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Stereochemistry of Cobalt(III) Complexes with Thioethers. I. Circular Dichroism Spectra of Complexes with Bi- or Terdentate Thioethers

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Five (bidentate-*N,S* or -*O,S*)bis(ethylenediamine)cobalt(III) complexes have been optically resolved and their absolute configurations deduced from their circular dichroism (CD) spectra, where bidentate-*N,S* or -*O,S* are $NH_2(CH_2)_2S^-$, $NH_2(CH_2)_2SR$ ($R=CH_3$ and C_2H_5), and $CH_3S(CH_2)_nCO_2^-$ ($n=1$ and 2). The chromatographic, CD, and NMR behaviors suggest that the thioether donor atoms are coordinated stereoselectively producing the Δ-(*S*) or Λ-(*R*) complexes. Three (terdentate-*N,S,O*)[1,1,1-tris(aminomethyl)ethane]cobalt(III) complexes of $NH_2(CH_2)_2SCH_2CO_2^-$, $NH_2(CH_2)_2S(CH_2)_2CO_2^-$, and L-$CH_3SCH_2CH(NH_2)CO_2^-$ have been prepared and the complexes of the former two ligands optically resolved; the absolute configurations have been discussed on the basis of the CD spectra.

Some bis(ethylenediamine)cobalt(III) complexes with a bidentate ligand containing a sulfur donor atom, such as 2-aminoethanethiol, mercaptoacetic acid, and the related thioethers, have been prepared and the absorption spectra have been discussed.[1-5] The contribution of the coordinated sulfur atom of the thioether ligands to CD spectra would be an interesting study. However, no report seems to have appeared on the circular dichroism (CD) spectra of these complexes.

Two series of mixed cobalt(III) complexes with a bi- or a terdentate ligand containing a thioether donor atom, [Co(bidentate-*N,S* or -*O,S*)$(en)_2]^{n+}$ and [Co(terdentate-*N,S,O*)(tame)$]^{2+}$ have been prepared and resolved into optical antipodes, and their absorption and CD spectra are discussed in relation to the absolute configurations. Abbreviations used for the ligands are as follows: Haet, 2-aminoethanethiol $NH_2(CH_2)_2SH$; mea, 2-(methylthio)ethylamine $NH_2(CH_2)_2SCH_3$; eea, 2-(ethylthio)ethylamine $NH_2(CH_2)_2SC_2H_5$; Hmta, (methylthio)acetic acid $CH_3SCH_2CO_2H$; Hmtp, 3-(methylthio)propionic acid $CH_3S(CH_2)_2CO_2H$; Haeta, (2-aminoethylthio)acetic acid $NH_2(CH_2)_2SCH_2CO_2H$; Haetp, 3-(2-aminoethylthio)propionic acid $NH_2(CH_2)_2S(CH_2)_2CO_2H$; L-Hsmc, *S*-methyl-L-cysteine $CH_3SCH_2CH(NH_2)CO_2H$; en, ethylenediamine $NH_2(CH_2)_2NH_2$; tame, 1,1,1-tris(aminomethyl)ethane $CH_3C(CH_2NH_2)_3$; *d*-H_4tart, *d*-tartaric acid $C_4O_6H_6$.

Experimental

Preparation of Ligands. *1,1,1-Tris(aminomethyl)ethane*: This ligand was prepared by the method of Fleischer *et al.*[6] Found: C, 26.61; H, 8.19; N, 18.34%. Calcd for $C_5H_{15}N_3\cdot 3HCl$: C, 26.51; H, 8.01; N, 18.55%.

(2-Aminoethylthio)acetic Acid: A solution of 77.2 g of 2-aminoethanethiol in 250 cm³ of water was mixed with a solution of 94.5 g of monochloroacetic acid and 56.1 g of potassium hydroxide in 200 cm³ of water with vigorous stirring at 80—85 °C on a water bath. The mixed solution was stirred for *ca.* 1 h and cooled in an ice bath. 185 cm³ of 60% perchloric acid was then added and the resulting deposit, $KClO_4$, was filtered off. The filtrate was concentrated in a vacuum evaporator until it became oily and the deposit, $KClO_4$, was again filtered off. This filtrate was cooled in a refrigerator overnight. The white needles precipitated were recrystallized from a small amount of ethanol and dried in a vacuum desiccator over $CaCl_2$. The second crop was obtained by standing the above filtrate in a refrigerator for several weeks. The total yield: 70%. Found: C, 30.71; H, 6.28; N, 9.09; S, 20.41; Cl, 11.55%. Calcd for $C_4H_9NSO_2\cdot 0.5HCl$: C, 30.52; H, 6.08; N, 8.90; S, 20.37; Cl, 11.26%.

