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Preparation and Stereochemistry of Bis(ethylenediamine)cobalt(III) Complexes with Selenium Donor Atom

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Five optically active cobalt(III) complexes of [Co(bidentate-*N,Se*)(en)$_2$] type were prepared; here bidentate-*N,Se* denotes 2-aminoethaneselenolato (aes), 2-aminoethaneselenenato (aesee), 2-(methylseleno)ethylamine (mseea), 2-(ethylseleno)ethylamine (eseea), and 2-(benzylseleno)ethylamine (bseea). These complexes were characterized from their absorption, CD and ^{1}H NMR spectra. Of these complexes, the crystal structure of $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$](ClO$_4$)$_3$ was determined by the X-ray diffraction method. The red plate crystal was orthorhombic, space group $P2_12_12_1$, a=12.220(15), b=19.224(7), c=8.977(11) Å, Z=4, and the final R value was 0.087. The coordinated selenium atom takes the (R) configuration for the Λ isomer. The absorption and CD spectra of the five complexes are discussed in comparison with those of the corresponding cobalt(III) complexes containing a coordinated sulfur atom.

A few cobalt(III) complexes with selenium-containing ligand have been investigated,[1–4] but little information concerning their spectrochemical and stereochemical properties has been reported up to now. It is favorable to compare the properties of cobalt(III) complexes containing a selenium donor atom with those of the corresponding complexes containing a sulfur donor atom, which have been extensively studied.[5–13]

This work is concerned with the preparation and stereochemistry of cobalt(III) complexes with a coordinated selenium atom. The cobalt(III) complex with 2-aminoethaneselenolato ($NH_2CH_2CH_2Se^-$), [Co(aes)(en)$_2$]$^{2+}$, was optically resolved, and the optically active cobalt(III) complexes with 2-aminoethaneselenenato ($NH_2CH_2CH_2SeO^-$), $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aesee)(en)$_2$]$^{2+}$, 2-(methylseleno)ethylamine ($NH_2CH_2CH_2SeCH_3$), $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$, 2-(ethylseleno) ethylamine ($NH_2CH_2CH_2SeC_2H_5$), $(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$]$^{3+}$, and 2-(benzylseleno)ethylamine ($NH_2CH_2CH_2SeCH_2C_6H_5$), $(+)^{\mathrm{CD}}_{500}$-[Co(bseea)(en)$_2$]$^{3+}$, were derived from $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$]$^{2+}$.[14] The crystal structure of the selenoether complex, $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$, was determined by X-ray diffraction and was compared to that of the corresponding thioether complex, [Co(mea)(en)$_2$]$^{3+}$ (mea=2-(methylthio)ethylamine).[9] This is the first example of the structural analysis of the cobalt(III) complex with a selenoether donor atom. The absorption and CD spectra of the present complexes are discussed in comparison with those of the corresponding [Co(bidentate-*N,S*)(en)$_2$] type complexes.[9–13]

Experimental

1) Preparation and Resolution of the Complexes. *a) $(+)^{\mathrm{CD}}_{500}$-(2-Aminoethaneselenolato)bis(ethylenediamine)cobalt(III) Perchlorate.* *$(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$*: [Co(aes)(en)$_2$](NO$_3$)$_2$ was prepared by the method of Deutsch *et al.*[1] A solution containing 2.0 g of K$_2$[Sb$_2$(*d*-tart)$_2$]·3H$_2$O in 20 cm^3 of water was added with stirring to a solution containing 2.4 g of [Co(aes)(en)$_2$](NO$_3$)$_2$ in 80 cm^3 of water at 50 °C. The solution was stirred for 5 min, though fine dark brown crystals soon began to appear. The crystals were collected by filtration and it was found from a CD measurement that the crystals were the $(+)^{\mathrm{CD}}_{500}$ diastereomer with a small amount of the $(-)^{\mathrm{CD}}_{500}$ type. After the $(-)^{\mathrm{CD}}_{500}$ diastereomer contamination was removed by grinding in a mortar several times with 10 cm^3 of an aqueous solution of NaClO$_4$ (1.5 mol dm^{-3}), the remaining $(+)^{\mathrm{CD}}_{500}$ diastereomer was dissolved in an aqueous solution of NaClO$_4$. The solution was concentrated with a rotary evaporator until fine needle crystals of the selenolato complex appeared. After cooling in a refrigerator, crystals of $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$ were collected by filtration, and washed with ethanol and ether. Found: C, 14.81; H, 4.32; N, 13.96%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$=$C_6H_{22}N_5O_8Cl_2SeCo$: C, 14.38; H, 4.42; N, 13.97%.

b) $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-(2-Aminoethaneselenenato)bis(ethylenediamine)cobalt(III) Perchlorate. *$(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aesee)(en)$_2$](ClO$_4$)$_2$*: A calculated amount of 0.31 cm^3 of 1% aqueous H$_2$O$_2$ was added dropwise to a solution containing 0.05 g of $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$ in 1 cm^3 of water and the solution was stirred for 15 min. An orange-yellow precipitate was obtained from the reaction solution after the addition of 2-propanol. This complex was recrystallized from a small amount of water by adding ethanol. The selenenato complex obtained showed the identical absorption and CD spectra with those of the reaction solution, indicating that the $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$ isomer was selectively formed. Found: C, 13.96; H, 4.04; N, 13.35%. Calcd for $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aesee)(en)$_2$](ClO$_4$)$_2$=$C_6H_{22}N_5O_9Cl_2SeCo$: C, 13.93; H, 4.28; N, 13.54%.

