the product was placed on the top of an SP-Sephadex column (ϕ2.7×120 cm). By elution with 0.2 mol/dm^3 Na$_2$SO$_4$, the orange band separated into four bands, I, II, III, and IV named in the order of elution, which were *mer-Δ*, *fac-Δ*, *mer-Λ*, and *fac-Λ* isomers of [Co(*R*-pen)$_3$]$^{3+}$, respectively. Each eluate was diluted with water and poured again on a small column of SP-Sephadex. After the column had been washed with 10^{-2} mol/dm^3 HCl (*ca.* 5 dm^3), the adsorbed complex was eluted with 1 mol/dm^3 HCl. The eluate was concentrated in a vacuum desiccator over P$_2$O$_5$ and NaOH to give orange crystals, which were filtered and washed with a small amount of water. The total yield was almost quantitative, and the formation ratio, I:II:III:IV was *ca.* 17:8:4:1. I. Found: C, 46.5; H, 6.6; N, 13.8%. II. Found: C, 46.6; H, 6.7; N, 13.8%. Calcd for [Co(R-pen)$_3$]Cl$_3$·2.5H$_2$O: C, 46.6; H, 6.7; N, 13.6%. III. Found: C, 45.6; H, 6.7; N, 13.6%. Calcd for [Co(R-pen)$_3$]Cl$_3$·3H$_2$O: C, 45.9; H, 6.7; N, 13.4%. IV. Found: C, 44.6; H, 6.3; N, 12.8%. Calcd for [Co(*R*-pen)$_3$]Cl$_3$·4H$_2$O: C, 44.6; H, 6.9; N, 13.0%.

mer-Λ- *and* fac-Λ-*[Co(*S-*dmbn)₃](ClO₄)₃·3H₂O.* The [Co(*S*-dmbn)$_3$]$^{3+}$ complex was prepared and separated into the isomers by a method similar to that for [Co(*R*-pen)$_3$]$^{3+}$, using *S*-dmbn which was obtained by neutralizing the dihydrochloride with an aqueous NaOH solution, instead of *R*-pen. Only two isomers, A(*mer-Λ*) and B(*fac-Λ*) were yielded in nearly the same amount, A being eluted faster than B in column chromatography. The isomers were isolated as perchlorates by use of 1.5 mol/dm^3 HClO$_4$ instead of 1 mol/dm^3 HCl. Yield: *ca.* 40% for each isomer. A. Found: C, 28.8; H, 7.1; N, 11.0%. B. Found: C, 28.5; H, 6.8; N, 11.0%. Calcd for [Co(S-dmbn)$_3$](ClO$_4$)$_3$·3H$_2$O: C, 28.5; H, 7.2; N, 11.1%.

The [Co(*S*-dmbn)$_3$]$^{3+}$ complex was also obtained by mixing a methanol solution (15 cm^3) of *trans*-[CoCl$_2$(pyridine)$_4$]Cl·6H$_2$O (0.59 g, 1 mmol)[8] and a methanol solution (15 cm^3) containing *S*-dmbn·2HCl (0.57 g, 3 mmol) and NaOCH$_3$ (0.32 g, 6 mmol). The reaction took place almost instantly to give a yellow solution. It was diluted with water and chromatographed by the same method as the above to give the *mer-Λ* and *fac-Λ* isomers. The formation ratio, *mer-Λ*: *fac-Λ* was 3:1, no *Δ* isomer being yielded.