3-(2-Aminoethylthio)propionic Acid. This was prepared as described above, except that 3-bromopropionic acid was used instead of monochloroacetic acid. The yield: 75%. Found: C, 25.52; H, 5.39; N, 5.87; S, 13.07; Br, 33.84%. Calcd for $C_5H_{11}NSO_2\cdot HBr\cdot 0.5H_2O$: C, 25.11; H, 5.48; N, 5.86; S, 13.41; Br, 33.41%.

Preparation and Resolution of Complexes. *(2-Aminoethanethiolato)bis(ethylenediamine)cobalt(III) Complexes, [Co(aet)(en)$_2$]Cl$_2\cdot H_2O$*: The chloride salt was prepared by the method of Hori.[1]

(+)$_{589}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$: The racemic chloride monohydrate (1 g) and the resolving agent $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ (0.99 g) were dissolved in 10 cm³ of water at 60 °C. On scratching the side of the flask with a glass rod, the brown diastereomer $(+)_{589}$-[Co(aet)(en)$_2$][Sb$_2$(*d*-tart)$_2$]$\cdot 2H_2O$ appeared. The mixture was cooled in an ice bath for *ca.* 10 min and then filtered off. The precipitate was washed with ice cold water, ethanol and acetone. Found: C, 20.05; H, 3.71; N, 8.66%. Calcd for $(+)_{589}$-[Co(aet)(en)$_2$][Sb$_2$(*d*-tart)$_2$]$\cdot 2H_2O = C_{14}H_{26}N_5SO_{12}CoSb_2$: C, 20.34; H, 3.66; N, 8.47%. The diastereomer (0.8 g) was ground in a mortar; water (60 cm³) was added and then excess sodium perchlorate (5 g), and the mixture was stirred for 10 min. After filtration, the solution was evaporated to 10 cm³ and cooled in an ice bath. The needle-shaped crystals were removed by filtration and washed with 50% ethanol and acetone. The yield was 0.3 g. Found: C, 15.96; H, 4.91; N, 15.31%. Calcd for $(+)_{589}$-[Co(aet)(en)$_2$](ClO$_4$)$_2 = C_6H_{22}N_5SO_8Cl_2Co$: C, 15.87; H, 4.88; N, 15.42%.

[2-(Methythio)ethylamine]bis(ethylenediamine)cobalt(III) Complexes, [Co(mea)(en)$_2$]Cl$_3\cdot H_2O$: The racemic complex was derived from the reaction of [Co(aet)(en)$_2$]Cl$_2\cdot H_2O$ and methyl iodide according to the method of Hori.[1]

(+)$_{589}$-[Co(mea)(en)$_2$]Cl$_3\cdot H_2O$: The racemic chloride monohydrate (1.91 g) and the resolving agent $Na_2[Sb_2(d\text{-tart})_2]\cdot 2H_2O$ (1.54 g) were dissolved in 10 cm³ of water at 50 °C. After being cooled to room temperature, the mixed solution was allowed to stand overnight in a refrigerator. The less soluble diastereomer deposited as orange precipitate was recrystallized from a small amount of hot water. Found: C, 20.40; H, 3.83; N, 8.06%. Calcd for $(+)_{589}$-[Co(mea)(en)$_2$]Cl[Sb$_2$(*d*-tart)$_2$]$\cdot 2H_2O = C_{15}H_{33}N_5SO_{14}ClCoSb_2$: C, 20.53; H, 3.79; N, 7.98%. The diastereomer was converted into the optically active chloride salt by use of

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an anion exchange resin (Dowex 1X8, Cl^- form). Found: C, 22.47; H, 7.24; N, 17.20%. Calcd for $(+)_{589}$-$[Co(mea)(en)_2]Cl_3\cdot H_2O\cdot 1/3C_2H_5OH = C_6H_{27}N_5SOCl_3Co\cdot 1/3C_2H_5OH$: C, 22.46; H, 7.13; N, 17.08%.

[2-(Ethylthio)ethylamine]bis(ethylenediamine)cobalt(III) Complexes, $[Co(eea)(en)_2]Cl_3\cdot 2H_2O$: This complex was obtained according to the above procedure, with use of ethyl iodide instead of methyl iodide.

$(+)_{589}$-$[Co(eea)(en)_2]^{3+}$: The resolution procedure was similar to that for $[Co(mea)(en)_2]Cl_3\cdot H_2O$. Found: C, 20.54; H, 4.33; N, 7.28%. Calcd for $(+)_{589}$-$[Co(eea)(en)_2]Cl[Sb_2(d\text{-tart})_2]\cdot 4.5H_2O = C_{16}H_{40}N_5SO_{16.5}ClCoSb_2$: C, 20.52; H, 4.31; N, 7.48%. The optically active chloride salt was obtained by use of an anion exchange resin (Dowex 1X8, Cl^- form). The CD spectrum of this complex was measured with the eluate, the concentration being calculated from the CD intensity referring to that of the diastereomer.

