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Preparation and Some Properties of Bis(trimethylenediamine)cobalt(III) Complexes with a Bidentate-*N,S* or -*N,Se* Ligand

Takumi KONNO,* Ken-ichi OKAMOTO, Hisahiko EINAGA,† and Jinsai HIDAKA
Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305
†*Institute of Materials Science, University of Tsukuba, Sakura, Ibaraki 305*
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Seven optically active cobalt(III) complexes of [Co(bidentate-*N,S* or -*N,Se*)(tn)$_2$] type were prepared for the first time; bidentate-*N,S* or -*N,Se* denotes 2-aminoethanethiolato (aet), 2-aminoethaneselenolato (aes), 2-aminoethanesulfenato (aese), 2-aminoethanesulfinato (aesi), 2-(methylthio)ethylamine (mea), and 2-(methylseleno)ethylamine (mseea). These complexes were characterized from their absorption, CD, and ^{1}H NMR spectra. All complexes obtained were assigned to the Λ configuration. The $(+)^{CD}_{550}$ mea isomer took selectively the Λ-(R) configuration in solution, while the $(+)^{CD}_{550}$ mseea isomer a mixture of the Λ-(R) and Λ-(S) ones. The absorption and CD spectra of the complexes are discussed in comparison with those of the corresponding bis(ethylenediamine)cobalt(III) complexes. The Λ-(R)- and Λ-(S)-[Co(aese)(tn)$_2$]$^{2+}$ isomers showed the CD spectral change with time and it was suggested that the epimerization at sulfur was accompanied by the racemization of the skew pair of chelate rings.

Bis(ethylenediamine)cobalt(III) complexes with a bidentate-*N,S* or -*N,Se* ligand have extensively been investigated,$^{1-12)}$ and these complexes showed some unique spectrochemical and stereochemical properties.$^{4-9)}$ However, it has not been clarified whether the properties depend on the sulfur- or selenium-containing ligand itself or on the ethylenediamine chelate ring. Therefore, it is worthwhile to study the corresponding cobalt(III) complexes with six-membered trimethylenediamine chelate ring, [Co(bidentate-*N,S* or -*N,Se*)(tn)$_2$]. No report has been presented for the trimethylenediamine complexes up to now.

In this paper, the bis(trimethylenediamine)cobalt(III) complexes with 2-aminoethanethiolato, [Co(aet)(tn)$_2$]$^{2+}$, and 2-aminoethaneselenolato, [Co(aes)(tn)$_2$]$^{2+}$, were prepared and optically resolved. The other optically active cobalt(III) complexes, $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$- and $(+)^{CD}_{550}\cdot(-)^{CD}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$, $(+)^{CD}_{500}$-[Co(aesi)(tn)$_2$]$^{2+}$, and $(+)^{CD}_{550}$-[Co(mea)(tn)$_2$]$^{3+}$, were derived from $(+)^{CD}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$, and $(+)^{CD}_{550}$-[Co(mseea)(tn)$_2$]$^{3+}$ was derived from $(+)^{CD}_{600}$-[Co(aes)(tn)$_2$]$^{2+}$.$^{13)}$ The absorption and CD spectra of these complexes were discussed in comparison with those of the corresponding bis(ethylenediamine)cobalt(III) complexes. The rate constants of the epimerization at sulfur and the racemization of the skew pair of chelate rings of the complex were estimated for $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$- and $(+)^{CD}_{550}\cdot(-)^{CD}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$.

Experimental

1) Preparation and Resolution of the Complexes. *a) $(+)^{CD}_{600}$-[Co(aet)(tn)$_2$](ClO$_4$)$_2$*: To a deoxygenated solution containing 4.0 g of $CoCl_2\cdot6H_2O$ in 15 cm^3 of water were successively added with stirring deoxygenated solutions containing 1.9 g of $(NH_2CH_2CH_2S\text{-})_2\cdot2HCl$ in 15 cm^3 of water and 4.0 g of $NH_2(CH_2)_3NH_2$ in 40 cm^3 of water. The mixture was continuously stirred under nitrogen atmosphere for 40 min in an ice bath. The dark brown solution was filtered and to the filtrate was added a solution containing 15 g of NaI in 50 cm^3 of ice-cold water. The solution was kept in a refrigerator overnight. The resultant dark brown crystals were collected by filtration and washed with ice-cold ethanol and ether. Found: C, 17.86; H, 4.89; N, 13.03%. Calcd for [Co(aet) (tn)$_2$]I$_2$=$C_8H_{26}N_5SCoI_2$: C, 17.88; H, 4.87; N, 13.03%.

One point five gram of [Co(aet)(tn)$_2$]I$_2$ was dissolved in 70 cm^3 of ice-cold water. To this were added with stirring a solution containing 1.0 g of K$_2$[Sb$_2$(d-tart)$_2$]$\cdot$H$_2$O in 20 cm^3 of water and 20 cm^3 of ethanol. The solution was stirred for 20 min in an ice bath, though fine reddish brown crystals began to appear after a few minutes. The crystals were collected by filtration and washed with ethanol and ether. Found: C, 22.60; H, 3.88; N, 8.26%. Calcd for [Co(aet)(tn)$_2$][Sb$_2$(d-tart)$_2$]$\cdot$1.5H$_2$O=$C_{16}H_{30}N_5O_{12}SCoSb_2\cdot1.5H_2O$: C, 22.72; H, 3.93; N, 8.28%.

