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Circular Dichroism Spectra and Racemization of Two Geometrical Isomers of the (2-Aminoethanesulfenato-*S*,*N*)[tris(2-aminoethyl)amine]cobalt(III) Ion

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Optically active *trans*(*t*-*N*,*S*)(*t*) and *cis*(*t*-*N*,*S*)(*p*) isomers of $[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ (tren=tris(2-aminoethyl)amine; *t*-*N*=tertiary amine nitrogen) were prepared, and their circular dichroism spectra were compared with those of Δ(*S* or *R*)- and Λ(*S* or *R*)-$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$ and two geometrical isomers of $[Co(R\text{-pn})(tren)]^{3+}$ (*R*-pn=(*R*)-1,2-propanediamine) and $[Co(S\text{-dmbn})(tren)]^{3+}$ (*S*-dmbn=(*S*)-3,3-dimethyl-1,2-butanediamine). Racemization or epimerization of these sulfenato complexes was studied in aqueous solutions with ionic strength of 1.0 ($NaClO_4$) in the pH and temperature ranges of 3.65—8.8 and 24.0—40.0 °C, respectively. The rates of *p*- and *t*-isomers of the tren complex are proportional to concentrations of the complex, but independent of pH, the latter isomer accompanying some decomposition during the course of racemization. The first-order rate constants of the *p*- and *t*-isomers are 9.92×10^{-5} and *ca.* 1.2×10^{-6} s^{-1} at 30.0 °C, respectively. No epimerization takes place in the en complexes under the same experimental conditions. The difference in rate of racemization or epimerization of these sulfenato complexes seems to be related closely to the crowding around the S=O group of the complex.

A sulfenate ion becomes chiral upon coordination to a metal ion through the sulfur atom, and a metal–sulfenato complex has a formal analogy with sulfoxides. Sulfoxides are in general optically stable, and typical barriers for the inversion lie in the range of 150 to 180 kJ mol^{-1}.[1)] The configurational stability of sulfur atoms in cobalt(III)–sulfenato complexes is also sufficient to support optical activity, and several stable diastereomers involving such chiral sulfur atoms have been obtained.[2–6)] However, neither optically active complexes in which a chiral sulfur atom is the sole source of optical activity nor studies on racemization of sulfenato complexes seem to have been reported.

In order to elucidate the optical activity and optical stability of a metal–sulfenato complex, it is desirable to prepare an optically active sulfenato complex whose activity arises only from a chiral sulfur atom. This paper reports resolution, absorption and circular dichroism (CD) spectra, and racemization of two geometrical (*p*- and *t*-)[7)] isomers of $[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ (Fig. 1; tren=tris(2-aminoethyl)amine) and related complexes, a pair of diastereomers of $[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$. Two geometrical isomers of $[Co(R\text{-pn})(tren)]^{3+}$ (*R*-pn=(*R*)-1,2-propanediamine) and $[Co(S\text{-dmbn})(tren)]^{3+}$ (*S*-dmbn =(*S*)-3,3-dimethyl-1,2-butanediamine) were also prepared in order to compare their CD spectra with those of *p*- and *t*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$.

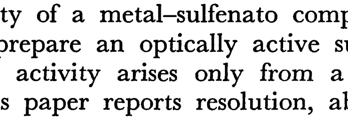
p-isomer t-isomer

Fig. 1. Two geometrical isomers of $[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$.

Experimental

The sulfenato complexes in solution were handled in the dark to minimize decomposition.

p- *and* t-*[Co(SCH₂CH₂NH₂)(tren)]ZnCl₄.* These thiolato complexes were prepared by the method of Jackson and Sargeson,[8)] and isolated as tetrachlorozincate salts by the same method as that for the corresponding (*R*)-cysteine complex.[8)] Found for the *p*-isomer: C, 19.63; H, 4.93; N, 14.34%. Found for the *t*-isomer: C, 19.68; H, 5.08; N, 14.40%. Calcd for $C_8H_{24}N_5Cl_4CoSZn$: C, 19.67; H, 4.95; N, 14.34%.