[(Methylthio)acetato]bis(ethylenediamine)cobalt(III) Complexes, $[Co(mta)(en)_2]Cl_2$: This complex was prepared by the reaction of methyl iodide and $[Co(SCH_2CO_2)(en)_2]Cl$, the latter being prepared according to the literature.[2)]

$(+)_{589}$-$[Co(mta)(en)_2]Cl_2\cdot 1.5H_2O$: The racemic chloride (0.71 g) was dissolved in 2 cm^3 of water at 40 °C. Freshly precipitated silver tartrate, $Ag_2(d\text{-}H_2tart)$ (0.27 g), was added and the mixture was stirred for 10 min. The silver chloride was filtered off, washed with water (1 cm^3). Then *d*-tartaric acid (0.15 g) was added to the filtrate and washing. The mixed solution was cooled in an ice bath. The red diastereomer thus precipitated was recrystallized from 2 cm^3 of hot water by addition of ethanol. Found: C, 29.45; H, 5.76; N, 9.02%. Calcd for $(+)_{589}$-$[Co(mta)(en)_2](d\text{-}H_3tart)_2\cdot 2H_2O = C_{15}H_{35}N_4SO_{16}Co$: C, 29.13; H, 5.70; N, 9.06%. The diastereomer was converted into the optically active chloride salt by use of an anion exchange resin (Dowex 1X8, Cl^- form). Found: C, 21.93; H, 6.25; N, 14.85%. Calcd for $(+)_{589}$-$[Co(mta)(en)_2]Cl_2\cdot 1.5H_2O = C_7H_{24}N_4SO_{3.5}Cl_2Co$: C, 22.00; H, 6.33; N, 14.66%.

[3-(Methylthio)propionato]bis(ethylenediamine)cobalt(III) Complexes, $[Co(mtp)(en)_2]Cl_2$: This complex was prepared according to the method described above, except that $[Co(SCH_2CH_2CO_2)(en)_2]Cl$ was used instead of $[Co(SCH_2CO_2)(en)_2]Cl$.

$(-)_{589}$-$[Co(mtp)(en)_2]Cl_2\cdot 0.5H_2O$: The racemic chloride (1.16 g) and the resolving agent $Na_2[Sb_2(d\text{-tart})_2]\cdot 2H_2O$ (0.93 g) were dissolved in 4 cm^3 water at 50 °C. After the solution had been cooled to room temperature, the diastereomer deposited was filtered and recrystallized from a small amount of hot water by addition of ethanol. Found: C, 20.48; H, 4.03; N, 6.29%. Calcd for $(-)_{589}$-$[Co(mtp)(en)_2][Sb_2(d\text{-tart})_2]\cdot 5H_2O = C_{16}H_{37}N_4SO_{19}CoSb_2$: C, 20.80; H, 4.04; N, 6.06%. The optically active chloride salt was obtained by use of an anion exchange resin (Dowex 1X8, Cl^- form). Found: C, 25.33; H, 6.44; N, 14.92%. Calcd for $(-)_{589}$-$[Co(mtp)(en)_2]Cl_2\cdot 0.5H_2O = C_8H_{24}N_4SO_{2.5}Cl_2Co$: C, 25.41; H, 6.40; N, 14.81%.

[(2-Aminoethylthio)acetato][1,1,1-tris(aminomethyl)ethane]cobalt(III) Complexes, $[Co(aeta)(tame)]Cl_2\cdot 0.5H_2O$: 1,1,1-Tris(aminomethyl)ethane (3.4 g) and sodium hydroxide (1.8 g) were added at 0°C to a green solution of tricarbonatocobaltate(III) prepared by the method of Shibata[7)] in a 3.6 g scale of $CoCl_2\cdot 6H_2O$. The mixture was then heated to 40 °C and stirred for 1.5 h. After addition of 3 g of (2-aminoethylthio)acetic acid hemihydrochloride, the solution was stirred at *ca.* 60 °C for 3 h, whereupon the solution turned from violet to red. 6 M acetic acid was then added until gas evolution ceased and the stirring was continued for 2 h at 80 °C. The resulting red solution was evaporated *in vacuo* and then cooled. The chloride salt thus precipitated was recrystallized from a small volume of water by addition of ethanol. Found: C, 27.52; H, 6.25; N, 14.77%. Calcd for $[Co(aeta)(tame)]Cl_2\cdot 0.5H_2O = C_9H_{24}N_4SO_{2.5}Cl_2Co$: C, 27.70; H, 6.20; N, 14.35%.