c) $(+)^{\mathrm{CD}}_{500}$-(2-(Methylseleno)ethylamine)bis(ethylenediamine)cobalt(III) Perchlorate. *$(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]ClO$_4$)$_3$*: To a solution containing 0.05 g of $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$ in 1 cm^3 of water was added 1 cm^3 of dimethyl sulfate. The mixture was allowed to stand in a refrigerator overnight and separated into two layers. The orange-red upper layer was poured onto a column of QAE-Sephadex A-25 (ClO$_4^-$ form, 2 cm×20 cm), and the column was eluted with water. The eluate was concentrated with a rotary evaporator until red crystals appeared. The resultant red complex was recrystallized from a small amount of water and obtained as fairly large plate crystals. A piece of a crystal was used in the X-ray diffraction study. Found: C, 13.89; H, 3.94; N, 11.39%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$](ClO$_4$)$_3$=$C_7H_{25}N_5O_{12}Cl_3SeCo$: C, 13.65; H, 4.09; N, 11.37%.

d) $(+)^{\mathrm{CD}}_{500}$-(2-(Ethylseleno)ethylamine)bis(ethylenediamine)cobalt(III) Perchlorate. *$(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$](ClO$_4$)$_3$*: To a solution containing 0.05 g of $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$ in 2 cm^3 of *N,N*-dimethylformamide was added 0.25 g of ethyl iodide. The mixture was allowed to stand in a refrigerator for two days, whereupon the color of the solution turned from dark brown to dark red. *N,N*-Dimethylformamide and unreacted ethyl iodide were extracted into ether and to the remaining dark red oil was added a small amount of water. This solution was poured onto a column of QAE-Sephadex

A-25 (ClO$_4^-$ form, 2 cm×20 cm) and the column was eluted with water. The eluate was concentrated almost to dryness with a rotary evaporator and to this was added a small amount of ethanol. After cooling in a refrigerator, the resultant crystals were collected by filtration and washed with ethanol–ether (1:1) and ether. Found: C, 15.15; H, 4.19; N, 10.98%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$](ClO$_4$)$_3$=$C_8H_{27}N_5O_{12}Cl_3SeCo$: C, 15.26; H, 4.32; N, 11.12%.

e) $(+)^{\mathrm{CD}}_{500}$-(2-(Benzylseleno)ethylamine)bis(ethylenediamine)cobalt(III) Perchlorate. *$(+)^{\mathrm{CD}}_{500}$-[Co(bseea)(en)$_2$](ClO$_4$)$_3$*: This complex was prepared by a procedure similar to that used for $(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$](ClO$_4$)$_3$ described in *d*), using benzyl chloride instead of ethyl iodide. Found: C, 21.57; H, 4.11; N, 9.88%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(bseea)(en)$_2$](ClO$_4$)$_3$·1.5H$_2$O=$C_{13}H_{29}N_5O_{12}Cl_3SeCo\cdot 1.5H_2O$: C, 21.73; H, 4.49; N 9.74%.

f) $(+)^{\mathrm{CD}}_{500}$-(2-Aminoethanethiolato)bis(ethylenediamine) cobalt(III) Perchlorate. *$(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$*: This complex was prepared by a procedure similar to that used for $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$ described in *a*). $(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$ showed the same CD pattern as that of Λ-[Co(aet)(en)$_2$]$^{2+}$ reported by Yamanari *et al.*,[5] but the CD intensity of the former ($\Delta\varepsilon_{522}$=+1.37) are much higher than that of the latter ($\Delta\varepsilon_{522}$=+0.54). Found: C, 15.86; H, 4.90; N, 15.51%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$=$C_6H_{22}N_5O_8SCl_2Co$: C, 15.86; H, 4.88; N, 15.42%.

g) $(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$- and $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-(2-Aminoethanesulfenato)bis(ethylenediamine)cobalt(III) Perchlorate. *$(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$- and $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$](ClO$_4$)$_2$*: A calculated amount of 1.24 cm^3 of 1% aqueous H$_2$O$_2$ was added dropwise to a solution containing 0.2 g of $(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$ in 4 cm^3 of water and the mixture was stirred for 15 min. An orange precipitate was obtained from the reaction solution after adding a large amount of 2-propanol. This complex was dissolved in a small amount of water and then 2-propanol was added until fine orange crystals began to appear. After cooling in a refrigerator overnight, the crystals of $(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$](ClO$_4$)$_2$ was collected by filtration. $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$](ClO$_4$)$_2$ was obtained from the filtrate by the addition of 2-propanol. These two isomers were recrystallized twice from water by adding 2-propanol. $(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$ and $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$ aese isomers showed the same CD spectra as Λ-(*S*)- and Λ-(*R*)-[Co(aese)(en)$_2$]$^{2+}$, respectively, reported by Kita *et al.*[11] The formation ratio of the two isomers, Λ-(*S*) : Λ-(*R*), was about 1:3, which was evaluated from the CD spectra of the reaction solution. Found for $(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$ isomer: C, 15.52; H, 4.52; N, 14.68%. Found for $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$ isomer: C, 15.45; H, 4.47; N, 14.77%. Calcd for $(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$- and $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$](ClO$_4$)$_2$=$C_6H_{22}N_5O_9SCl_2Co$: C, 15.32; H, 4.71; N, 14.89%.