p-*[Co{S(O)CH₂CH₂NH₂}(tren)](ClO₄)₂·2H₂O and* t-*[Co{S(O)CH₂CH₂NH₂}(tren)](ClO₄)₂.* These sulfenato complexes were prepared by stoichiometric oxidation of the corresponding thiolato complexes. To a suspension of *p*-$[Co(SCH_2CH_2NH_2)(tren)]ZnCl_4$ (1.95 g, 4 mmol) in a mixture of water (5 cm^3) and 70% $HClO_4$ (1 cm^3) was added an equimolar amount of 35% H_2O_2 (0.39 g, 4 mmol) in 3 cm^3 of water dropwise with stirring. The color of the solution changed immediately from brown to red-orange, and the starting material dissolved completely by reaction with the peroxide. The addition of $NaClO_4$ and cooling led to crystallization of the desired product. It was filtered and recrystallized from water by adding dropwise ethanol saturated with $LiClO_4$. Yield: 1.1 g (52%). Found: C, 18.11; H. 4.94; N, 13.20%. Calcd for $C_8H_{28}N_5Cl_2CoO_{11}S$: C, 18.05; H, 5.30; N, 13.16%.

The *t*-isomer was prepared by a similar procedure, but the complex perchlorate was not precipitated by the addition of $NaClO_4$. The red-orange mixture was diluted with water and passed through a column of SP-Sephadex C-25. After washing the column with water, the product adsorbed was eluted with 1 mol/dm^3 $NaClO_4$, and the effluent was evaporated to a small volume under reduced pressure. The addition of a small amount of ethanol led to crystallization of the desired product. It was filtered and recrystallized by the same method as that for the *p*-isomer. Yield: 30%. Found: C, 19.42; H, 4.94; N, 14.33%. Calcd for $C_8H_{24}N_5Cl_2CoO_9S$: C, 19.36; H, 4.87; N, 14.11%.

Resolution of the p-*[Co{S(O)CH₂CH₂NH₂}(tren)]²⁺ Isomer.* To an aqueous solution (15 cm^3) of *p*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)](ClO_4)_2\cdot2H_2O$ (1.16 g, 2 mmol) was added an aqueous solution (10 cm^3) of potassium *d*-tartrate hemihydrate (0.47 g, 2 mmol). The solution was stirred for 30 min and filtered to remove potassium perchlorate precipitated. The filtrate was evaporated to about 5 cm^3 under reduced pressure and filtered again. The filtrate was mixed with 20 cm^3 of methanol and cooled in a refrigerator. After 3 h the orange, crude product was filtered, washed with methanol, and recrystallized twice from water (2 cm^3) by adding 3 cm^3 of methanol. Yield: 0.35 g. No change in the $\Delta\varepsilon$ value was observed with further recrystallization. Found: C, 29.87; H, 6.86; N, 14.66%. Calcd for $C_{12}H_{32}N_5CoO_9S$=[Co{S(O)$CH_2CH_2NH_2$}(tren)]($C_4H_4O_6$)·$2H_2O$: C, 29.94; H, 6.70; N, 14.55%.

This diastereomer was converted into perchlorate by use of a DEAE-Sephadex (ClO_4^- form) column. The perchlorate was not isolated and the effluent was used for measurements without delay, because the complex racemizes at a moderate rate (*vide post*). The concentration of the solution was determined by reference to the optical density of the racemate.

Resolution of the t-*[Co{S(O)CH$_2$CH$_2$NH$_2$}(tren)]$^{2+}$ Isomer.* An aqueous solution of *t*-[Co{S(O)$CH_2CH_2NH_2$}(tren)](ClO_4)$_2$ (*ca.* 15 mg) was poured onto a column (ϕ 2.7×50 cm) of SP-Sephadex C-25 and the adsorbed band was eluted with 0.1 mol/dm^3 Na_2[Sb_2(*d*-tartrate)$_2$]. The band was separated into two, the $(+)_{589}$-isomer being eluted faster. Each effluent was diluted with water, passed through an SP-Sephadex column (ϕ 1.5×3 cm), and the complex adsorbed was eluted with 1.0 mol/dm^3 $NaClO_4$. The optically active complex was not isolated because the amount was very small. The $\Delta\varepsilon$ value was determined with the aid of the ε value of the racemate.