$(+)_{589}$-$[Co(aeta)(tame)]Cl_2\cdot 1.5H_2O$: The racemic chloride (0.39 g) was dissolved in 5 cm^3 of water at 40 °C. Potassium tris(L-cysteinesulfinato-*N*,*S*)cobaltate(III) 6-hydrate, $K_3[Co(\text{L-cysu})_3]\cdot 6H_2O$[8)] (0.22 g) dissolved in 5 cm^3 of water was added with stirring. The mixed solution was kept in a refrigerator for *ca.* 1 h. The orange yellow diastereomer precipitated was filtered and then recrystallized from a large amount of water. Found: C, 23.73; H, 5.59; N, 11.28%. Calcd for $(+)_{589}$-$[Co(aeta)(tame)]_3[Co(\text{L-cysu})_3]_2\cdot 14H_2O\cdot 2KCl = C_{45}H_{127}N_{18}S_9O_{44}Cl_2Co_5K_2$: C, 23.91; H, 5.66; N, 11.15%. The optically active chloride salt was obtained by use of an anion exchange resin (Dowex 1X8, Cl^- form). Found: C, 24.97; H, 6.20; N, 13.18%. Calcd for $(+)_{589}$-$[Co(aeta)(tame)]Cl_2\cdot 1.5H_2O\cdot 1/4KCl = C_9H_{26}N_4SO_{3.5}Cl_2Co\cdot 1/4KCl$: C, 25.32; H, 6.14; N, 13.13%.

[3-(2-Aminoethylthio)propionato][1,1,1-tris(aminomethyl)ethane]cobalt(III) Complexes, $[Co(aetp)(tame)]Br_2\cdot 1.5H_2O$: This complex was prepared according to the method described above, with use of 3-(2-aminoethylthio)propionic acid monohydrobromide instead of (2-aminoethylthio)acetic acid hemihydrochloride. Found: C, 23.45; H, 5.90; N, 11.35%. Calcd for $[Co(aetp)(tame)]Br_2\cdot 1.5H_2O = C_{10}H_{28}N_4SO_{3.5}Br_2Co$: C, 23.48; H, 5.52; N, 10.96%.

$(-)_{589}$-$[Co(aetp)(tame)]^{2+}$: The racemic bromide was optically resolved by the same method as that for $[Co(aeta)(tame)]Cl_2$. The CD spectrum of this complex was measured with the eluate and the concentration was calculated from the optical density referring to that of the racemic complex.

Trinitro[1,1,1-tris(aminomethyl)ethane]cobalt(III), $[Co(NO_2)_3(tame)]$: 1,1,1-Tris(aminomethyl)ethane trihydrochloride (4.5 g) and sodium hydroxide (2.4 g) were dissolved in 15 cm^3 of water and the mixture was transferred to a separatory funnel. The solution was added dropwise to a solution of $Na_3[Co(NO_2)_6]$[9)] (8.1 g) in 20 cm^3 of water at 70 °C. A yellow precipitate was formed readily and removed by filtration. The crude product was recrystallized from a small amount of hot water. The yield was 2 g. Found: C, 19.05; H, 4.92; N, 26.78%. Calcd for $[Co(NO_2)_3(tame)] = C_5H_{15}N_6O_6Co$: C, 19.12; H, 4.81; N, 26.75%.

Trichloro[1,1,1-tris(aminomethyl)ethane]cobalt(III), $[CoCl_3(tame)]\cdot 0.75H_2O$: Trinitro[1,1,1-tris(aminomethyl)ethane]cobalt(III) (2.5 g) was added to 80 cm^3 of ethanol saturated with hydrogen chloride and gently stirred until the evolution of nitrogen oxide ceased. The solution was kept standing overnight at room temperature. The deep blue precipitate was filtered off and washed with ethanol and ether repeatedly until the washings became colorless. The reaction proceeded almost quantitatively; the yield was 1.9 g. Found: C, 20.13; H, 5.43; N, 14.25%. Calcd for $[CoCl_3(tame)]\cdot 0.75H_2O = C_5H_{16.5}N_3O_{0.75}Cl_3Co$: C, 20.29; H, 5.62; N, 14.20%.

(S-Methyl-L-cysteinato)[1,1,1-tris(aminomethyl)ethane]cobalt(III) Chloride, $[Co(\text{L-smc})(tame)]Cl_2$: Trichloro[1,1,1-tris(aminomethyl)ethane]cobalt(III) (0.9 g) was suspended in water (10 cm^3); silver perchlorate (1.98 g) was added and the mixture was shaken for 10 min. The resulting solution was filtered in order to remove the silver chloride. The solution obtained by dissolving *S*-methyl-L-cysteine (0.41 g) and sodium hydroxide (0.13 g) in 10 cm^3 of water was then added. The mixed solution was heated to 70 °C and stirred for 3 h. The reaction mixture was poured into a column of SP-Sephadex C-25 (3×40 cm, Na^+ form). The adsorbed band was eluted with 0.15 M NaCl solution at the rate of *ca.* 0.5 cm^3/min. The second orange-red eluate was evaporat-

ed and the deposit, NaCl, was filtered off. To the filtrate was added a large amount of ethanol. The crude product thus obtained was recrystallized from a minimum quantity of water by addition of ethanol, and washed with ethanol and then acetone, and dried in a vacuum desiccator. Found: C, 21.09; H, 4.65; N, 11.31%. Calcd for [Co(L-smc)(tame)]-$Cl_2 \cdot 2NaCl = C_9H_{23}N_4SO_2Cl_2Co \cdot 2NaCl$: C, 21.70; H, 4.65; N, 11.25%.