Λ-*[Co(*SS-*2,3-bn)₃]Cl₃·1.5H₂O and* Δ-*[Co(*SS-*2,3-bn)₃]Cl₃·5H₂O.* Two isomers of [Co(*SS*-2,3-bn)$_3$]$^{3+}$ were obtained by a method similar to that for [Co(*R*-pen)$_3$]$^{3+}$ using *SS*-2,3-bn instead of *R*-pen. The formation ratio of the *Λ(lel₃)* to the *Δ(ob₃)* isomers was *ca.* 10:1. The *Λ* isomer. Found: C, 31.7; H, 8.6; N, 18.1%. Calcd for [Co(*SS*-2,3-bn)$_3$]Cl$_3$·1.5H$_2$O: C, 31.7; H, 8.6; N, 18.4%. The *Δ* isomer. Found: C, 28.0; H, 8.7; N, 16.5%. Calcd for [Co(*SS*-2,3-bn)$_3$]Cl$_3$·5H$_2$O: C, 27.7; H, 8.9; N, 16.2%.

*[Co(NH₃)₄(*R-*pen)](ClO₄)₃·2H₂O and [Co(NH₃)₄(*S-*dmbn)](ClO₄)₃.* These complexes were prepared from [Co(NH$_3$)$_5$(H$_2$O)](ClO$_4$)$_3$ and *R*-pen or *S*-dmbn·2HCl in dimethyl sulfoxide (DMSO) by a method similar to that reported.[9,10] Yield: *ca.* 20% (*R*-pen complex). *ca.* 10% (*S*-dmbn complex). The *R*-pen complex. Found: C, 16.2; H, 4.7; N, 14.1%. Calcd for [Co(NH$_3$)$_4$(*R*-pen)](ClO$_4$)$_3$·2H$_2$O: C, 16.1; H, 4.7; N, 14.1%. The *S*-dmbn complex. Found: C, 13.4; H, 5.1; N, 15.8%. Calcd for [Co(NH$_3$)$_4$-

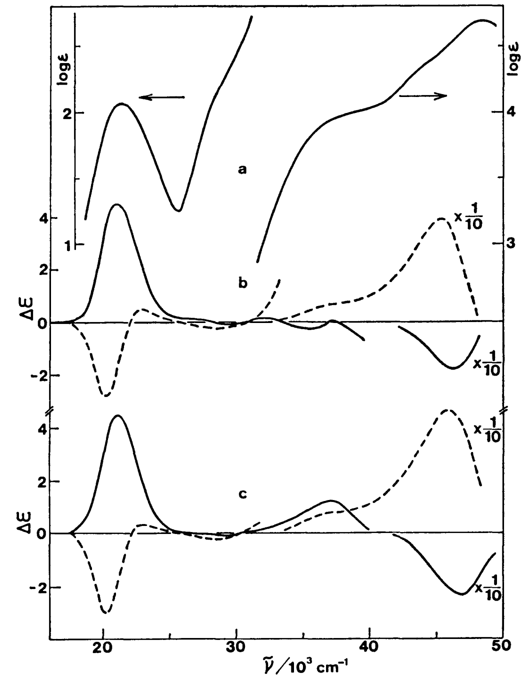

Fig. 1. a: Absorption spectrum of *fac*-Λ-$[\mathrm{Co}(R\text{-pen})_3]^{3+}$ (IV). b: CD spectra of *fac*-Λ-$[\mathrm{Co}(R\text{-pen})_3]^{3+}$ (IV) (——) and *fac*-Δ-$[\mathrm{Co}(R\text{-pen})_3]^{3+}$ (II) (----). c: CD spectra of *mer*-Λ-$[\mathrm{Co}(R\text{-pen})_3]^{3+}$ (III) (——) and *mer*-Δ-$[\mathrm{Co}(R\text{-pen})_3]^{3+}$ (I) (----).

(S-dmbn)]$(\mathrm{ClO_4})_3$: C, 13.3; H, 5.2; N, 15.8%.