Preparation and Resolution of [Co{S(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$. The complex was prepared by the method of Adzamli *et al.*[4] The reaction mixture was chromatographed by use of an SP-Sephadex C-25 column. By elution with 0.15 mol/dm^3 Na_2SO_4, the orange band was separated into two, I and II in the order of elution. Bands I and II contain racemates of a pair of diastereomers, $\Delta(S)$ and $\Lambda(R)$, and $\Delta(R)$ and $\Lambda(S)$, respectively. The racemates were isolated as perchlorate by a method similar to that for *t*-[Co{S(O)$CH_2CH_2NH_2$}(tren)](ClO_4)$_2$. The total yield was about 80%, and the formation ratio, I:II, was *ca.* 2:1. Isomer II is less stable toward decomposition in water. Found for I: C, 15.48; H, 4.84; N, 14.80%. Found for II: C, 15.30; H, 4.71; N, 14.90%. Calcd for $C_6H_{22}N_5Cl_2CoO_9S$: C, 15.33; H, 4.72; N, 14.89%. The racemates were resolved by the same chromatographic method as that for *t*-[Co{S(O)$CH_2CH_2NH_2$}(tren)]$^{2+}$. The faster eluted enantiomers of I and II are $\Lambda(R)$ (I-1) and $\Lambda(S)$ (II-1), respectively. The isomers obtained from the slower eluted bands are thus $\Delta(S)$ (I-2) and $\Delta(R)$ (II-2). The absolute configurations of the isomers were assigned by comparing the CD spectra with that of $\Delta(S)$-[Co(*R*-cysO)(en)$_2$]$^+$ (*R*-cysO=(*R*)-2-amino-3-sulfenatopropanoate-*N,S*),[3] the absolute configuration of which has been determined by the X-ray method.[2] The $\Delta(S)$-isomer (I-2) was isolated as perchlorate by the same method as that for the racemate. Found: C, 15.27; H, 4.59; N, 15.07%. Calcd for $C_6H_{22}N_5Cl_2CoO_9S$: C, 15.33; H, 4.72; N, 14.89%. The enantiomers of isomer II were not isolated because of their instability. Each effluent of the resolved isomer II was loaded on SP-Sephadex C-25, eluted with 1 mol/dm^3 $NaClO_4$, and the effluent was used for measurements.

[Co(R-pn)(tren)](ClO$_4$)$_3$·1.5H$_2$O (P-I) and [Co(R-pn)(tren]Br$_3$ (P-II). A mixture of (*R*)-1,2-propanediamine dihydrochloride (*R*-pn·2HCl) (0.74 g, 5 mmol) and sodium methoxide (0.54 g, 10 mmol) in methanol (5 cm^3) was stirred for *ca.* 0.5 h. Sodium chloride which deposited was filtered off and washed with a small amount of methanol. The combined filtrate and washings were added to a dimethyl sulfoxide solution (15 cm^3) of [$CoCl_2$(tren)]Cl[9] (1.56 g, 5 mmol), and the mixture was stirred for a day at room temperature. The resulting orange-brown solution was diluted with water and poured onto a column (ϕ2.7×3 cm) of SP-Sephadex C-25. A small portion of the Sephadex charged with the product was placed on the top of a column (ϕ2.7×120 cm) of SP-Sephadex C-25, and the product was eluted with 0.2 mol/dm^3 Na_2SO_4. The column showed several bands. The effluents of the third (P-I) and fourth (P-II) bands were collected separately. Each effluent was diluted ten times with water and passed again through an SP-Sephadex C-25 column (ϕ1.5×3 cm). Isomer P-II was eluted with 1 mol/dm^3 NaBr, and the effluent was evaporated under reduced pressure to give orange crystals, which were recrystallized from water. Found: C, 20.64; H, 5.68; N, 16.24%. Calcd for $C_9H_{28}N_6Br_3Co$: C, 20.83; H, 5.44; N, 16.19%.