Measurements. The electronic absorption spectra were measured on a Shimadzu UV-200 spectrophotometer in aqueous solution. The CD spectra were recorded with a Jasco MOE-1 spectropolarimeter, with a cell of 1 cm pathlength. A Jasco DIP-4 digital polarimeter was used to check the optical rotations. The proton magnetic resonance spectra were recorded in deuterium oxide on a Varian XL-100-15 NMR spectrometer with DSS as an internal reference. All measurements were carried out at room temperature.

Results and Discussion

Absorption Spectra. The first absorption maximum of $[Co(aet)(en)_2]^{2+}$, which belongs to $[Co(N)_5(S)]$ type having a thiolato group, appears at 20800 cm^{-1} with a shoulder on the low energy side (Fig. 1 and Table 1). The spectrum is very similar to the spectra of [Co(L-cyst)$(en)_2$]I, [Co(L-Hcyst)$(en)_2$]ICl, and [Co(L-cystee)$(en)_2$]I_2[4] (L-H_2cyst=L-cysteine and L-Hcystee=L-cysteine ethyl ester), in which the sulfur containing ligands are coordinated through the amino and thiolato groups. Based on the approximate C_{4v} symmetry, the lower energy band is assigned to the transition $^1A_1 \rightarrow {}^1E$, and the higher band to $^1A_1 \rightarrow {}^1A_2$. The ligand field strength of the thiolato group is very weak and falls close to iodide in the spectrochemical series.

On the other hand, the complexes $[Co(mea)(en)_2]^{3+}$ and $[Co(eea)(en)_2]^{3+}$ which belong to $[Co(N)_5(S)]$ type having a thioether donor atom, show a single band at 20500 cm^{-1} (Fig. 2 and Table 1). The energy corresponds to that for the $[Co(N)_5(O)]$ type complexes, $[Co(gly)(en)_2]^{2+}$, [Co(L-ala)$(en)_2]^{2+}$, and $[Co(sar)(en)_2]^{2+}$ (gly=glycinate, L-ala=L-alaninate, and sar=*N*-methyl glycinate). As seen in Fig. 3, the first absorption maxima of the thioether complexes $[Co(mta)(en)_2]^{2+}$ and $[Co(mtp)(en)_2]^{2+}$, which belong to $[Co(N)_4(O)(S)]$ type, appear at 20000 and 20100 cm^{-1}, respectively, in line with that of $[Co(ox)(en)_2]^+$ which belongs to a $[Co(N)_4(O)_2]$ type. Thus, the thioether R–S–R seems to lie close to the COO^- group in the spectrochemical series. The three tame complexes also belong to the $[Co(N)_4(O)(S)]$ type having the first absorption maxima at 20300—20400 cm^{-1} (Fig. 4 and

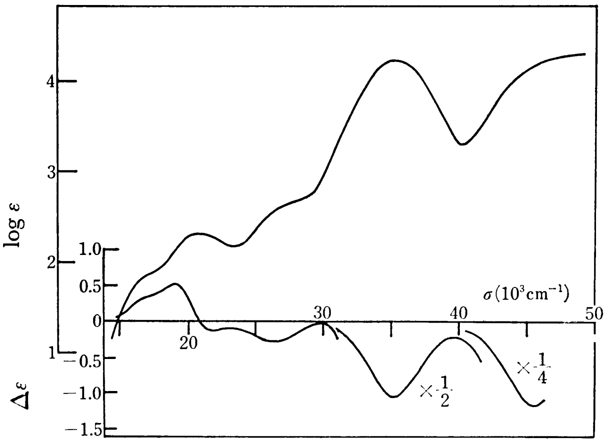


Fig. 1. Absorption and CD spectra of $(+)_{589}$-[Co(aet)-$(en)_2](ClO_4)_2$.