Zero point seven gram of $(+)^{CD}_{600}$-[Co(aet)(tn)$_2$][Sb$_2$(d-tart)$_2$]$\cdot$1.5H$_2$O was dissolved in 20 cm^3 of an aqueous solution containing 4.0 g of NaClO$_4$ with stirring in an ice bath. When the solution was continuously stirred for 10 min, fine dark brown crystals appeared. The resultant crystals were collected by filtration and washed with ice-cold ethanol and ether. The concentration of this isomer was evaluated from the extinction coefficient of the racemic iodide salt.

b) $(+)^{CD}_{600}$-[Co(aes)(tn)$_2$](ClO$_4$)$_2$: This complex was prepared by a procedure similar to that used for $(+)^{CD}_{600}$-[Co(aet)(tn)$_2$](ClO$_4$)$_2$ described in *a)*, using $(NH_2CH_2CH_2Se)_2\cdot H_2SO_4$$^{14)}$ instead of $(NH_2CH_2CH_2S\text{-})_2\cdot2HCl$. The concentration of this isomer was evaluated from the extinction coefficient of the racemic iodide salt. Found: C, 15.69; H, 4.91; N, 11.86%. Calcd for [Co(aes)(tn)$_2$]I$_2$$\cdot$H$_2$O=$C_8H_{26}N_5CoSeI_2\cdot H_2O$: C, 15.96; H, 4.69; N, 11.63%. Found: C, 21.19; H, 3.73; N, 7.72%. Calcd for [Co(aes)(tn)$_2$][Sb$_2$(d-tart)$_2$]$\cdot$2H$_2$O=$C_{16}H_{30}N_5O_{12}CoSeSb_2\cdot2H_2O$: C, 21.31; H, 3.80; N, 7.77%.

c) $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$-[Co(aese)(tn)$_2$](ClO$_4$)$_2$ and $(+)^{CD}_{550}\cdot(-)^{CD}_{370}$-[Co(aese)(tn)$_2$]I$_2$: The preparation procedure was operated without light. To a solution containing 0.2 g of $(+)^{CD}_{600}$-[Co(aet)(tn)$_2$](ClO$_4$)$_2$ in 2 cm^3 of ice-cold water was added a calculated amount of 2% H$_2$O$_2$ (0.6 cm^3). The mixture was stirred for 20 min in an ice bath and the resultant precipitate of the $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$ aese isomer was collected by filtration. To the filtrate was soon added 0.5 g of NaI and the solution was stirred for 10 min in an ice bath. The resultant precipitate, which was found from the CD measurement to be the $(+)^{CD}_{550}\cdot(-)^{CD}_{370}$ aese isomer containing a small amount of the $(+)^{CD}_{550}\cdot(+)^{CD}_{370}$ one, was filtered off. To the filtrate were added 1.0 g of NaI and a large amount of 2-propanol–ether (2:1), and then the solution was stood in a refrigerator overnight. The resultant orange-red precipitate of the (+)$^{CD}_{550}$·(−)$^{CD}_{370}$ aese isomer was collected by filtration. The formation ratio of the two isomers, (+)$^{CD}_{550}$·(+)$^{CD}_{370}$:(+)$^{CD}_{550}$·(−)$^{CD}_{370}$, was about 6:5, which was evaluated from the CD spectra of the reaction solution. Found for (+)$^{CD}_{550}$·(+)$^{CD}_{370}$ isomer: C, 19.31; H, 5.23; N, 14.03%. Calcd for $[Co(aese)(tn)_2](ClO_4)_2=C_8H_{26}N_5O_9SCl_2Co$: C, 19.28; H, 5.26; N, 14.05%. Found for (+)$^{CD}_{550}$·(−)$^{CD}_{370}$ isomer: C, 16.61; H, 4.60; N, 12.04%. Calcd for $[Co(aese)(tn)_2]I_2\cdot H_2O=C_8H_{26}N_5OSCoI_2\cdot H_2O$: C, 16.83; H, 4.94; N, 12.26%.

d) (+)$^{CD}_{600}$-[Co(aesi)(tn)$_2$](ClO$_4$)$_2$: To a solution containing 0.1 g of (+)$^{CD}_{600}$-[Co(aet)(tn)$_2$](ClO$_4$)$_2$ in 2 cm^3 of ice-cold water was added an excess amount of 10% H_2O_2 (0.6 cm^3), followed by the addition of 0.3 cm^3 of 60% $HClO_4$. The solution was stirred for 20 min in an ice bath and stood in a refrigerator for 2 d. The solution was poured onto a column of QAE-Sephadex A-25 (ClO_4^- from, 2 cm×20 cm) and the adsorbed band was eluted with water. The eluate was concentrated to a small volume with a rotary evaporator and to this was added an appropriate amount of ethanol. The solution was kept in a refrigerator for several days and the resultant crystals were collected by filtration. Found: C, 18.59; H, 5.12; N, 13.51%. Calcd for $[Co(aesi)(tn)_2](ClO_4)_2=C_8H_{26}N_5O_{10}SCl_2Co$: C, 18.68; H, 5.09; N, 13.61%.