Isomer P-I was isolated as perchlorate, because the bromide was highly soluble. The column charged with isomer P-I was washed with a large amount of 10^{-2} mol/dm^3 HBr, and then the isomer was eluted with 1 mol/dm^3 HBr. The effluent was concentrated to a small volume under reduced pressure. On addition of concd $HClO_4$ the concentrate gave large crystals of the perchlorate, which were filtered and washed with ethanol. Found: C, 17.80; H, 5.08; N, 14.11%. Calcd for $C_9H_{31}N_6Cl_3CoO_{13.5}$: C, 17.88; H, 5.17; N, 13.90%. The formation ratio, P-I:P-II, was *ca.* 1:2, and the total yield was *ca.* 40%.

*[Co(*S*-dmbn)(tren)]Br$_3$·2.5H$_2$O(B-I) and [Co(*S*-dmbn)(tren)]Br$_3$·H$_2$O (B-II).* These complexes were prepared by the same method as that for the above *R*-pn complexes, except that (*S*)-3,3-dimethyl-1,2-butanediamine dihydrochloride[10] was used instead of *R*-pn·2HCl. The separation of bands for isomers B-I and B-II was insufficient in chromatography by use of 0.2 mol/dm^3 Na_2SO_4, B-I being eluted faster. The orange effluent containing both isomers B-I and B-II was chromatographed again with 0.15 mol/dm^3 Na_2[Sb_2(*d*-tartrate)$_2$]. Isomers B-II and B-I were eluted separately in this order, and isolated as bromide by the same method as that for isomer P-II of the *R*-pn complex. The formation ratio, B-I:B-II, was *ca.* 1:1, and the total yield was *ca.* 60%. Found for B-I: C, 23.83; H, 6.42; N, 13.95%. Calcd for $C_{12}H_{39}N_6Br_3CoO_{2.5}$: C, 23.77; H, 6.48; N, 13.86%. Found for B-II: C, 24.88; H, 6.41; N, 14.54%. Calcd for $C_{12}H_{36}N_6Br_3CoO$: C, 24.89; H, 6.27; N, 14.51%.

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. Optical rotations at 589 nm were measured with a JASCO DIP-4 polarimeter.

Kinetics. All kinetic experiments were carried out in the dark in the pH region of 3.65 (acetate buffer) to 8.8 (phosphate buffer) maintained at constant ionic strength of 1.0 with $NaClO_4$. The complex concentrations were in the range of 1.0×10^{-4} to 2.7×10^{-3} mol/dm^3. The temperatures of the solutions were kept constant in a constant temperature water bath. The racemization or epimerization of the complexes was followed by monitoring CD change as a function of reaction time. Portions of the reacting solution were withdrawn at timed intervals and then their CD spectra were recorded in the range of 400 to 260 nm. CD strengths at two maxima, *ca.* 380 and 280 nm, were used for calculation. Optical densities of bands at *ca.* 370 nm, which are characteristic of the S-bonded sulfenato moiety, were also measured to check the stability of the complexes toward decomposition.

Results and Discussion

Absorption and CD Spectra. Two geometrical isomers of [Co{S(O)$CH_2CH_2NH_2$}(tren)]$^{2+}$ can be prepared easily from the corresponding isomers of [Co-