Table 1. Absorption and CD data of bis(ethylenediamine) complexes

Complex	σ_{max}[a)] (log ε)	σ_{ext}[a)] (Δε)
$(+)_{589}$-[Co(aet)$(en)_2$]-$(ClO_4)_2$	17 (1.85)[c)]	17 (+0.36)[c)]
	20.8 (2.31)	19.1 (+0.54)
		21.8 (−0.12)
	27 (2.62)[c)]	26.5 (−0.28)
	35.4 (4.24)	35.1 (−2.12)
		45.7 (−4.70)
$(+)_{589}$-[Co(mea)-$(en)_2$]Cl_3	20.5 (2.25)	20.1 (+3.22)
	28 (2.35)[c)]	26.0 (+0.06)
		28.1 (−0.13)
	35.5 (3.92)	35.5 (+5.09)
	45.8 (4.21)	47.2 (−11.2)
$(+)_{589}$-[Co(eea)-$(en)_2]^{3+}$	20.5 (2.25)[b)]	20.0 (+2.84)
	28 (2.37)[b,c)]	26.0 (−0.05)
		28.0 (−0.08)
	35.5 (3.94)[b)]	35.4 (+6.73)
	45.3 (4.22)[b)]	46.4 (−22.2)
$(+)_{589}$-[Co(mta)$(en)_2$]Cl_2	20.0 (2.20)	18.9 (+2.28)
		21.1 (+2.43)
	28 (2.35)[c)]	27.5 (−0.77)
	35.7 (3.85)	33.9 (−1.59)
		38.0 (+4.44)
	43.7 (4.14)	43.9 (−23.4)
$(-)_{589}$-[Co(mtp)$(en)_2$]Cl_2	20.1 (2.27)	19 (−0.65)[c)]
		21.2 (−2.15)
	27 (2.36)[c)]	27.2 (+0.99)
	34.6 (3.93)	33.7 (+2.93)
	44.5 (4.15)	44 (+7.38)[c)]

a) The wave numbers are given in 10^3 cm^{-1} unit. b) The racemate. c) A shoulder.

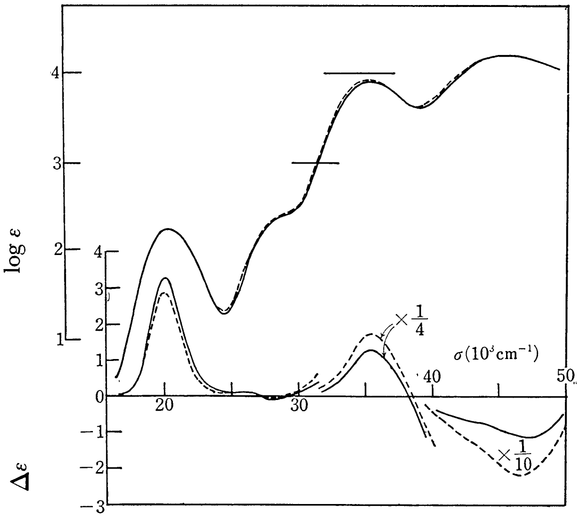


Fig. 2. Absorption and CD spectra of $(+)_{589}$-[Co-(mea)$(en)_2$]Cl_3 (——) and $(+)_{589}$-[Co(eea)$(en)_2$]Cl_3 (----).

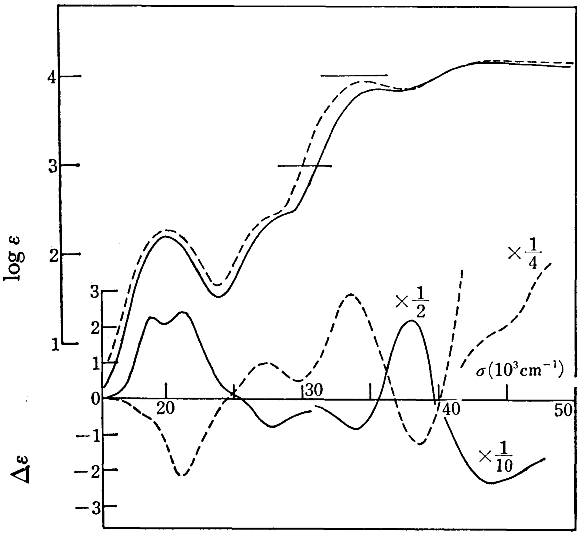


Fig. 3. Absorption and CD spectra of $(+)_{589}$-[Co(mta)(en)$_2$]Cl$_2$ (——) and $(-)_{589}$-[Co(mtp)(en)$_2$]Cl$_2$ (----).

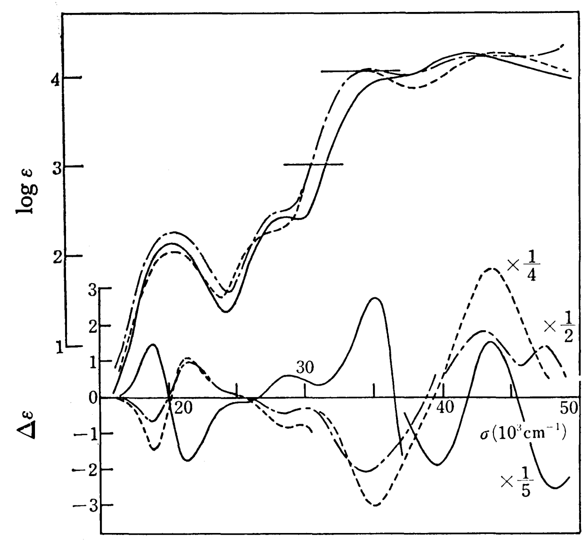


Fig. 4. Absorption and CD spectra of $(+)_{589}$-[Co(aeta)(tame)]$^{2+}$ (——), $(-)_{589}$-[Co(aetp)(tame)]$^{2+}$ (————), and $(-)_{589}$-[Co(L-smc)(tame)]$^{2+}$ (----).