$[\mathrm{Co(NH_3)_4}$(SS-2,3-bn)$](\mathrm{ClO_4})_3$. This complex was prepared by a method similar to that of Mizukami *et al.*[11] for the corresponding (R,R)-2,4-pentanediamine complex. The method for the above R-pen and S-dmbn complexes gives a large amount of $[\mathrm{Co}(SS\text{-2,3-bn})_3]^{3+}$ owing to disproportionation. The $\mathrm{NH_4[Co(SO_3)_2(NH_3)_2}(SS\text{-2,3-bn})]$ complex (not analyzed) prepared from $\mathrm{NH_4[Co(SO_3)_2(NH_3)_4]}$[12] and SS-2,3-bn was allowed to react with 47% hydrobromic acid to yield *trans*(Br,Br)-$[\mathrm{CoBr_2(NH_3)_2}(SS\text{-2,3-bn})]\mathrm{Br}$ (not analyzed). It was dissolved in liquid ammonia to give an orange solution. A crude complex which remained on evaporation of the liquid ammonia was purified by column chromatography with SP-Sephadex. The complex was isolated as perchlorate by a method similar to that for $[\mathrm{Co}(S\text{-dmbn})_3]^{3+}$. Yield: *ca.* 10%. Found: C, 9.2; H, 4.6; N, 16.7%. Calcd for $[\mathrm{Co(NH_3)_4}(SS\text{-2,3-bn})](\mathrm{ClO_4})_3$: C, 9.4; H, 4.7; N, 16.4%.

Equilibrium Studies. Each isomer of *mer*-Λ- and *fac*-Λ-$[\mathrm{Co}(S\text{-dmbn})_3](\mathrm{ClO_4})_3$ was refluxed in water (50 cm³) in the presence of active charcoal (0.1 g) for 3—8 h. The charcoal was filtered off and the filtrate was subjected to SP-Sephadex column chromatography in order to see the distributions of isomers. The ratio, *mer*-Λ:*fac*-Λ=1:1 was obtained, no formation of the Δ isomer being observed. The Λ-$[\mathrm{Co}(SS\text{-2,3-bn})_3]\mathrm{Cl_3\cdot 1.5H_2O}$ complex was equilibrated by the same method, giving the ratio, Λ:Δ=10:1. The ratios for both complexes thus obtained are the same as the respective formation ratios obtained when the complexes were prepared in the presence of active charcoal. Equilibration of $[\mathrm{Co}(R\text{-pen})_3]^{3+}$ by the same method as the above was accompanied with reduction of Co(III) to Co(II).

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. ^{1}H NMR spectra in DMSO-d_6 solutions and ^{13}C NMR spectra in DMSO solutions were obtained with a JEOL PMX-60 and a JEOL FX-60 spectrometer, respectively.

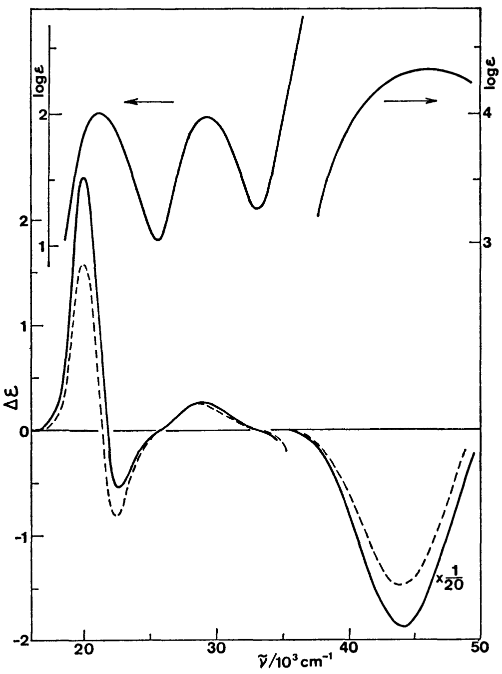

Fig. 2. Absorption spectrum of *mer*-Λ-$[\mathrm{Co}(S\text{-dmbn})_3]^{3+}$ (A), and CD spectra of *mer*-Λ-$[\mathrm{Co}(S\text{-dmbn})_3]^{3+}$ (A) (——) and *fac*-Λ-$[\mathrm{Co}(S\text{-dmbn})_3]^{3+}$ (B) (----).