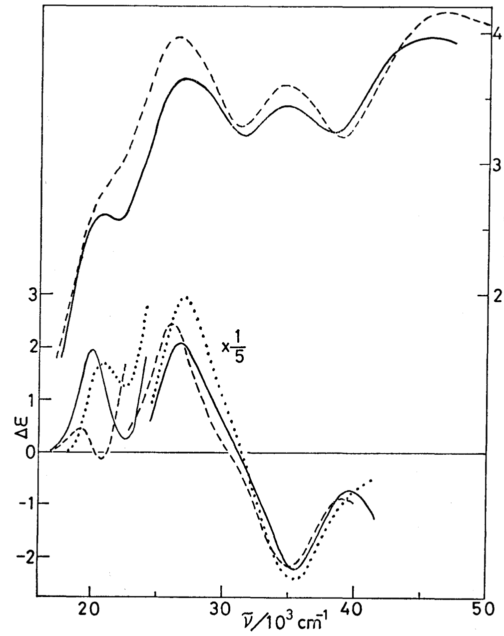

Fig. 2. Absorption and CD spectra of $(+)_{589}$-*p* (——) and$(+)_{589}$-*t* (----) isomers of $[Co\{S(O)CH_2CH_2NH_2\}$-$(tren)]^{2+}$, and calculated CD curve, $1/2\{\Delta\varepsilon(\Delta(S)$-$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+})+\Delta\varepsilon(\Lambda(S)$-$[Co\{S(O)$-$CH_2CH_2NH_2\}(en)_2]^{2+})\}$ (……).

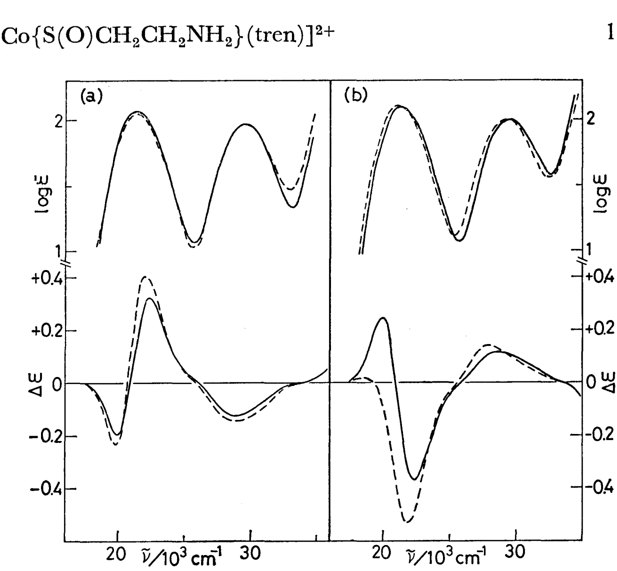

Fig. 3. Absorption and CD spectra of (a) P-I (——) and P-II (----) isomers of $[Co(R\text{-pn})(tren)]^{3+}$ and (b) B-I (——) and B-II (----) isomers of $[Co(S\text{-dmbn})(tren)]^{3+}$.

$(SCH_2CH_2NH_2)(tren)]^{2+}$ [8] by stoichiometric oxidation with hydrogen peroxide. The sulfenato complexes thus obtained should have the same geometrical configuration as those of the respective parent thiolato complexes. The *p*- and *t*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ isomers show absorption spectra fairly different from each other as seen in Fig. 2 and Table 1. The *p*-isomer gives a more distinct first d-d band (20830 cm^{-1}) and much weaker Co–S charge transfer bands (27030 and 34600 cm^{-1})[4] than the corresponding bands of the *t*-isomer. The first d-d band of the former appears at the higher energy side than that of the latter. In analogous tren complexes of glycinate[11] and (*S*)-alaninate[12] ions, the *p*-isomer also shows the first d-d band at high energy as compared with that of the *t*-isomer. Such a spectral difference in the d-d band region between the *p*- and *t*-isomers may be attributed to the difference in ligand field strength between the tertiary amine and other primary amine nitrogens. Mitsui *et al.*[11] suggested that in [Co(glycinate)(tren)]$^{2+}$ the tertiary amine nitrogen exerts a weaker ligand field than the primary amine nitrogen.