TABLE 2. ABSORPTION AND CD DATA OF [Co(terdentate-N,S,O)(tame)]$^{2+}$ COMPLEXES

Complex	$\sigma_{max}{}^{a)}$ (log ε)	$\sigma_{ext}{}^{a)}$ (Δε)
$(+)_{589}$-[Co(aeta)(tame)]Cl$_2$	20.3(2.12)$^{b)}$	18.8(+1.46)
		21.3(−1.75)
	28.6(2.41)$^{b)}$	28.8(+0.61)
	35.7(3.93)$^{b,c)}$	35.1(+2.79)
	42.4(4.22)$^{b)}$	39.6(−9.08)
		43.7(+7.89)
		48.1(−12.7)
$(-)_{589}$-[Co(aetp)(tame)]$^{2+}$	20.3(2.24)$^{b)}$	18.7(−0.66)
		21.4(+0.99)
	28 (2.43)$^{b,c)}$	28.3(−0.40)
	35.0(4.03)$^{b)}$	34.7(−2.03)
	44.0(4.18)$^{b)}$	42.9(+3.76)
		47.5(+3.14)
$(-)_{589}$-[Co(L-smc)(tame)]Cl$_2$	20.4(2.05)	18.7(−1.39)
		21.2(+1.08)
	28 (2.25)$^{c)}$	28.4(−0.79)
	34.7(4.02)	34.8(−11.9)
	44.4(4.21)	43.5(+14.3)

a) The wavenumbers are given in 10^3 cm^{-1} unit. b) The racemate. c) A shoulder.

Table 2). These maxima are somewhat shifted to higher energy than those of the bis(ethylenediamine) complexes.

In the near-ultraviolet region, the complexes show intense bands (log $\varepsilon \approx 4.0$). Such bands appear always for the cobalt(III) complexes containing sulfur donor atoms,[10–12] and are considered to be the charge transfer bands due to the lone-pair electrons on the sulfur donor.

CD Spectra of the Bis(ethylenediamine) Complexes. The optical isomer of the complex containing a thiolato group, $(+)_{589}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$ which has only a chirality due to the skew pair of chelate rings, exhibits three weak CD bands in the first absorption band region (Fig. 1). Based on the assignment of the absorption components, two low energy positive bands can be assigned to be the split components of $^1A_1 \rightarrow {}^1E$ and a higher energy negative one $^1A_1 \rightarrow {}^1A_2$. This complex can be assigned to Λ configuration on the basis of the sign of $^1A_1 \rightarrow {}^1E$ components.

For each of the four complexes containing a thioether donor atom, four optical isomers, Δ-(R), Δ-(S), Λ-(R), and Λ-(S), are possible; both chiralities due to the skew pair of chelate rings (Δ and Λ) and due to the coordinated sulfur atom ((R) and (S)) contribute to the CD spectra. The optical isomers of the [Co(N)$_5$(S)] type, $(+)_{589}$-[Co(mea)(en)$_2$]$^{3+}$, and $(+)_{589}$-[Co(eea)(en)$_2$]$^{3+}$ which were obtained from the less soluble diastereomers, show one strong positive CD band in the first absorption band region and two weak CD bands of positive and negative signs in the second d-d absorption band region (Fig. 2). The CD spectra are strikingly similar to each other, indicating that the S-alkyl groups of both the complexes are in analogous environments. A similar trend has been found for some N,N'-dialkylethylenediaminediacetato complexes[13] which have two asymmetric nitrogen donor atoms. The complexes belonging to the [Co(N)$_4$(O)(S)] type, $(+)_{589}$-[Co(mta)(en)$_2$]$^{2+}$ and $(-)_{589}$-[Co(mtp)(en)$_2$]$^{2+}$, show two CD bands of the same sign in the first absorption band region (Fig. 3). The chiralities arising from the skew pair of chelate rings can be assigned to the present four complexes on the basis of the CD sign in the first absorption band region;[14] namely, Λ,Λ,Λ, and Δ configurations for $(+)_{589}$-[Co(mea)(en)$_2$]$^{3+}$, $(+)_{589}$-[Co(eea)(en)$_2$]$^{3+}$, $(+)_{589}$-[Co(mta)(en)$_2$]$^{2+}$, and $(-)_{589}$-[Co(mtp)(en)$_2$]$^{2+}$, respectively.