e) (+)$^{CD}_{550}$-[Co(mea)(tn)$_2$](NO$_3$)$_3$. To a solution containing 0.1 g of (+)$^{CD}_{600}$-[Co(aet)(tn)$_2$](ClO$_4$)$_2$ in 2 cm^3 of ice-cold water was added 2 cm^3 of ice-cold dimethyl sulfate. When the mixture was allowed to stand in a refrigerator overnight, it was separated into two layers. The red upper layer was poured onto a column of QAE-Sephadex A-25 (NO_3^- form, 2 cm×20 cm) and the adsorbed band was eluted with water. The eluate was concentrated to a small volume with a rotary evaporator and to this was added a small amount of ethanol. After cooling in a refrigerator overnight, the resultant crystals were collected by filtration and washed with ethanol and ether. Found: C, 22.01; H, 6.09; N, 22.77%. Calcd for $[Co(mea)(tn)_2](NO_3)_3\cdot 0.5H_2O=C_9H_{29}N_8O_9SCo\cdot 0.5H_2O$: C, 21.91; H, 6.13; N, 22.71%.

f) (+)$^{CD}_{550}$-[Co(mseea)(tn)$_2$](NO$_3$)$_3$. This complex was prepared by a procedure similar to that used for (+)$^{CD}_{550}$-[Co(mea)(tn)$_2$](NO$_3$)$_3$ described in *e)*, using (+)$^{CD}_{600}$-[Co(aes)(tn)$_2$](ClO$_4$)$_2$ instead of (+)$^{CD}_{600}$-[Co(aet)(tn)$_2$](ClO$_4$)$_2$. Found: C, 19.10; H, 5.74; N, 19.61%. Calcd for $[Co(mseea)(tn)_2](NO_3)_3\cdot 2H_2O=C_9H_{29}N_8O_9CoSe\cdot 2H_2O$: C, 19.05; H, 5.86; N, 19.75%.

*g) Λ-[Co(aet)(en)$_2$](ClO$_4$)$_2$, Λ-(*R*)- and Λ-(*S*)-[Co(aese)(en)$_2$](ClO$_4$)$_2$, Λ-[Co(aesi)(en)$_2$](ClO$_4$)$_2$, and Λ-(*R*)-[Co(mea)(en)$_2$](NO$_3$)$_3$.* These bis(ethylenediamine)cobalt(III) complexes were prepared by the methods described in previous papers.[8,11]

2) Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra with a JASCO J-20 spectropolarimeter. All measurements were carried out in an aqueous solution at room temperature. The ^1H NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 NMR spectrometer at probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference. The absorption and CD spectral changes for the epimerization and racemization were followed at 24 °C in the room light which was (4.7±0.3)×10^2 lx with a lux-meter ANA-999 of Tokyo Photo-electric Co., Ltd.

Results and Discussion

Absorption and CD Spectra. Figures 1—4 and Tables 1 and 2 show the absorption and CD spectra of the bis(trimethylenediamine)cobalt(III) complexes. The absorption spectral behavior of the present complexes with a sulfur- or selenium-containing ligand is quite similar to that of the corresponding [Co(bidentate-*N,S* or -*N,Se*)(en)$_2$] type complexes.[4—11] All com-

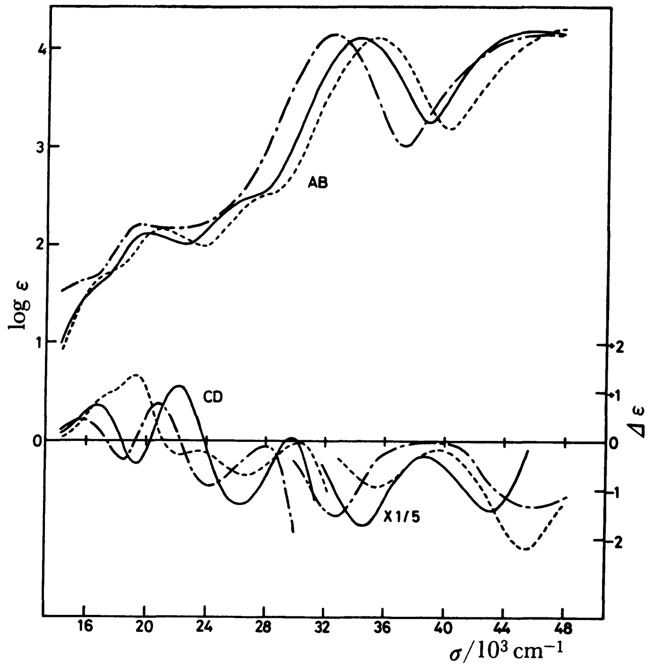

Fig. 1. Absorption and CD spectra of (+)$^{CD}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$ (——), (+)$^{CD}_{600}$-[Co(aes)(tn)$_2$]$^{2+}$ (—·—), and *Λ*-[Co(aet)(en)$_2$]$^{2+}$ (-----).