Results and Discussion

Four isomers (I, II, III, IV) of the $[\mathrm{Co}(R\text{-pen})_3]^{3+}$ complex are easily assigned on the basis of the ^{13}C NMR and CD spectra. II and IV give only one kind of signal for each resonance of the methylene (II, 49.3 ppm; IV, 49.8 ppm) and methine (II, 61.2 ppm; IV 60.4 ppm) carbons, while I and III show more than two signals (unresolved peaks) for each of the corresponding carbons. Thus the former two and the latter two can be assigned to the *fac*(C_3) and *mer*(C_1) configurations, respectively. In the first absorption band region, I and II show a negative main CD band, and III and IV a strong positive CD band (Fig. 1). Thus I, II, III, and IV are assigned to the *mer*-Δ, *fac*-Δ, *mer*-Λ, and *fac*-Λ isomers, respectively. The $[\mathrm{Co}(S\text{-dmbn})_3]^{3+}$ complex yielded only two isomers, A and B out of four possible isomers. ^{1}H NMR spectra of A and B exhibit two and one signals, respectively, in the resonance region of the t-butyl group. Both isomers show a similar CD pattern which is characteristic of the Λ configuration (Fig. 2). Thus A and B can be assigned to the *mer*-Λ and *fac*-Λ isomers, respectively.

The Δ- and Λ-$[\mathrm{Co}(R\text{-pen})_3]^{3+}$, and Λ-$[\mathrm{Co}(S\text{-dmbn})_3]^{3+}$ complexes have the *lel*$_3$, *ob*$_3$, and *lel*$_3$ structures, respectively, since the R-pen and S-dmbn chelate rings should be stabilized in the λ and δ conformations, respectively, with the phenyl or t-butyl group disposed equatorially. For a $[\mathrm{Co(1,2\text{-}diamine)_3}]^{3+}$ complex, the *lel*$_3$ isomer is known to be more stable than the *ob*$_3$ one.[13] The relative amounts of the *lel*$_3$ to the *ob*$_3$-