h) $(+)^{\mathrm{CD}}_{500}$-(2-(Methylthio, Ethylthio or Benzylthio)ethylamine)bis(ethylenediamine)cobalt(III) Nitrate. *$(+)^{\mathrm{CD}}_{500}$-[Co(mea, eea or bea)(en)$_2$](NO$_3$)$_3$*: These thioether complexes were prepared by a procedure similar to those used for selenoether complexes described in *c)—e)*, using $(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$](ClO$_4$)$_2$ instead of $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$](ClO$_4$)$_2$. The nitrate salts were obtained by the use of an anion exchange resin (QAE-Sephadex A-25, NO$_3^-$ form). $(+)^{\mathrm{CD}}_{500}$-[Co(mea or eea)(en)$_2$](NO$_3$)$_3$ showed the same CD spectra as Λ-(*R*)-[Co(mea or eea)(en)$_2$]$^{3+}$, reported by Yamanari *et al.*[5] Found for $(+)^{\mathrm{CD}}_{500}$ mea complex: C, 18.68; H, 5.53; N, 24.45%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(mea)(en)$_2$](NO$_3$)$_3$=$C_7H_{25}N_8O_9SCo$: C, 18.42; H, 5.52; N, 24.55%. Found for $(+)^{\mathrm{CD}}_{500}$ eea complex: C, 21.00; H 5.92; N, 22.97%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(eea)(en)$_2$](NO$_3$)$_3$·0.25C$_2$H$_5$OH=$C_8H_{27}N_8O_9SCo\cdot 0.25C_2H_5OH$: C, 21.19; H, 5.96; N, 23.25%. Found for $(+)^{\mathrm{CD}}_{500}$ bea complex: C, 28.23; H, 5.66; N, 20.23%. Calcd for $(+)^{\mathrm{CD}}_{500}$-[Co(bea)(en)$_2$](NO$_3$)$_3$·H$_2$O=$C_{13}H_{29}N_8O_9SCo\cdot H_2O$: C, 28.37; H, 5.68; N, 20.36%.

2) General Data. 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 ^{1}H 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 calculations were carried out on a FACOM M-200 computer at University of Tsukuba.

3) X-Ray Characterization. The unit cell parameters and intensity data were measured on a Rigaku-denki four circle diffractometer (AFC-5) with a graphite-monochromatized Mo *Kα* radiation. The unit cell parameters were determined by least-squares refinement based on 24 reflections. The systematic absences led to the space group P2$_1$2$_1$2$_1$. Crystal data: $C_7H_{25}N_5O_{12}Cl_3SeCo$, *M.W.*=615.6, a=12.220 (15), b=19.224(7), c=8.977(11) Å, V=2108.9(11) Å^3, orthorhombic, space group P2$_1$2$_1$2$_1$, d_x=1.91 g cm^{-3}, d_c=1.92 g cm^{-3}, and Z=4.

The intensity data were collected by the ω–2θ scan technique up to 2θ=60° with a scan rate of 4° min^{-1}. The intensity data were converted to the F_o data in the usual manner. Absorption corrections were not applied. A total of 2176 independent reflections with $|F_o|>3\sigma(|F_o|)$ were considered as 'observed' and used for the structure analysis.

4) Determination of the Crystal Structure. The positions of the cobalt and selenium atoms were obtained from the three-dimensional Patterson function. The difference-Fourier maps based on the cobalt and selenium positions revealed all non-hydrogen atom. The structure was refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms (program RFINE by L. W. Finger, which was modified by H. Horiuchi, was used). The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.[15] The final residual values were R=0.090 and R_w=0.119, respectively. We attempted to determine the absolute configuration of the complex cation by an anomalous-scattering technique. When the refinements were carried out by use of a set of the atomic parameters containing the Λ configuration of the complex cation, the residual values converged to R=0.087 and R_w=0.114, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the Δ configuration) resulted in the residual values of R=0.095 and R_w=0.124, respectively. These facts suggest that the former is probably the correct choice, namely, the complex cation has the Λ configuration. This absolute configuration coincides with the result that $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$ is assigned to the Λ configuration based on the CD spectral behavior (*vide infra*).

The final positional parameters are listed in Table 1. List of structure factors (Table A), anisotropic thermal parameters (Table B), bond lengths and angles for perchlorate ion (Table C), and the projected figure of the crystal structure, which indicated distance in the range of 2.90—3.04 Å, are kept at the Chemical Society of Japan (Document No. 8445).

Results and Discussion

Structure of $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$. The perspective drawing of the $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$ ion is shown in Fig. 1. The bond lengths and angles are summarized in Table. 2. The coordination geometry around the cobalt atom is approximately octahedral. The selenium atom coordinates to the cobalt atom and the mseea ligand acts as a bidentate. The asymmetric selenium atom in $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$, which has the Λ configuration, takes the (*R*) configuration. This result supports the prediction that a steric interaction occurs between the methyl group and the ethylenediamine chelate ring, N2-C4-C5-N3, if the asymmetric selenium donor atom takes the (*S*) configuration. The methyl group of this isomer takes the axial orientation, which causes the chelate ring of 2-(methylseleno)ethylamine, Se-C2-C3-N1, to have the gauche form with λ conformation (Fig. 1 and Table 3), though the methyl group is expected to take the equatorial orientation in general.[16,17] This fact seems to point out that the methyl group and the amino groups, N3 and N4, repel each other, if the methyl group takes the equatorial orientation. The ethylenediamine chelate ring, N4-C6-C7-N5, takes the reasonable gauche form with δ conformation (Fig. 1 and Table 3). The other ethylenediamine chelate ring, N2-C4-C5-N3, takes the unusual gauche form with λ conformation (Fig. 1 and Table 3).