Figure 2 shows CD spectra of $(+)_{589}$-*p*- and $(+)_{589}$-*t*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$. In the Co–S charge transfer band region (23000—39000 cm^{-1}), both enantiomers give CD patterns very similar to that of $\Delta(S)$-$[Co(R\text{-cysO})(en)_2]^{+}$.[3] Another $\Lambda(R)$-diastereomer of the *R*-cysO complex shows an almost enantiomeric CD pattern in this region. Thus the sulfur atoms in both $(+)_{589}$-enantiomers can be assigned to the *S* configuration. The optical activity of both *p*- and *t*-isomers originates from only the chiral sulfur atom of the sulfenate ligand. Thus these CD spectra represent the vicinal effect of a coordinated chiral sulfur atom in a $[CoSN_5]$-type complex. In Fig. 2 are compared the spectra with the calculated vicinal CD curve for the (*S*)-sulfur atom derived from CD spectra of $\Delta(S)$- and $\Lambda(S)$-$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$. The curve and two spectra are very similar in the Co–S charge transfer region. In the first d-d band region, the CD spectrum of the *p*-isomer resembles the calculated curve, but that of the *t*-isomer is fairly different from it, although all of the main CD bands show the positive sign.

Akamatsu *et al.*[12] reported that each pair of the *p*- and *t*-isomers of $[Co\{(S)\text{-alaninate}\}(tren)]^{2+}$ and a similar type complex $[Co\{(S)\text{-alaninate}\}(nitrilotriacetate)]^{-}$ give CD spectra almost enantiomeric to each other in the d-d band region. They attributed this remarkable feature to the mutually quasi-enantiomeric configuration in the isomers, and called such optical activity the "quasi-enantiomeric" effect. The *p*- and *t*-isomers of these alaninato complexes seem to be quasi-enantiomeric to each other. However, they are mutually geometrical isomers having the tertiary amine nitrogen and oxygen donor atoms in the cis and trans positions, and exhibit absorption spectra fairly different from each other. Consequently, the isomers would inevitably give CD spectra different from each other. The complexes given by Akamatsu *et al.*[12] would not be suitable for estimating how the quasi-enantiomeric effect contributes to CD spectra.

In order to estimate this effect, we have prepared two isomers of $[Co(R\text{-pn})(tren)]^{3+}$ and $[Co(S\text{-dmbn})$-$(tren)]^{3+}$ and measured their CD spectra. Each of *R*-pn and *S*-dmbn has two different nitrogen donor atoms, but the difference in ligand field strength between these two nitrogen atoms should be negligibly small as compared with that between the oxygen and nitrogen donor atoms of the (*S*)-alaninate ligand. Molecular models indicate that there is no remarkable difference in strain or non-bonded interaction between the isomers of both *R*-pn and *S*-dmbn complexes. Figure 3 shows absorption and CD spectra of the two isomers of these complexes. The differences in ab-

Table 1. Absorption and CD spectral data

Complex	Absorption $\tilde{\nu}_{max}$/cm^{-1} (log ε)	CD $\tilde{\nu}_{ext}$/cm^{-1}($\Delta\varepsilon$)
$(+)_{589}$-*p*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$	20830(2.60)	19960(+1.99)
	27030(3.63)	26670(+10.6)
	34600(3.46)	35210(−11.3)
	45660(3.97)	
$(+)_{589}$-*t*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$	20000(2.63)[a]	19160(+0.437)
		20830(−0.146)
	26320(3.94)	26180(+12.0)
	34600(3.56)	34970(−10.6)
	46510(4.15)	
$\Delta(S)$-$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$	21100(2.67)	19120(−1.39)
		21690(+2.88)
	27400(3.83)	27320(+17.3)
	35030(3.57)	35590(−12.2)
	49500(4.21)	
$\Lambda(S)$-$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$	21190(2.85)	19800(+2.76)
	27030(3.81)	26670(+12.2)
	35150(3.60)	35460(+12.0)
	50000(4.23)	
(P-I)-$[Co(R\text{-}pn)(tren)]^{3+}$	21320(2.07)	19880(−0.203)
		22270(+0.329)
	29540(1.97)	28740(−0.119)
	45250(4.29)	44640(+3.27)
(P-II)-$[Co(R\text{-}pn)(tren)]^{3+}$	21280(2.04)	19690(−0.227)
		22120(+0.408)
	29540(1.98)	28570(−0.139)
	45450(4.34)	45660(+3.66)
(B-I)-$[Co(S\text{-}dmbn)(tren)]^{3+}$	21320(2.10)	19840(+0.248)
		22320(−0.375)
	29590(2.02)	28490(+0.118)
	45450(4.30)	43860(−4.01)
(B-II)-$[Co(S\text{-}dmbn)(tren)]^{3+}$	21190(2.11)	18660(+0.015)
		21740(−0.536)
	29330(1.99)	27930(+0.137)
	44540(4.32)	43670(−5.64)