Table 1. Absorption (AB) and CD spectral data

Complex	$\tilde{\nu}^{AB}/10^3$ cm^{-1}(log ε)	$\tilde{\nu}^{CD}/10^3$ cm^{-1}(Δ ε)
mer-Δ-[Co(*R*-pen)$_3$]$^{3+}$	21.20(2.10)	20.24(−2.94)
		23.04(+0.34)
	29.0 (2.2)sh	28.20(−0.16)
	37.0 (3.9)sh	
	48.50(4.73)	45.90(+48)
fac-Δ-[Co(*R*-pen)$_3$]$^{3+}$	21.20(2.06)	20.16(−2.79)
		22.90(+0.52)
	29.0 (2.1)sh	28.25(−0.19)
	37.0 (4.0)sh	
	48.50(4.75)	45.20(+39)
mer-Λ-[Co(*R*-pen)$_3$]$^{3+}$	21.20(2.07)	21.05(+4.50)
	29.0 (2.1)sh	28.99(−0.03)
	37.0 (4.0)sh	37.00(+1.25)
	48.50(4.72)	46.50(−23)
fac-Λ-[Co(*R*-pen)$_3$]$^{3+}$	21.20(2.08)	21.05(+4.46)
	29.0 (2.3)sh	29.07(−0.07)
		31.25(+0.14)
	37.0 (3.9)sh	35.60(−0.27)
		37.00(+0.10)
	48.50(4.69)	46.10(−18)
mer-Λ-[Co(*S*-dmbn)$_3$]$^{3+}$	21.16(2.02)	20.08(+2.42)
		22.62(−0.55)
	29.28(1.99)	28.82(+0.26)
	46.50(4.33)	44.20(−37.9)
fac-Λ-[Co(*S*-dmbn)$_3$]$^{3+}$	21.16(2.02)	19.96(+1.57)
		22.37(−0.82)
	29.28(1.99)	28.57(+0.25)
	46.50(4.34)	43.90(−29.5)
Λ-[Co(*SS*-2,3-bn)$_3$]$^{3+}$	21.51(2.00)	20.41(+2.73)
		23.09(−0.56)
	29.63(1.97)	28.99(+0.32)
	47.60(4.45)	46.70(−41)
Δ-[Co(*SS*-2,3-bn)$_3$]$^{3+}$	21.51(1.99)	21.28(−3.47)
	29.63(1.96)	27.00(−0.068)
		29.24(+0.94)
		32.05(−0.29)
	46.90(4.49)	41.00(−0.94)
		47.10(+25.5)
fac-Δ-[Co(*R*-pn)$_3$]$^{3+}$ [19]	21.39(2.00)	20.28(−2.44)
		22.83(+0.75)
	29.50(1.96)	28.99(−0.32)
	47.30(4.40)	47.00(+48)
mer-Λ-[Co(*R*-pn)$_3$]$^{3+}$ [18]	21.39(1.95)	21.05(+2.48)
	29.40(1.90)	27.30(+0.078)
		29.30(−0.031)
		31.70(+0.036)
	47.00(4.43)	41.50(+1.35)
		47.20(−20.1)
[Co(NH$_3$)$_4$(*R*-pen)]$^{3+}$	21.19(1.89)	19.05(−0.037)
		21.60(+0.465)
	29.8 (1.9)sh	28.20(−0.007)
	39.0 (3.6)sh	
	49.00(4.59)	46.10(+5.9)
[Co(NH$_3$)$_4$(*S*-dmbn)]$^{3+}$	21.19(1.84)	19.53(+0.037)
		21.65(−0.386)
	29.46(1.77)	29.40(+0.014)
	50.00(4.39)	46.90(−5.54)
[Co(NH$_3$)$_4$(*SS*-2,3-bn)]$^{3+}$	21.28(1.84)	19.42(+0.075)
		21.74(−0.345)
	29.46(1.77)	29.41(+0.012)
	49.60(4.43)	47.80(−4.92)
[Co(NH$_3$)$_4$(*R*-pn)]$^{3+}$ [19]	21.19(1.85)	19.31(−0.066)
		21.69(+0.326)
	29.50(1.78)	29.15(−0.02)
	50.30(4.44)	47.00(+5.4)

sh: Shoulder.

isomers in equilibrium at 373 K for [Co(*R*-pn)$_3$]$^{3+}$ (*R*-pn=(*R*)-1,2-propanediamine),[14] [Co(*SS*-2,3-bn)$_3$]$^{3+}$, and [Co(*RR*-chxn)$_3$]$^{3+}$ (*RR*-chxn=(*R*,*R*)-*trans*-1,2-cyclohexanediamine)[15] are 8.8:1, 10:1, and 14:1, respectively. In the present study, [Co(*S*-dmbn)$_3$]$^{3+}$ yielded only the *lel*$_3$ form by either preparative method and by heating the complex in water with active charcoal (Experimental). The relative stability of the *ob*$_3$ to the *lel*$_3$ isomers seems to decrease as the substituent becomes larger and the number of the substituent increases.