The bond lengths and angles are similar to those for the [Co(L)(en)$_2$] type complexes, where L denotes selenium- or sulfur-containing ligand such as 2-aminoethaneselenolato,[1] 2-aminoethaneseleninato,[2] and 2-(methylthio)ethylamine.[9] The average Co-N

TABLE 1. POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	$B_{eq}/Å^2$ [a]
Co	0.0383(2)	−0.1444(1)	0.3033(2)	3.02
Se	−0.1078(1)	−0.0720(1)	0.2191(3)	5.22
N1	0.0308(12)	−0.0951(7)	0.4976(16)	4.18
N2	−0.0741(10)	−0.2122(8)	0.3687(17)	3.77
N3	0.0402(12)	−0.1953(9)	0.1192(16)	4.90
N4	0.1552(10)	−0.0840(7)	0.2349(19)	4.60
N5	0.1569(10)	−0.2016(8)	0.3859(18)	4.11
C1	−0.0400(24)	0.0092(13)	0.1150(33)	8.69
C2	−0.1316(19)	−0.0357(13)	0.4196(26)	7.06
C3	−0.0253(20)	−0.0257(12)	0.4917(28)	6.69
C4	−0.1130(28)	−0.2463(22)	0.2291(44)	16.71
C5	−0.0166(23)	−0.2645(12)	0.1284(27)	7.43
C6	0.2663(14)	−0.1210(11)	0.2548(29)	6.42
C7	0.2664(14)	−0.1606(13)	0.3903(29)	6.95
CL1	0.3085(4)	−0.3489(3)	0.2018(5)	4.63
CL2	0.7182(5)	−0.4203(3)	0.1679(7)	5.74
CL3	0.5909(4)	−0.1714(3)	0.3222(7)	5.86
O11	0.3504(15)	−0.3295(9)	0.3385(20)	8.29[b]
O12	0.3859(26)	−0.3664(16)	0.1078(36)	16.08[b]
O13	0.2657(22)	−0.2884(14)	0.1209(31)	13.74[b]
O14	0.2218(33)	−0.3944(19)	0.2235(45)	21.41[b]
O21	0.8232(35)	−0.4252(23)	0.1180(49)	22.83[b]
O22	0.7268(21)	−0.4373(13)	0.3151(30)	13.04[b]
O23	0.6918(27)	−0.3592(18)	0.1146(40)	17.93[b]
O24	0.6404(30)	−0.4566(20)	0.1096(43)	20.41[b]
O31	0.6914(22)	−0.1624(13)	0.3681(30)	13.27[b]
O32	0.5252(24)	−0.1708(16)	0.4616(33)	14.55[b]
O33	0.5692(27)	−0.2453(20)	0.3186(38)	18.25[b]
O34	0.5343(38)	−0.1474(24)	0.2063(51)	25.84[b]

a) B_{eq} is the equivalent isotropic temperature factors defined by Hamilton.[19] b) Isotropic temperature factor.

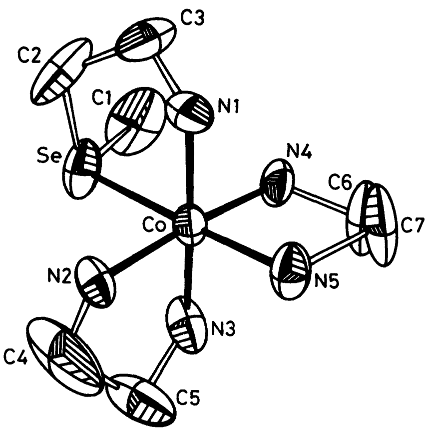

Fig. 1. A perspective drawing of Δ-$(+)^{CD}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$ with the numbering scheme of atoms.

TABLE 2. INTERMOLECULAR DISTANCES AND BOND ANGLES (WITH e.s.d.'s)

	(a) Bond distances (l/Å)		
Co-Se	2.386(3)	Co-N1	1.987(15)
Co-N2	1.983(14)	Co-N3	1.921(15)
Co-N4	1.940(14)	Co-N5	1.964(14)
Se-C1	1.999(26)	Se-C2	1.952(24)
N1-C3	1.501(27)	N2-C4	1.492(42)
N3-C5	1.503(29)	N4-C6	1.543(22)
N5-C7	1.554(23)	C2-C3	1.464(34)
C4-C5	1.525(45)	C6-C7	1.435(36)
	(b) Bond angles (ϕ/°)		
Se-Co-N1	88.0(4)	Se-Co-N2	87.7(4)
Se-Co-N3	91.9(5)	Se-Co-N4	95.8(4)
Se-Co-N5	176.2(5)	N1-Co-N2	91.2(6)
N1-Co-N3	177.1(6)	N1-Co-N4	91.5(7)
N1-Co-N5	88.2(6)	N2-Co-N3	85.9(7)
N2-Co-N4	175.6(6)	N2-Co-N5	91.7(6)
N3-Co-N4	91.4(7)	N3-Co-N5	91.8(7)
N4-Co-N5	84.9(6)	Co-Se-C1	107.1(8)
Co-Se-C2	91.6(7)	C1-Se-C2	102.3(11)
Co-N1-C3	114.4(13)	Co-N2-C4	105.1(17)
Co-N3-C5	113.5(13)	Co-N4-C6	109.6(11)
Co-N5-C7	111.1(12)	Se-N2-C3	108.7(16)
N1-C3-C2	107.8(18)	N2-C4-C5	110.6(25)
N3-C5-C4	100.8(21)	N4-C6-C7	110.1(16)
N5-C7-C6	104.3(16)		

TABLE 3. DISPLACEMENTS OF ATOMS FROM THE LEAST-SQUARES PLANE (d/Å)