a) Shoulder.

sorption and CD spectra between the isomers are very small in the *R*-pn complex, while appreciably large in the *S*-dmbn complex. However, the isomers of this *S*-dmbn complex show still the same CD pattern. These observations suggest that the quasi-enantiomeric effect contributes very little to optical activity of metal complexes. The enantiomeric CD spectra reported by Akamatsu *et al.*12) seem to result from a difference in the order of energies of the d-d transition components between the *p*- and *t*-geometrical isomers. No assignment was made for the geometrical isomers of the *R*-pn and *S*-dmbn complexes.

Racemization at Sulfur Atoms. CD changes of *p*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ were recorded over the temperature range of 24.0 to 40.0 °C at I=1.0 ($NaClO_4$) in the pH region of 3.65 to 8.8. A representative spectral change is given in Fig. 4. In every kinetic run the plot of log(ΔOD_{376}) and log(ΔOD_{285}) against time gave a straight line for at least two half-lives, from which the first-order rate constant k_r/s^{-1} was obtained. No detectable change in the absorption spectrum was observed during the measurements. However, over a longer time period the complex underwent decomposition; the absorbance at 380 nm diminished by 2.3% at 30 °C in 1.0 mol/dm^3 $NaClO_4$ in a day, *i.e.*, 12 half-lives. Eyring treatments of log(k_r/T) *vs.* T^{-1} yielded an activation enthalpy of 130±3 kJ mol^{-1} and an activation entropy of 109±9 J mol^{-1} K^{-1}. The first-order rate constant is 9.92×10^{-5} s^{-1} at 30.0 °C. The rate was independent of pH. Thus it can be assumed that the racemization takes place intramolecularly. The activation enthalpy of 130 kJ mol^{-1} is smaller by 20—50 kJ mol^{-1} than those reported for sulfoxides.1) A fairly large difference in activation enthalpy was also observed for the racemization between metal–sulfide complexes (40—60 kJ mol^{-1})13–19) and sulfonium ions (100—120 kJ mol^{-1}).1)

The racemization of the *t*-isomer was studied by

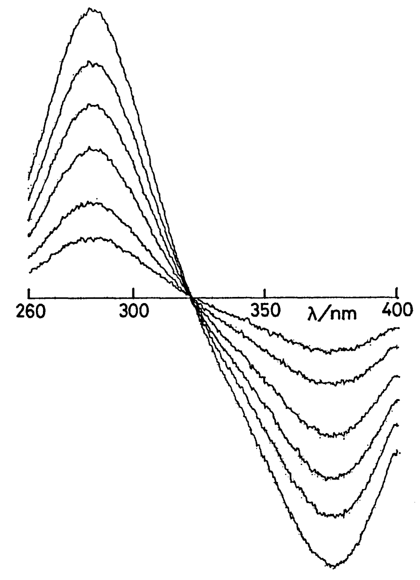

Fig. 4. CD spectral change of *p*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ in 1.0 mol/dm^3 $NaClO_4$ at 30.0 °C in a period of 264 min.