On the other hand, the formation ratio of the *lel*$_3$ to the *ob*$_3$ isomers of [Co(*R*-pen)$_3$]$^{3+}$ was 5:1. Although the equilibration study was unsuccessful because of decomposition of the complex, this value can be regarded as that at equilibrium, since the reaction was carried out by prolonged heating in the presence of active charcoal (Experimental). The value of 5:1 indicates that the *ob*$_3$ isomer of [Co(*R*-pen)$_3$]$^{3+}$ is fairly stable as compared with those of the other complexes given above, despite the ligand has a bulky phenyl substituent. Bosnich and Harrowfield[16] reported that for the [Co{(−)-dpen}$_3$]$^{3+}$ complex ((−)-dpen=(−)-1,2-diphenyl-1,2-ethanediamine), in which each chelate ring has two phenyl substituents, the (−)-isomer predominates to the extent of at least 90% over the (+)-isomer at equilibrium. Later Kuroda and Mason[17] determined the absolute configuration of (+)-[Co{(−)-dpen}$_3$]$^{3+}$ by X-ray analysis to be Λ(*lel*$_3$)-[Co(*SS*-dpen)$_3$]$^{3+}$. These reports show that in [Co(*SS*-dpen)$_3$]$^{3+}$ the *ob*$_3$ isomer is much more stable than the *lel*$_3$ one. Thus it is concluded that tris-type complexes of 1,2-diamines with phenyl substituents tend to stabilize the *ob*$_3$ isomer, contrary to those of 1,2-diamines with alkyl substituents.

It is known that the *mer* and *fac* isomers of [Co(*R*-pn)$_3$]$^{3+}$ with the same absolute configuration give essentially the same CD spectra.[18] The corresponding isomers of [Co(*R*-pen)$_3$]$^{3+}$ show a small difference in the CD spectra, but there is a fairly large difference between *mer*- and *fac*-Λ-[Co(*S*-dmbn)$_3$]$^{3+}$. In the first absorption band region, the CD patterns of Δ(*lel*$_3$) and Λ(*ob*$_3$) isomers of [Co(*R*-pen)$_3$]$^{3+}$ (*mer* and *fac*)

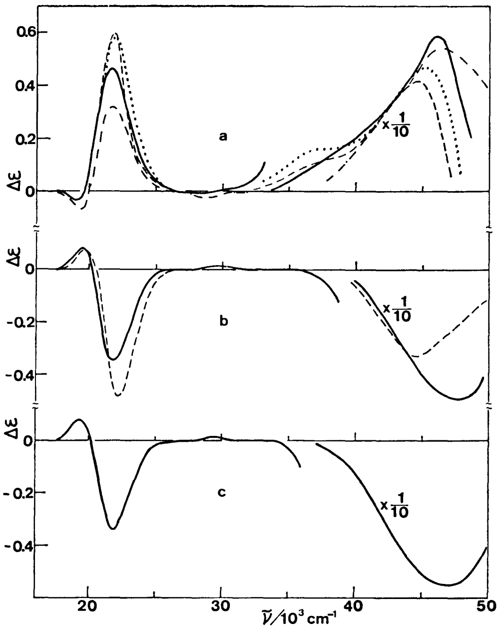

Fig. 3. a: Observed CD spectra of [Co(NH_3)$_4$(*R*-(pen)]$^{3+}$ (——) and [Co(NH_3)$_4$(*R*-pn)]$^{3+}$ (—·—·—), and calculated CD curves, 1/6{$\Delta\varepsilon$(*fac*-Λ-[Co(*R*-pen)$_3$]$^{3+}$)+$\Delta\varepsilon$(*fac*-Δ-[Co(*R*-pen)$_3$]$^{3+}$)} (----) and 1/6{$\Delta\varepsilon$(*mer*-Λ-[Co(*R*-pen)$_3$]$^{3+}$) + $\Delta\varepsilon$(*mer*-Δ-[Co(*R*-pen)$_3$]$^{3+}$)} (....). b: Observed CD spectrum of [Co(NH_3)$_4$(*SS*-2,3-bn)]$^{3+}$ (——) and calculated CD curve, 1/6{$\Delta\varepsilon$(Λ-[Co(*SS*-2,3-bn)$_3$]$^{3+}$)+$\Delta\varepsilon$(Δ-[Co-(*SS*-2,3-bn)$_3$]$^{3+}$)} (----). c: CD spectrum of [Co-(NH_3)$_4$(*S*-dmbn)]$^{3+}$.