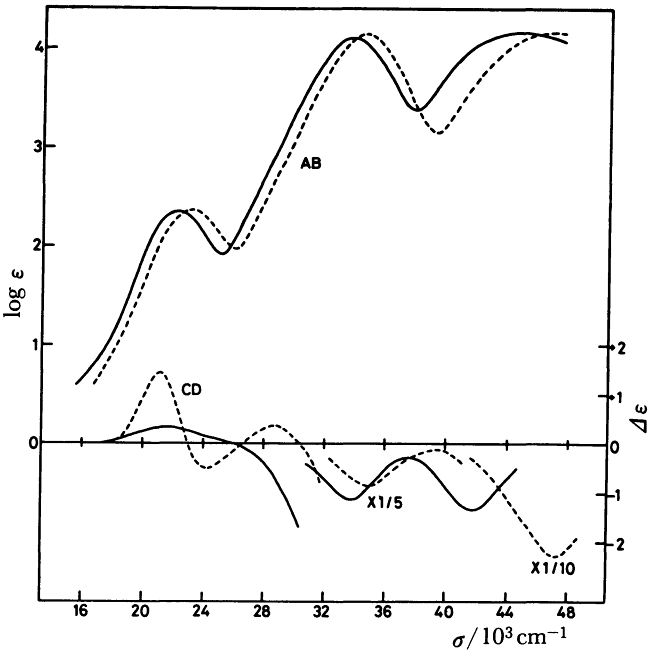

Fig. 2. Absorption and CD spectra of (+)$^{CD}_{500}$-[Co(aesi)(tn)$_2$]$^{2+}$ (——), and *Λ*-[Co(aesi)(en)$_2$]$^{2+}$ (-----).

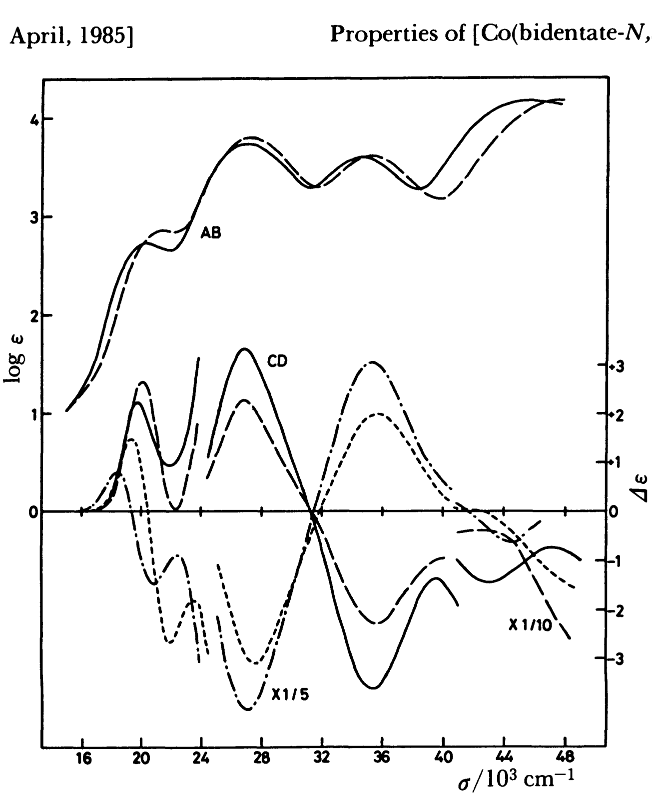

Fig. 3. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$ (——), $(+)^{\mathrm{CD}}_{550}\cdot(-)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$ (—·—), Λ-(*S*)-[Co(aese)(en)$_2$]$^{2+}$ (———), and Λ-(*R*)-[Co(aese)(en)$_2$]$^{2+}$ (-----).

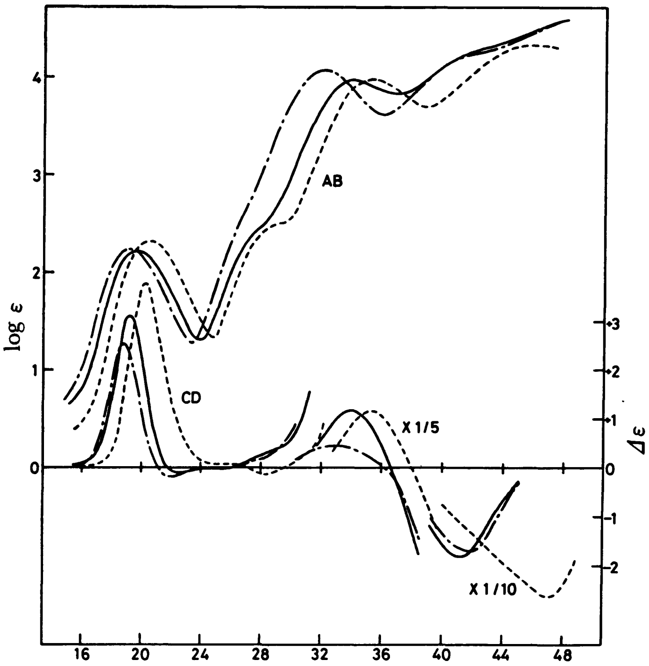

Fig. 4. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{550}$-[Co(mea)(tn)$_2$]$^{3+}$ (——), $(+)^{\mathrm{CD}}_{550}$-[Co(mseea)(tn)$_2$]$^{3+}$ (—·—), and Λ-(*R*)-[Co(mea)(en)$_2$]$^{3+}$ (-----).

plexes show the chalcogen-to-metal charge transfer band at 32—35×10^3 cm^{-1}, which shifts to lower energy than that of the corresponding bis(ethylenediamine) complexes. As for [Co(aese)(tn)$_2$]$^{2+}$, another characteristic charge transfer band appears at *ca.* 27×10^3 cm^{-1}, as in the case for [Co(aese)(en)$_2$]$^{2+}$.[6,8–10] The first absorption band of the [Co(bidentate-*N,S* or -*N,Se*)(tn)$_2$] type complexes shifts to lower energy than that of the corresponding [Co(bidentate-*N,S* or -*N,Se*)(en)$_2$] ones,[4–11] in analogous with the fact that the [Co(L)(tn)$_2$] type complexes show the first absorption band at lower energy as compared with that of the corresponding [Co(L)(en)$_2$] ones; L denotes a bidentate ligand such as glycinate and oxalate.[15,16]