The NMR spectra of the resolved complexes show a single peak in the S-methyl proton region (Fig. 5). In the chromatographic separation of isomers of each resolved complex, all the fractions had the same CD spectra. The results and molecular model examination suggest that the thioether ligands are coordinated stereoselectively. The S-alkyl group in the configuration Δ-(R) or Λ-(S) has appreciable nonbonded atomic

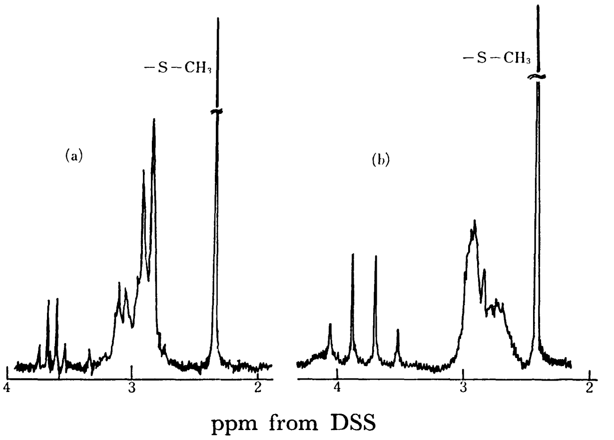


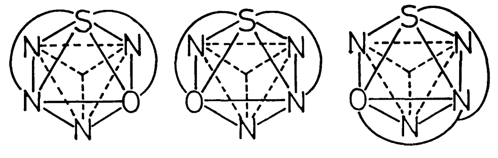
Fig. 5. The NMR spectra of (+)$_{589}$-[Co(mea)(en)$_2$]Cl$_3$ (a) and (+)$_{589}$-[Co(mta)(en)$_2$]Cl$_2$ (b) in D$_2$O.

interactions with the adjacent en chelate ring in contrast to that in the configuration Δ-(S) or Λ-(R). Thus, it is concluded that the configurations of the resolved complexes are Δ-(S) or Λ-(R).

In the region of the lower energy thioether charge transfer band, the mea and eea complexes show only one CD band; on the other hand, the mta and mtp complexes show two CD bands of opposite signs. Namely, for the [Co(N)$_5$(S)] type, the Λ-(R) and Δ-(S) complexes show (+) and (−) bands, respectively. The Λ-(R) complex of the [Co(N)$_4$O(S)] type shows (−) and (+) CD bands from low energy side, and Δ-(S) one (+) and (−).

CD Spectra of the tame Complexes. 1,1,1-Tris(aminomethyl)ethane is a typical tripod-like ligand and coordinates facially to a Co(III) ion. When three remaining coordination sites are occupied by the three non-equivalent ligating atoms, a kind of chirality due to the arrangement of these donor atoms is expected;[15,16] this kind of chirality contributes dominantly to the CD spectra of [Co(NH$_2$CHRCO$_2$)NH$_3$(tame)]$^{2+}$.[15] In the present system, the terdentate-*N,S,O* ligands occupy the three remaining coordination sites but there is no chirality arising from the skew pair of chelate rings. These complexes have a chirality due to the arrangement of three different donor atoms and another due to the central donor sulfur atom, though both chiralities are associated with each other.

Three tame complexes, (+)$_{589}$-[Co(aeta)(tame)]$^{2+}$, (−)$_{589}$-[Co(aetp)(tame)]$^{2+}$, and (−)$_{589}$-[Co(L-smc)(tame)]$^{2+}$, exhibit two CD bands of opposite signs in the first absorption band region (Fig. 4): L-smc and aetp (−)$_{589}$-complexes show (−) and (+) bands in the order of increasing energy, but aeta (−)$_{589}$-one shows the reverse CD pattern. As is shown in Fig. 6, the optical isomers of the aeta and aetp complexes have the structure (a) or (b), while the L-smc complex takes the structure (c) because of the complete stereoselectivity due to the L-smc ligand. The arrangement chirality of (b) and (c) are the same but that of (a) is the opposite. Accordingly, by analogy of the CD patterns absolute configurations are assigned as (a) for (+)$_{589}$-[Co(aeta)(tame)]$^{2+}$ and (b) for (−)$_{589}$-[Co(aetp)(tame)]$^{2+}$.



(a) (b) (c)

Fig. 6. Optical isomers of [Co(terdentate-*N,S,O*)(tame)]$^{2+}$, (a) and (b), and the structure of (−)$_{589}$-[Co(L-smc)(tame)]$^{2+}$ (c).

In the lower energy thioether charge transfer band region, the aeta (+)$_{589}$- and aetp (−)$_{589}$-complexes show a positive and a negative band, respectively, which corresponds to the fact that the two complexes have the opposite absolute configurations.

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