quite resemble those of Δ- and Λ-[Co(*R*-pn)$_3$]$^{3+}$ (*mer* and *fac*), respectively, although the CD strengths of Λ(*ob*$_3$) isomers of the *R*-pen complex are much larger than those of the corresponding isomers of the *R*-pn complex (Table 1). The CD strength of *mer*-Λ(*ob*$_3$)-[Co(*R*-pen)$_3$]$^{3+}$ reported by Bernth and Larsen1) is about 2.5 times as small as ours. For tris(1,2-diamine)–cobalt(III) complexes reported so far, the *ob*$_3$ isomer gives always stronger CD than does the *lel*$_3$ one in the first absorption band region.

The vicinal CD curve of *R*-pen derived from the CD spectra of *fac*-Δ and *fac*-Λ (or *mer*-Δ and *mer*-Λ) isomers of [Co(*R*-pen)$_3$]$^{3+}$ is similar to the observed CD spectrum of [Co(NH_3)$_4$(*R*-pen)]$^{3+}$ over the whole region (Fig. 3). The CD patterns of [Co(NH_3)$_4$-(*R*-pen)]$^{3+}$ and [Co(NH_3)$_4$(*R*-pn)]$^{3+}$ are very similar in the first absorption band region, although the CD strength of the former is fairly larger than that of the latter. The vicinal CD curve of *SS*-2,3-bn derived from Δ- and Λ-[Co(*SS*-2,3-bn)$_3$]$^{3+}$ resembles the observed CD spectrum of [Co(NH_3)$_4$(*SS*-2,3-bn)]$^{3+}$. The CD patterns of [Co(NH_3)$_4$(*SS*-2,3-bn)]$^{3+}$ and [Co(NH_3)$_4$(*S*-dmbn)]$^{3+}$ are almost mirror images of those of the corresponding *R*-pen and *R*-pn complexes. These results indicate that the *R*-pen and *S*-dmbn chelate rings are stabilized in the λ and δ gauche conformations, respectively, and that the vicinal effects of chiral 1,2-diamines in the [CoN_6]-type complexes are little dependent on the kind and the number of substituents on skeletal carbon atoms.

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References

1) N. Bernth and E. Larsen, *Acta Chem. Scand., Ser. A*, **32**, 545 (1978).

2) S. Yano, M. Saburi, S. Yoshikawa, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **49**, 101 (1976).

3) H. Reihlen, E. Weinbrenner, and G. V. Hessling, *Ann.*, **494**, 143 (1932).

4) C. J. Hawkins and R. M. Peachey, *Aust. J. Chem.*, **29**, 33 (1976).

5) W. E. Cooley, C. F. Liu, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 4189 (1959).

6) E. J. Billo and J. R. Vitiello, *Inorg. Chim. Acta*, **26**, L10 (1978).

7) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

8) A. Werner and R. Feenstra, *Ber.*, **39**, 1538 (1906).

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

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

11) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **45**, 2129 (1972).

12) A. Werner and H. Gruger, *Z. Anorg. Allg. Chem.*, **16**, 398 (1898).

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

14) S. E. Harnung, S. Kallesoe, A. M. Sargeson, and C. E. Schaffer, *Acta Chem. Scand., Ser. A*, **28**, 385 (1974).

15) S. E. Harnung, B. S. Sørensen, I. Creaser, H. Maegaard, U. Pfenninger, and C. E. Schaffer, *Inorg. Chem.*, **15**, 2123 (1976).

16) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3426 (1972).

17) R. Kuroda and S. F. Mason, *J. Chem. Soc., Dalton Trans.*, **1977**, 1016.

18) T. E. MacDermott, *Inorg. Chim. Acta*, **2**, 81 (1968); M. Kojima, Y. Yoshikawa, and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **9**, 689 (1973).

19) M. Kojima and J. Fujita, Unpublished data.