The Δ and Λ isomers are possible for each of [Co(aet)(tn)$_2$]$^{2+}$, [Co(aes)(tn)$_2$]$^{2+}$, and [Co(aesi)(tn)$_2$]$^{2+}$. As shown in Fig. 1, the CD spectrum of $(+)^{\mathrm{CD}}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$ agrees well with that of Λ-[Co(aet)(en)$_2$]$^{2+}$,[4,8] except for the two bands at higher energy in the first absorption band region (*ca.* 19 and 22×10^3 cm^{-1}). Furthermore, the stoichiometric oxidation of $(+)^{\mathrm{CD}}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$ generated Λ-(*R*)- and Λ-(*S*)-[Co(aese)(tn)$_2$]$^{2+}$ (*vide infra*), as in the oxidation reaction of Λ-[Co(aet)(en)$_2$]$^{2+}$.[7–9] These facts suggest that the starting thiolato complex, $(+)^{\mathrm{CD}}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$, takes the Λ configuration. As shown in Fig. 1, $(+)^{\mathrm{CD}}_{600}$-[Co(aes)(tn)$_2$]$^{2+}$ exhibits a CD spectra quite similar to that of Λ-$(+)^{\mathrm{CD}}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$ over the whole region, and then can be assigned to the Λ configuration. The $(+)^{\mathrm{CD}}_{500}$ aesi isomer, which is the oxidation product from Λ-$(+)^{\mathrm{CD}}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$, shows a positive CD band in the first absorption band region (Fig. 2), being also assigned to the Λ configuration. These facts indicate that the oxidation reaction for the starting thiolato complex proceeded with retention of its absolute configuration, as in the case for the bis(ethylenediamine) cobalt(III) complexes.[7–9,11] In the present bis(trimethylenediamine)cobalt(III) complexes, Λ-[Co(aet) (tn)$_2$]$^{2+}$, Λ-[Co(aes)(tn)$_2$]$^{2+}$, and Λ-[Co(aesi)(tn)$_2$]$^{2+}$, which have no chirality due to the coordinated chalcogen atom, commonly show a negative CD band in the chalcogen-to-metal charge transfer band region similar to that of the corresponding bis(ethylenediamine) complexes, though the CD spectra in the first absorption band region are different from one another (Fig. 1 and 2).[4,7,8,11] This may suggest that the configurational chirality due to the skew pair of chelate rings can be deduced from the CD pattern in the chalcogen-to-metal charge transfer band region as for the bis(diamine)cobalt(III) complexes with the aet, aes or aesi ligand.

Taking the asymmetric chalcogen donor atom, (*R*) and (*S*), into consideration, four isomers, Δ-(*R*), Δ-(*S*), Λ-(*R*), and Λ-(*S*), are possible for each of [Co(aese)(tn)$_2$]$^{2+}$, [(Co(mea)(tn)$_2$]$^{3+}$, and [Co(mseea)(tn)$_2$]$^{3+}$. The two isomers, $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$- and $(+)^{\mathrm{CD}}_{550}\cdot(-)^{\mathrm{CD}}_{370}$-[Co(aese)(tn)$_2$]$^{2+}$, which are formed by the stoichiometric oxidation reaction of $(+)^{\mathrm{CD}}_{600}$-[Co(aet)(tn)$_2$]$^{2+}$ with aqueous H_2O_2, show the CD spectra quite similar to those of Λ-(*S*)- and Λ-(*R*)-[Co(aese)(en)$_2$]$^{2+}$, respectively, over the whole region (Fig. 3).[8,9] This fact suggests that the $(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$ and $(+)^{\mathrm{CD}}_{550}\cdot(-)^{\mathrm{CD}}_{370}$ aese isomers take the

Table 1. Absorption data of $[\mathrm{Co(bidentate\text{-}}N,S\mathrm{\ or\ \text{-}}N,Se\mathrm{)(tn)_2}]$ type complexes

Complex	First band	Second band	Charge transfer band
$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{Co(aet)(tn)_2}]^{2+}$	16.9 (1.61 sh)	27.3 (2.51 sh)	34.13 (4.12)
	19.92 (2.11)		45.35 (4.20)
$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{Co(aes)(tn)_2}]^{2+}$	16.0 (1.64 sh)		32.36 (4.16)
	19.70 (2.21)		46.30 (4.16)
$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aesi)(tn)_2}]^{2+}$	22.15 (2.36)		33.67 (4.12)
			44.64 (4.17)
$(+)^{\mathrm{CD}}_{550}\cdot(-)^{\mathrm{CD}}_{370}$-$[\mathrm{Co(aese)(tn)_2}]^{2+}$	20.68 (2.66)		26.95 (3.81)
			34.48 (3.62)
			44.15 (4.63)
$(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-$[\mathrm{Co(aese)(tn)_2}]^{2+}$	20.20 (2.73)		26.88 (3.74)
			34.42 (3.61)
			45.15 (4.19)
$(+)^{\mathrm{CD}}_{550}$-$[\mathrm{Co(mea)(tn)_2}]^{3+}$	19.67 (2.22)	28.3 (2.52 sh)	34.07 (3.97)
			43.9 (4.33 sh)
			49.02 (4.60)
$(+)^{\mathrm{CD}}_{550}$-$[\mathrm{Co(mseea)(tn)_2}]^{3+}$	19.16 (2.24)		32.15 (4.07)
			43.1 (4.28 sh)
			48.78 (4.57)

Wave numbers and logε values (in parentheses) are given in $10^3\,\mathrm{cm^{-1}}$ and $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, respectively. Sh denotes a shoulder.