2-(Methylseleno)ethylamine chelate ring

Plane 1, $0.66326X-0.67175Y-0.32990Z+2.45197=0$
Co 0.0000 Se −0.0000 N1 −0.0000 C1 1.9064
C2 −0.3179 C3 0.4590

Ethylenediamine chelate ring

Plane 2, $-0.71865X-0.59399Y-0.36156Z+2.96969=0$
Co 0.0000 N2 0.0000 N3 0.0000 C4 0.4060
C5 −0.3208
Plane 3, $0.04888X+0.51340Y-0.85676Z+0.88497=0$
Co −0.0001 N4 0.0001 N5 0.0001 C6 0.2782
C7 −0.3723

The X, Y, and Z coordinates in Å are referred to the crystallographic axes.

length is 1.959 Å and no significant trans effect is observed, as well as the cobalt(III) complexes with coordinated thioether sulfur atom.[9,18] The bond lengths of Co-Se, Se-Cl, and Se-C2 (2.386, 1.999, and 1.952 Å) are longer than the bond lengths of Co-S (2.267) and S-C (1.817 and 1.834 Å) in the corresponding [Co(mea)(en)$_2$]$^{3+}$,[9] and this results in a smaller bond angle of Co-Se-C2 (91.6°) that the angle of the corresponding Co-S-C (97.9°).[9] The other two bond angles around the selenium atom (Co-Se-Cl=107.1° and Cl-Se-C2=102.3°) are reasonable for the tetrahedral geometry in contrast to those around the sulfur atom in [Co(mea)(en)$_2$]$^{3+}$ (Co-S-C=114.2° and C-S-C=99.4°).[9] This fact seems to depend on the longer bond lengths of Se-Co and Se-Cl.

Absorption and CD Spectra. The electronic absorption and CD spectra of the selenolato complex, $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$]$^{2+}$, selenenato complex, $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aesee)(en)$_2$]$^{2+}$, and selenoether complexes, $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$, $(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$]$^{3+}$, and $(+)^{\mathrm{CD}}_{500}$-[Co(bseea)(en)$_2$]$^{3+}$, are shown in Figs. 2—5, together with those of the corresponding [Co(bidentate-*N*,*S*)(en)$_2$] type complexes; the data are summarized in Tables 4 and 5. The absorption spectral behavior of the cobalt(III) complexes which belong to [Co(*N*)$_5$(*Se*)] type is quite similar to those of the corresponding [Co(*N*)$_5$(*S*)] type complexes (Figs. 2—6).[5,9—12] The intense absorption bands at around 32—36×10^3 cm^{-1} are assigned to the charge transfer ones due to the coordinated selenium atom, which correspond to the so-called sulfur-to-metal charge transfer band.[5,9—12] The charge transfer bands of the selenolato, selenenato and selenoether complexes commonly shift to a lower energy than those of the corresponding thiolato, sulfenato and thioether ones, respectively (Figs. 2—6).[5,9—12] Of these complexes, [Co(aesee)(en)$_2$]$^{2+}$ shows another intense band at 27.55×10^3 cm^{-1} (Fig. 3). This band corresponds well with the characteristic band (*ca.* 27.0×10^3 cm^{-1}) of the sulfenato complex, [Co(aese)(en)$_2$]$^{2+}$ (Fig. 3).[10—12] Therefore, the band at 27.55×10^3 cm^{-1} seems to be characteristic for the selenenato complex as well as for the sulfenato complex.

In the first absorption band region, [Co(aes)(en)$_2$]$^{2+}$ shows an explicit shoulder on the lower energy side of the major peak (*ca.* 16.6×10^3 cm^{-1}) as well as [Co(aet)(en)$_2$]$^{2+}$ (Fig. 2).[5] This kind of shoulder was also observed in the absorption spectra of the cobalt(III) complexes with thiolato-type ligand such as L-cysteinate[7,8] and D- or L-penicillaminate,[8,13] and

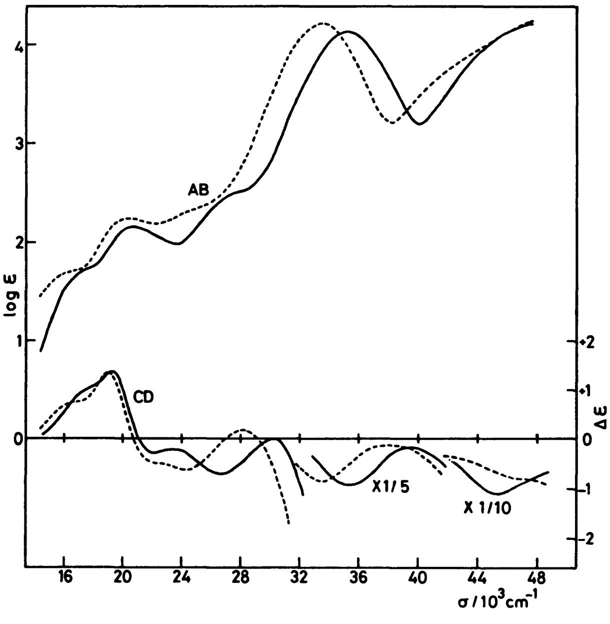

Fig. 2. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$]$^{2+}$ (----) and $(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$]$^{2+}$ (——).