the same procedure. However, the rate was not determined accurately, because the complex decomposed during the course of racemization. In 1.0 mol/dm^3 $NaClO_4$ at 30.0 °C, the CD strength (382, 286 nm) and absorbance (380 nm) of the complex decreased by 18 and 9.7%, respectively, in a day. When we took the absorbance at 380 nm as a quantitative measure for the concentration of the *t*-isomer, the rate constant of the racemization is approximately 1.2×10^{-6} s^{-1} at 30.0 °C. This value is smaller than that of the *p*-isomer by a factor of *ca.* 80. Thus it is concluded that the *p*-isomer racemizes much faster than the *t*-isomer does, while the former is more stable than the latter toward decomposition. For the analogous $[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ complex, the *t*- and *p*-isomers seem also to have similar relative stability toward racemization; the former was resolved by column chromatography, while the latter was not.[20]

Turley and Haake[21] studied the inversion at sulfur in several platinum(II)–sulfide complexes, and proposed a mechanism involving simultaneous bond making between the metal ion and the other lone-pair on sulfur as the original coordinate bond breaks. This mechanism seems to be a current view on inversion of the sulfur in metal–sulfide complexes. However, Jackson and Sargeson[22] pointed out that the mechanism is the same in principle as the pyramidal inversion mechanism for free sulfoxides and sulfonium ions, which proceeds *via* a trigonal planar intermediate. If we assume that the racemization of $[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ proceeds by the pyramidal inversion at the sulfur atom, the difference in rate of racemization of the *p*- and *t*-isomers seems to stem from a difference in structure around the S=O group between them. According to X-ray analyses on the two $[Co(glycinate)(tren)]^{2+}$ isomers,[11] the cis position to the tertiary amine nitrogen is hindered by atoms H(a) and H(b) as shown in Fig. 5. The trans position is free from such hindrance. Consequently, the cis ligand is much more labile in substitution reactions than the trans ligand.[23,24] The S=O group in the *p*-isomer of $[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ is situated at such a hindered position, and the oxygen atom points close at atom H(a) or H(b). The *t*-isomer seems to have no such hindrance around the S=O group. In the trigonal planar transition state, on the other hand, both *p*- and *t*-isomers seem to have similar structural situation involving no particular steric hindrance around the S=O group. Accordingly, the *p*-isomer will have a lower energy barrier for the inversion than that of the *t*-isomer, and racemizes faster than the *t*-isomer does.

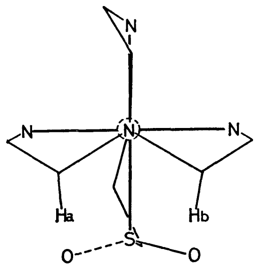

Fig. 5. A schematic structure of *p*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ viewed from the *t*-N–Co bond axis.

The epimerization at sulfur of a pair of diastereomers, *Δ*(*S*)- and *Λ*(*S*)-$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$ was examined by the same procedure and the results compared with the racemization of the tren complex. Both en and tren complexes have the same $[CoN_5S]$ type. The structures around the S=O groups of the diastereomers are similar to each other and to that of *t*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$, and there is no particular steric hindrance among the S=O group and other atoms in these isomers. For the *Δ*(*S*)-diastereomer, neither the absorption nor CD spectrum in 1.0 mol/dm^3 $NaClO_4$ showed detectable change in a day at 30.0 °C. On the other hand, the *Λ*(*S*)-diastereomer in 1.0 mol/dm^3 $NaClO_4$ decreased both absorbance (370 nm) and CD strength (375 nm) by the same quantity, 26%, at 30.0 °C in a period of 340 min, being less stable toward decomposition than the *Δ*(*S*)-diastereomer. Jackson and Sargeson[22] reported that the *Δ*-(*R*) and *Δ*(*S*) diastereomers do not convert into each other over a period of at least 12 h at 25 °C. These results shows that the sulfur atoms in these diastereomers are stable toward racemization like the one in *t*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$. The *p*-$[Co\{S(O)CH_2CH_2NH_2\}(tren)]^{2+}$ isomer whose S=O group is hindered by H(a) or H(b) atom racemizes much faster than these isomers do. Thus it is concluded that the rate of racemization of the sulfenate ligand in cobalt(III)–amine complexes is governed by a steric factor, if the racemization proceeds by the pyramidal inversion at the sulfur atom.

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