Table 2. CD data of $[\mathrm{Co(bidentate\text{-}}N,S\mathrm{\ or\ \text{-}}N,Se\mathrm{)(tn)_2}]$ type complexes

Complex	First band	Second band	Charge transfer band
$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{Co(aet)(tn)_2}]^{2+}$	16.67 (+0.70)	30.21 (−1.30)	34.42 (−8.72)
	19.23 (−0.46)		43.1 (−7.0)
	22.08 (+1.13)		
$(+)^{\mathrm{CD}}_{600}$-$[\mathrm{Co(aes)(tn)_2}]^{2+}$	15.70 (+0.43)	24.21 (−0.89)	32.68 (−7.56)
	18.45 (−0.36)		45.5 (−6.6)
	20.79 (+0.76)		
$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aese)(tn)_2}]^{2+}$	21.51 (+0.33)		33.56 (−5.45)
			41.67 (−6.6)
$(+)^{\mathrm{CD}}_{550}\cdot(-)^{\mathrm{CD}}_{370}$-$[\mathrm{Co(aese)(tn)_2}]^{2+}$	18.38 (+0.85)		27.03 (−20.18)
	20.70 (−1.48)		35.27 (+15.26)
			44.3 (−6.1)
$(+)^{\mathrm{CD}}_{550}\cdot(+)^{\mathrm{CD}}_{370}$-$[\mathrm{Co(aese)(tn)_2}]^{2+}$	19.67 (+2.25)		26.81 (+16.71)
			35.34 (−17.95)
			44.76 (−14.2)
$(+)^{\mathrm{CD}}_{550}$-$[\mathrm{Co(mea)(tn)_2}]^{3+}$	19.23 (+3.14)	29.4 (−0.43 sh)	34.13 (+5.68)
	22.47 (−0.11)		41.32 (−18.4)
$(+)^{\mathrm{CD}}_{550}$-$[\mathrm{Co(mseea)(tn)_2}]^{3+}$	18.80 (+2.57)		32.15 (+2.31)
	21.98 (−0.18)		41.59 (−17.2)

Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in $10^3\,\mathrm{cm^{-1}}$ and $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, respectively. Sh denotes a shoulder.

Λ-(*S*) and Λ-(*R*) configurations, respectively. This assignment is confirmed by comparing the vicinal CD due to the asymmetric sulfur atom and the configurational CD due to the skew pair of chelate rings for $[\mathrm{Co(aese)(tn)_2}]^{2+}$ with those for $[\mathrm{Co(aese)(en)_2}]^{2+}$. Figure 5 shows the (*S*) vicinal and the Λ configurational CD curves calculated from the observed CD curves of Λ-(*R*)- and Λ-(*S*)-$[\mathrm{Co(aese)(tn)_2}]^{2+}$, together with those calculated from Λ-(*R*)- and Λ-(*S*)-$[\mathrm{Co(aese)(en)_2}]^{2+}$. The (*S*) vicinal CD curve for $[\mathrm{Co(aese)(tn)_2}]^{2+}$ is quite similar to that for $[\mathrm{Co(aese)(en)_2}]^{2+}$, showing two bands, (−) and (+), from lower energy in the first absorption band region, and two bands, (+) and (−), from lower energy in the sulfur-to-metal charge transfer band region. A similar relation is also observed for the Λ configurational CD curves; the dominant positive CD band is observed at the lower energy side of the first absorption band region and a negative band in the sulfenato charge transfer band region (*ca.* $28\times10^3\,\mathrm{cm^{-1}}$), though the CD intensity for $[\mathrm{Co(aese)(tn)_2}]^{2+}$ is weaker than that for $[\mathrm{Co(aese)(en)_2}]^{2+}$ in the first absorption band region. The formation ratio of the two isomers, Λ-(*R*):Λ-(*S*), is about 5:6 for $[\mathrm{Co(aese)(tn)_2}]^{2+}$ and this ratio is in contrast to the case for $[\mathrm{Co(aese)(en)_2}]^{2+}$ (Λ-(*R*):Λ-(*S*)=3:1).[8] This may be due to the absence of the effective intramolecular hydrogen bond between the sulfenato oxygen atom and the adjacent amine proton in $[\mathrm{Co(aese)(tn)_2}]^{2+}$, because of the flexibility of the six-membered trimethylenediamine cheate ring.