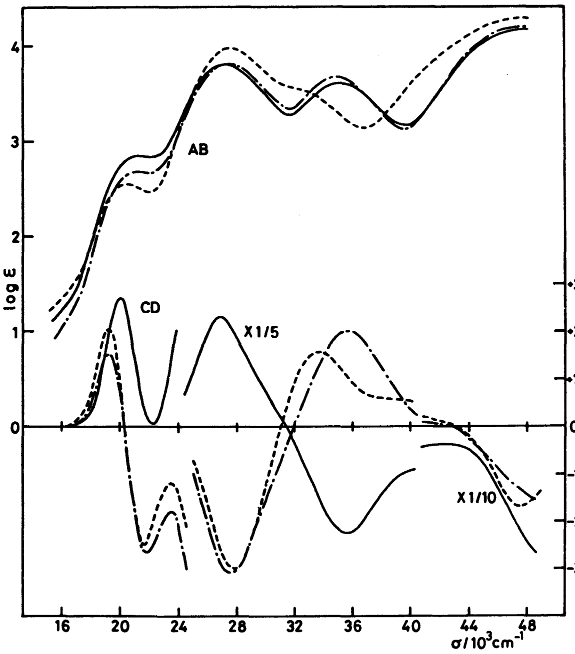

Fig. 3. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aesee)(en)$_2$]$^{2+}$ (----), $(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$]$^{2+}$ (— — —) and $(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$]$^{2+}$ (——).

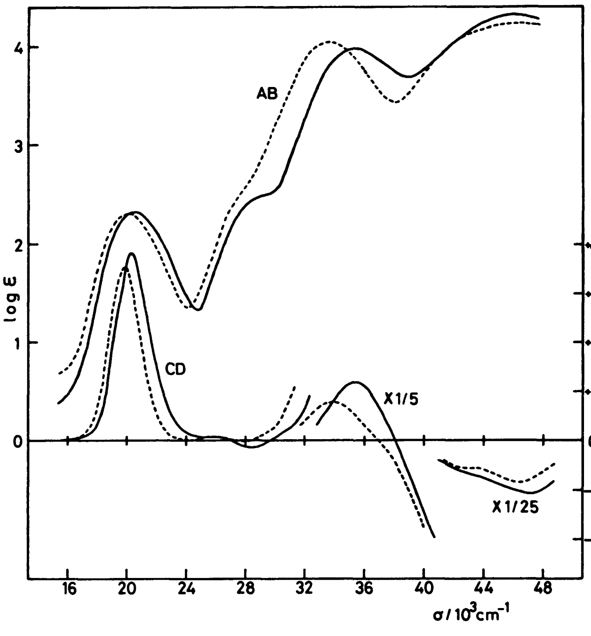

Fig. 4. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$ (----) and $(+)^{\mathrm{CD}}_{500}$-[Co(mea)(en)$_2$]$^{3+}$ (——).

accordingly, this band seems to be also characteristic for the selenolato coordination. The mseea, eseea and bseea complexes show a rather sharp first absorption band without a shoulder as the case of the corresponding thioether complexes (Figs. 4—6).[5,9]

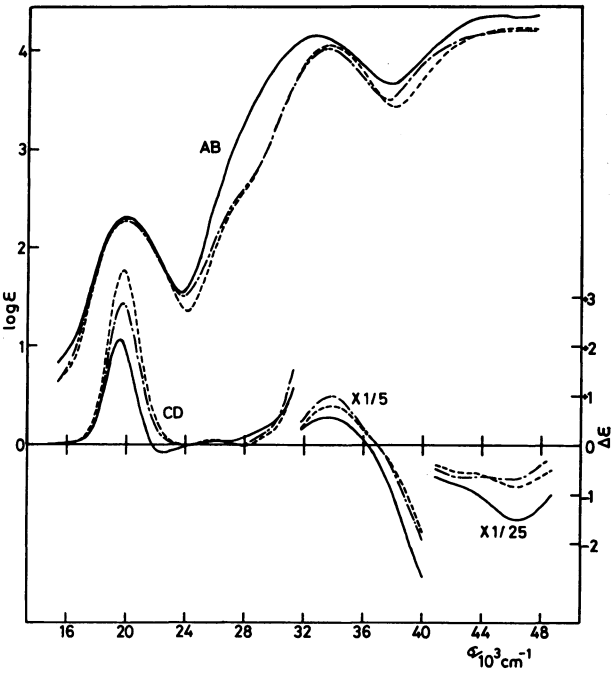

Fig. 5. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$ (----), $(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$]$^{3+}$ (—–—), and $(+)^{\mathrm{CD}}_{500}$-[Co(bseea)(en)$_2$]$^{3+}$ (——).

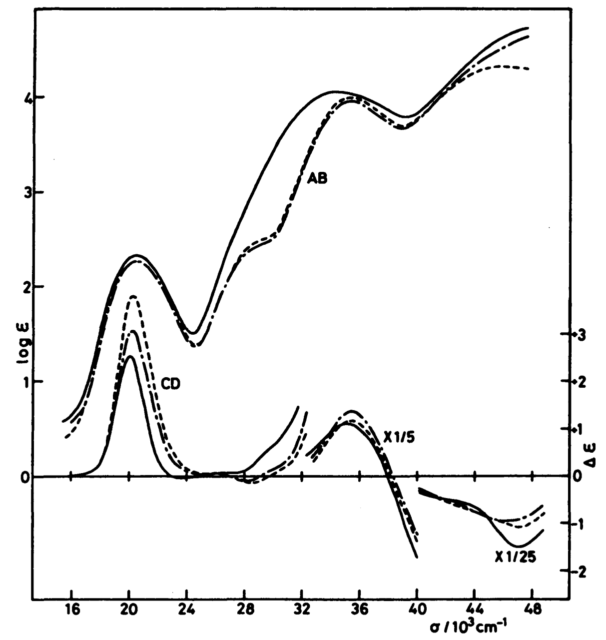

Fig. 6. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{500}$-[Co(mea)(en)$_2$]$^{3+}$ (----), $(+)^{\mathrm{CD}}_{500}$-[Co(eea)(en)$_2$]$^{3+}$ (—–—), and $(+)^{\mathrm{CD}}_{500}$-[Co(bea)(en)$_2$]$^{3+}$ (——).