Each of $(+)^{\mathrm{CD}}_{550}$-$[\mathrm{Co(mea)(tn)_2}]^{3+}$ and $(+)^{\mathrm{CD}}_{550}$-$[\mathrm{Co(mseea)(tn)_2}]^{3+}$, which is the methylation product of Λ-$[\mathrm{Co(aet)(tn)_2}]^{2+}$ and Λ-$[\mathrm{Co(aes)(tn)_2}]^{2+}$, respectively, shows a major positive CD band in the first absorp-

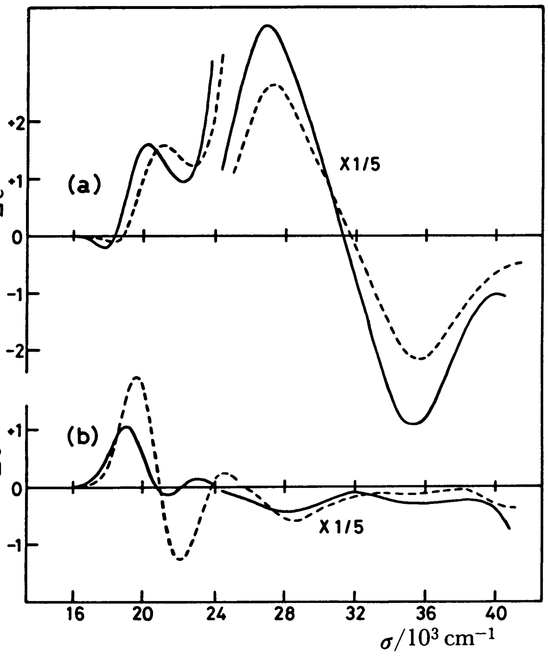

Fig. 5. (a): Vicinal CD curves ($\Delta\varepsilon(S)=1/2\{\Delta\varepsilon[\Lambda\text{-}(S)]-\{\Delta\varepsilon[\Lambda\text{-}(R)]\}\}$) of $[Co(aese)(tn)_2]^{2+}$ (——) and $[Co(aese)(en)_2]^{2+}$ (-----).
(b): Configurational CD curves ($\Delta\varepsilon(\Lambda)=1/2\{\Delta\varepsilon[\Lambda\text{-}(S)]+\{\Delta\varepsilon[\Lambda\text{-}(R)]\}\}$) of $[Co(aese)(tn)_2]^{2+}$ (——) and $[Co(aese)(en)_2]^{2+}$ (-----).

tion band region, as well as Λ-$(+)^{CD}_{500}$-$[Co(mea)(en)_2]^{3+}$ and Λ-$(+)^{CD}_{500}$-$[Co(mseea)(en)_2]^{3+}$ (Fig. 4).[4,7,8] Therefore, it is suggested that no isomerization occurs during the methylation procedure and the $(+)^{CD}_{550}$ mea and mseea isomers take the Λ configuration. The ^{1}H NMR spectrum of Λ-$(+)^{CD}_{550}$-$[Co(mea)(tn)_2]^{3+}$ exhibits a single peak in the methyl protons region (2.26 ppm from DSS), suggesting that the $(+)^{CD}_{550}$ mea isomer takes either the (*R*) or (*S*) configuration in solution. It is probable that the Λ-$(+)^{CD}_{550}$ mea isomer prefers to the (*R*) configuration as Λ-$(+)^{CD}_{500}$-$[Co(mea)(en)_2]^{3+}$,[4,8] because there is a nonbonded interaction between the methyl group and the adjacent diamine chelate ring when Λ-$[Co(mea)(tn)_2]^{3+}$ takes the (*S*) configuration. In the sulfur-to-metal charge transfer band region, Λ-$(+)^{CD}_{550}$-$[Co(mea)(tn)_2]^{3+}$ shows a positive CD band similar to that of Λ-(*R*)-$[Co(mea)(en)_2]^{3+}$ (Fig. 4). The CD band in this region is closely related to the chirality due to the chalcogen donor atom.[8] From these facts, it is suggested that $(+)^{CD}_{550}$-$[Co(mea)(tn)_2]^{3+}$ takes selectively the Λ-(*R*) configuration in solution. For Λ-$(+)^{CD}_{550}$-$[Co(mseea)(tn)_2]^{3+}$, the ^{1}H NMR spectrum shows two peaks in the methyl protons region (2.19 and 2.32 ppm, in the ratio 4:1). This indicates that the Λ-$(+)^{CD}_{550}$ mseea isomer takes a mixture of the Λ-(*R*) and Λ-(*S*) configurations in solution, contrary to the case of Λ-$(+)^{CD}_{550}$-$[Co(mea)(tn)_2]^{3+}$, although the (*R*) configuration seems to be dominant for the Λ-$(+)^{CD}_{550}$ mseea isomer. It is considered that the nonbonded interaction between the methyl group and the adjacent diamine chelate ring in Λ-(*S*)-$[Co(mseea)(tn)_2]^{3+}$ is not so conspicuous as that in Λ-(*S*)-$[Co(mea)(tn)_2]^{3+}$, because of the longer bond lengths of Co–Se and Se–C than those of Co–S and S–C.[8] The CD spectrum of Λ-$(+)^{CD}_{550}$-$[Co(mseea)(tn)_2]^{3+}$ shows a positive band in the chalcogen-to- metal charge transfer band region (*ca.* $32\times10^3\,cm^{-1}$) as well as Λ-(*R*)-$[Co(mea)(tn)_2]^{3+}$, though the CD intensity of the former is weaker than that of the latter (Fig. 4). This supports that the Λ-$(+)^{CD}_{550}$ mseea isomer has dominantly the (*R*) configuration, because a negative CD band will appear in the chalcogen-to-metal charge transfer band region if not so.[8,12] The Λ-$(+)^{CD}_{550}$ mseea isomer chromatographed on SP-Sephadex column gave only one adsorbed band and all of its fractions showed the same CD spectra in the whole region. This suggests that the inversion at selenium in Λ-$(+)^{CD}_{550}$-$[Co(mseea)(tn)_2]^{3+}$ occurs as in the case for thioether or selenoether cobalt(III) complexes.[17–19]

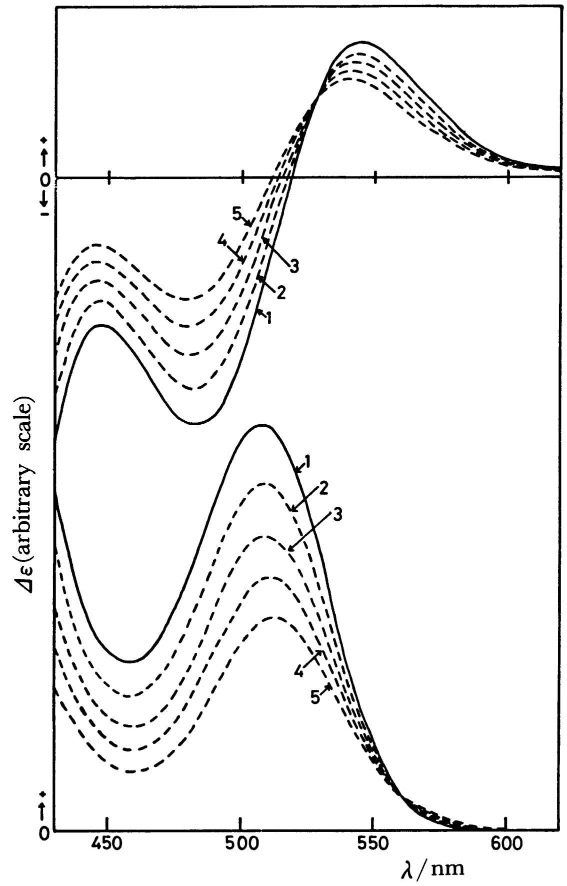

Fig. 6. CD spectral change with time for Λ-(*R*)-$[Co(aese)(tn)_2]^{2+}$ (upper) and Λ-(*S*)-$[Co(aese)(tn)_2]^{2+}$ (lower) in water at 24 °C. The curves 1—5 were measured at 0, 60, 120, 180, and 240 min, respectively.

Epimerization and Racemization of Λ*-(*R*)- and* Λ*-(*S*)-$[Co(aese)(tn)_2]^{2+}$.* Of the bis(trimethylenediamine)-cobalt(III) complexes in the present work, Λ-(*R*)- and Λ-(*S*)-$[Co(aese)(tn)_2]^{2+}$ exhibited the CD spectral change with time in water. Figure 6 shows the CD spectral change of Λ-(*R*)-$[Co(aese)(tn)_2]^{2+}$ (2.72×10^{-3} mol dm^{-3}) and Λ-(*S*)-$[Co(aese)(tn)_2]^{2+}$ (3.05×10^{-3} mol dm^{-3}) at 24 °C in the room light. Though the absorption spectral change was also observed for the isomers, the change was negligibly small as compared with the CD spectral change. The isodichroic point was recognized at 528 nm for the Λ-(R) isomer and at 561 nm for the Λ-(S) one for at least 1.5 half-lives. These facts indicate that not only the epimerization at sulfur but the racemization of the skew pair of chelate rings takes place for these isomers under these conditions. The CD intensity change was also observed in the dark. However, this change was only 15% in the room light at the same intervals, and the rate constant could not be obtained because of the decomposition for the complex. Thus, the rate constants for the epimerization and racemization were tentatively estimated from the CD spectral change in the room light. The CD intensity change at 455 nm or 483 nm ($\Delta\varepsilon[\Lambda\text{-}(R)]=-\Delta\varepsilon[\Lambda\text{-}(S)]$) should be regarded as being caused by the epimerization at sulfur and that at 543 nm ($\Delta\varepsilon[\Lambda\text{-}(R)]=\Delta\varepsilon[\Lambda\text{-}(S)]$) by the racemization of the skew pair of chelate rings (Fig. 3). At these wavelengths, the plots of the logarithmic CD intensity change against time gave a straight line, from which the first-order rate constant was obtained; $4.9\times10^{-5}\,\mathrm{s}^{-1}$ for the Λ-(R) isomer and $6.7\times10^{-5}\,\mathrm{s}^{-1}$ for the Λ-(S) one at 455 nm, and $5.0\times10^{-5}\,\mathrm{s}^{-1}$ for the Λ-(R) isomer and $7.2\times10^{-5}\,\mathrm{s}^{-1}$ for the Λ-(S) one at 483 nm. These values may be taken as about the same, considering that the epimerization is affected by the light. The rate constant for the racemization obtained from the CD spectral change at 543 nm is $2.4\times10^{-5}\,\mathrm{s}^{-1}$ for both of the Λ-(R) and Λ-(S) isomers. This value is smaller than that of the epimerization at sulfur and it is suggested that the epimerization at sulfur was accompanied by the racemization of the skew pair of chelate rings.

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13) Abbreviation used for ligands are as follows: aet, 2-aminoethanethiolate $NH_2CH_2CH_2S^-$; aes, 2-aminoethane selenolate $NH_2CH_2CH_2Se^-$; aese, 2-aminoethanesulfenate $NH_2CH_2CH_2SO^-$; aesi, 2-aminoethanesulfinate $NH_2CH_2CH_2SO_2^-$; mea, 2-(methylthio)ethylamine $NH_2CH_2CH_2SCH_3$; mseea, 2-(methylseleno)ethylamine $NH_2CH_2CH_2SeCH_3$.

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