TABLE 4. ABSORPTION DATA OF [Co(bidentate-*N,Se* OR -*N,S*)(en)$_2$] TYPE COMPLEXES

Complex	First band	Second band	Charge transfer band
$(+)^{\mathrm{CD}}_{500}$-[Co(aes)(en)$_2$]$^{2+}$	16.5 (1.71 sh) 20.35 (2.24)	24.7 (2.33 sh)	33.44 (4.22)
$(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aesee)(en)$_2$]$^{2+}$	20.45 (2.55)		27.55 (3.99) 32.0 (3.55 sh) 47.85 (4.30)
$(+)^{\mathrm{CD}}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$	20.00 (2.30)		33.56 (4.06) 46.30 (4.24)
$(+)^{\mathrm{CD}}_{500}$-[Co(eseea)(en)$_2$]$^{3+}$	19.96 (2.27)		33.44 (4.03) 46.51 (4.22)
$(+)^{\mathrm{CD}}_{500}$-[Co(bseea)(en)$_2$]$^{3+}$	19.92 (2.31)		32.57 (4.16) 44.84 (4.36)
$(+)^{\mathrm{CD}}_{500}$-[Co(aet)(en)$_2$]$^{2+}$	17.5 (1.72 sh) 20.66 (2.16)	28.2 (2.52 sh)	35.21 (4.13) 48.78 (4.22)
$(+)^{\mathrm{CD}}_{500}\cdot(-)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$]$^{2+}$	21.12 (2.68)		27.32 (3.82) 34.84 (3.68) 49.26 (4.21)
$(+)^{\mathrm{CD}}_{500}\cdot(+)^{\mathrm{CD}}_{360}$-[Co(aese)(en)$_2$]$^{2+}$	21.12 (2.85)		26.99 (3.81) 35.03 (3.61) 49.26 (4.18)
$(+)^{\mathrm{CD}}_{500}$-[Co(mea)(en)$_2$]$^{3+}$	20.47 (2.32)	29.3 (2.50 sh)	35.34 (3.99) 45.66 (4.32)
$(+)^{\mathrm{CD}}_{500}$-[Co(eea)(en)$_2$]$^{3+}$	20.45 (2.26)	29.4 (2.45 sh)	35.34 (3.95) 48.90 (4.63)
$(+)^{\mathrm{CD}}_{500}$-[Co(bea)(en)$_2$]$^{3+}$	20.45 (2.33)		34.31 (4.05) 49.0 (4.75 sh)

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

TABLE 5. CD DATA OF [Co(bidentate-N,Se OR -N,S)(en)$_2$] TYPE COMPLEXES

Complex	First band	Second band	Charge transfer band
$(+)^{\rm CD}_{500}$-[Co(aes)(en)$_2$]$^{2+}$	16.6 (+0.75 sh)	24.45 (−0.61)	33.44 (−4.26)
	19.01 (+1.35)	28.17 (+0.18)	
	22.2 (−0.47 sh)		
$(+)^{\rm CD}_{500}\cdot(-)^{\rm CD}_{360}$-[Co(aesee)(en)$_2$]$^{2+}$	19.23 (+2.04)		27.78 (−15.04)
	22.12 (−2.25)		33.56 (+7.80)
			38.5 (+2.95 sh)
			47.62 (−16.9)
$(+)^{\rm CD}_{500}$-[Co(mseea)(en)$_2$]$^{3+}$	19.80 (+3.55)	25.97 (+0.10)	33.90 (+3.98)
			46.3 (−20.8)
$(+)^{\rm CD}_{500}$-[Co(eseea)(en)$_2$]$^{3+}$	19.76 (+2.87)	25.97 (+0.08)	33.90 (+5.05)
			45.7 (−16.8)
$(+)^{\rm CD}_{500}$-[Co(bseea)(en)$_2$]$^{3+}$	19.61 (+2.15)	26.32 (+0.07)	33.56 (+2.85)
	22.47 (−0.15)		46.3 (−37.2)
$(+)^{\rm CD}_{500}$-[Co(aet)(en)$_2$]$^{2+}$	17.5 (+1.00 sh)	26.67 (−0.71)	35.34 (−4.62)
	19.27 (+1.37)		45.5 (−11.1)
	22.08 (−0.29)		
$(+)^{\rm CD}_{500}\cdot(-)^{\rm CD}_{360}$-[Co(aese)(en)$_2$]$^{2+}$	19.27 (+1.53)		27.55 (−15.39)
	21.83 (−2.65)		35.59 (+10.24)
			41.7 (+0.64 sh)
			48.8 (−15.8)
$(+)^{\rm CD}_{500}\cdot(+)^{\rm CD}_{360}$-[Co(aese)(en)$_2$]$^{2+}$	19.96 (+2.72)		26.88 (+11.56)
			35.59 (−11.29)
			40.5 (−4.28 sh)
$(+)^{\rm CD}_{500}$-[Co(mea)(en)$_2$]$^{3+}$	20.20 (+3.82)	28.41 (−0.15)	35.46 (+5.92)
			47.1 (−27.5)
$(+)^{\rm CD}_{500}$-[Co(eea)(en)$_2$]$^{3+}$	20.20 (+3.08)	28.17 (−0.10)	35.46 (+6.90)
			45.9 (−23.1)
$(+)^{\rm CD}_{500}$-[Co(bea)(en)$_2$]$^{3+}$	20.04 (+2.54)		35.09 (+5.47)
	23.53 (−0.02)		47.2 (−37.6)

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

The aesee complex shows the first absorption band with a large molar absorption coefficient and it seems to be affected by the intense charge transfer band at 27.55×10^3 cm^{-1} (Fig. 3). The first absorption bands of the selenolato, selenenato, and selenoether complexes shift to a lower energy than those of the corresponding thiolato, sulfenato, and thioether complexes,[5,9–12] respectively (Figs. 2—6), indicating that the order of the ligand field strength is $S>Se$.

The Δ and Λ isomers are possible for [Co(aes)(en)$_2$]$^{2+}$. As shown in Fig. 2, the CD spectrum of $(+)^{\rm CD}_{500}$-[Co(aes)(en)$_2$]$^{2+}$ agrees with that of Λ-$(+)^{\rm CD}_{500}$-[Co(aet)(en)$_2$]$^{2+}$ in the whole region,[5] and then the $(+)^{\rm CD}_{500}$ aes isomer is assignable to the Λ configuration. Taking the asymmetric selenium donor atom, (R) and (S), into consideration, four isomers, Δ-(R), Δ-(S), Λ-(R), and Λ-(S), are possible for each of [Co(aesee)(en)$_2$]$^{2+}$, [Co(mseea)(en)$_2$]$^{3+}$, [Co(eseea)(en)$_2$]$^{3+}$, and [Co(bseea)(en)$_2$]$^{3+}$. In contrast to the fact that two isomers, Λ-(R) and Λ-(S), were formed for [Co(aese)(en)$_2$]$^{2+}$ (Λ-(R):Λ-(S)=3:1), $(+)^{\rm CD}_{500}\cdot(-)^{\rm CD}_{360}$-[Co(aesee)(en)$_2$]$^{2+}$ was selectively formed by the stoichiometric oxidation reaction of Λ-$(+)^{\rm CD}_{500}$-[Co(aes)(en)$_2$]$^{2+}$ with H_2O_2. The $(+)^{\rm CD}_{500}\cdot(-)^{\rm CD}_{360}$ aesee isomer shows quite similar CD spectrum to that of the Λ-(R) aese isomer (Fig. 3),[11] and then it is suggested that the $(+)^{\rm CD}_{500}\cdot(-)^{\rm CD}_{360}$ aesee isomer takes the Λ-(R) configuration. This stereoselectivity may suggest that there is an intramolecular hydrogen bond between the selenenato or sulfenato oxygen atom and the adjacent amino proton in Λ-(R)-[Co(aesee or aese)(en)$_2$]$^{2+}$ and the hydrogen bond stabilizes the Λ-(R) configuration. The hydrogen bond is more favorable for the Λ-(R) aesee isomer than for the Λ-(R) aese one, because the bond lengths of Co–Se and Se–O are longer than those of Co–S and S–O, respectively.[1,2] The $(+)^{\rm CD}_{500}$ mseea, eseea and bseea isomers, which were derived from Λ-$(+)^{\rm CD}_{500}$-[Co(aes)(en)$_2$]$^{2+}$, show a positive CD band (*ca.* 19.7×10^3 cm^{-1}) whose intensity decreases with the order of the mseea, eseea, and bseea isomers, though the bseea isomer shows a weak negative CD band at the higher energy side in the first absorption band region. A similar CD spectral behavior was observed for a series of the corresponding thioether isomers, $(+)^{\rm CD}_{500}$ mea, eea, and bea (Fig. 6). Taking these facts and the assignments of the $(+)^{\rm CD}_{500}$ mea and eea isomers[5] into consideration, the $(+)^{\rm CD}_{500}$ mseea, eseea, bseea, and bea isomers are assigned to the Λ configuration. The ^{1}H NMR spectrum of the $(+)^{\rm CD}_{500}$ mseea isomer exhibits a single peak in the methyl protons region (2.26 ppm from DSS) and that of the $(+)^{\mathrm{CD}}_{500}$ eseea isomer one set of triplet peaks (centered at 1.57 ppm). The $(+)^{\mathrm{CD}}_{500}$ bseea isomer shows a single peak due to the aromatic protons (7.52 ppm). The ^{1}H NMR spectral behavior of the selenoether isomers is in line with that of the corresponding thioether isomers.[5,9] Molecular model constructions of the selenoether and thioether complexes reveal that the Λ-(R) configuration is preferable, because the *Se*- or *S*-alkyl group in the Λ-(S) configuration have a nonbonding interaction with the adjacent ethylenediamine chelate ring. Moreover, the X-ray structural analysis indicates that the $(+)^{\mathrm{CD}}_{500}$ mseea isomer has the (R) configuration for the coordinated selenium atom when the isomer takes the Λ configuration. Based on these results, it is suggested that the $(+)^{\mathrm{CD}}_{500}$ selenoether and thioether isomers take selectively the Λ-(R) configuration in solution.

In the charge transfer band region, the Λ-(R) selenoether and thioether isomers show one positive CD band, while Λ-$[\mathrm{Co(aes)(en)_2}]^{2+}$, Λ-$[\mathrm{Co(aet)(en)_2}]^{2+}$ and Λ-$[\mathrm{Co(aesi}\text{-}N,S)(en)_2]^{2+}$ (aesi=2-aminoethanesulfinato),[2] which have no chirality due to the chalcogen donor atom, show a negative one (Figs. 2 and 4—6). This fact suggests that the CD band in this region is contributed by not only the configurational chirality due to the skew pair of chelate rings but also the chirality of the selenium or sulfur donor atom.

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