Characterization of Cobalt(III) Complex with 2-Aminoethaneseleninate. Spontaneous Resolution and Crystal Structure of $(-)^{CD}_{500}$-(2-Aminoethaneseleninato)bis(ethylenediamine)cobalt(III) Nitrate

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The crystal structure and the absolute configuration of the spontaneously resolved title complex cation, $(-)^{CD}_{500}$-$[Co(aesei)(en)_2]^{2+}$, has been determined by X-ray diffraction. The red crystalline needle was monoclinic, space group $P2_1$, $a=9.572(4)$, $b=10.410(3)$, $c=8.838(5)$ Å, $\beta=115.35(3)°$, $Z=2$, and the final R value was 0.035 for 2358 independent reflections with $|F_0|>3\sigma(|F_0|)$. The crystal used showed a negative CD value at 500 nm and had Δ configuration. The 2-aminoethaneseleninate is bound to the cobalt atom by the nitrogen and oxygen atoms, and the asymmetric selenium atom takes an S configuration. The value of the protonation constant (pKa) was determined to be 1.91 ± 0.05, on the basis of the major absorption spectral change at 304 nm of the title complex by spectrophotometric titration ($\mu=1.0$ mol dm^{-3} ($NaClO_4$) and 25 °C). The electronic absorption and CD spectral behavior were compared with those of the related sulfinato complexes, in which the *S*-bonded sulfinato complex, $(+)^{CD}_{500}$-$[Co(S(O)_2CH_2CH_2NH_2)(en)_2]^{2+}$, was resolved in this work.

The structure and bonding for the cobalt(III) complexes with selenium- or sulfur-containing bidentate ligands have been studied in some detail.[1-12] These complexes have only Co–Se or Co–S bonding, except for the (2-aminoethanesulfinato-N,O)bis(ethylenediamine)cobalt(III), $[Co(aesi-N,O)(en)_2]^{2+}$, obtained by photochemical preparation.[6,7] The (2-aminoethaneseleninato)bis(ethylenediamine)-cobalt(III), $[Co(aesei)(en)_2]^{2+}$, was obtained by treatment of the (2-aminoethaneselenolato)bis(ethylenediamine)cobalt(III), $[Co(aes)(en)_2]^{2+}$, with excess hydrogen peroxide. The aesei acts as a bidentate ligand and takes either of the two coordination modes, aesei-N,Se or aesei-N,O. The *S*-bonded sulfinato complex, which is obtained by a similar procedure to the aesei complex, takes up the nitrogen and sulfur coordinations, and the primary coordination sphere of the cobalt atom remains intact throughout the oxidation process.[2,10] Therefore, there has been no real evidence for the coordination mode of the seleninato complex except for the anticipation on the basis of the electronic absorption spectra of the related sulfinato complexes.[2,6,7]

The present paper deals with the preparation and spontaneous resolution of $[Co(aesei)(en)_2](NO_3)_2$. The crystal structure and absolute configuration of the $(-)^{CD}_{500}$ aesei isomer are established by X-ray diffraction studies and an investigation based on the CD spectra. The electronic absorption and CD spectra in solution of the aesei complex are discussed in comparison with the related sulfinato complexes, in which the $[Co(aesi-N,S)(en)_2]^{2+}$ isomer was resolved in this work. A preliminary report has been presented.[12]

Experimental

1) Preparation and Resolution of the Complexes. a) Spontaneous Resolution of $[Co(aesei)(en)_2](NO_3)_2$: An excess amount of 5% aqueous H_2O_2 (5 cm^3) was added to a solution containing 0.4 g of $[Co(aes)(en)_2](NO_3)_2$[3] in 7 cm^3 of water, followed by addition of 2 cm^3 of 15% HNO_3. The solution was stirred for 20 min and stood in a refrigerator for a day. The solution was adjusted to pH 7 by the addition of an queous solution of NaOH and concentrated with a rotary evaporator. The resultant seleninato complex was collected by filtration. The spontaneous resolution of the nitrate salt was observed for the needle crystals as follows; the racemic nitrate was dissolved in a small amount of water at room temperature and when the solution was kept in a refrigerator overnight, the spontaneously resolved red complex was obtained as fairly large needle crystals. A piece of one of these crystals was used for the X-ray diffraction study.

b) $(+)^{CD}_{500}$-[Co(aesei)(en)$_2$](ClO$_4$)$_2$: The $(+)^{CD}_{500}$ aesei isomer was obtained by the same procedure as that used in a), using the $(+)^{CD}_{500}$-$[Co(aes)(en)_2](ClO_4)_2$ isomer[11] instead of the racemic nitrate. This isomer shows the identical electronic absorption and CD spectra as the spontaneously resolved $(+)^{CD}_{500}$ isomer. Found: C, 13.21; H, 4.27; N, 12.94%. Calcd for $[Co(aesei)(en)_2](ClO_4)_2\cdot0.5H_2O=CoC_6H_{22}N_5O_{10}SeCl_2\cdot0.5H_2O$: C, 13.29; H, 4.28; N, 12.92%.

c) $(+)^{CD}_{500}$-[Co(asei-N,S)(en)$_2$](ClO$_4$)$_2$: This $(+)^{CD}_{500}$ aesi isomer was obtained by the same procedure as that used in b), using the $(+)^{CD}_{500}$-$[Co(SCH_2CH_2NH_2)(en)_2](ClO_4)_2$ isomer[9] instead of the $(+)^{CD}_{500}$-$[Co(aes)(en)_2](ClO_4)_2$ one. The analytical result was obtained from the racemic nitrate salt. Found: C, 16.71; H, 5.62; N, 22.91%. Calcd for $[Co(aesi-N,S)(en)_2](NO_3)_2\cdot H_2O=CoC_6H_{22}N_7O_8S\cdot H_2O$: C, 16.79; H, 5.63; N, 22.84%.

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 aqueous solution at room temperature. The calculations were carried out on a FACOM M-200 computer at the University of Tsukuba. The protonation constant was determined by measuring the adsorbance at 304 nm in aqueous media at 25 °C and $\mu=1.0$ mol dm^{-3} ($NaClO_4$). The hydrogen ion concentration was measured with a HORIBA pH meter (F7-SS).

3) X-Ray Characterization. The unit cell parameters and intensity data were measured on a Rigaku-denki automated four-circle diffractometer (AFC-5) with a graphitemonochromatized Mo $K\alpha$ radiation ($\lambda=0.710690$ Å). A spontaneously resolved needle crystal with approximate dimensions of $0.03\times0.07\times0.7$ mm^3 was used for the intensity measurements. The unit cell parameters were determined by least-squares refinement based on 20 reflections. The systematic absence led to the space group $P2_1$. Crystal data: $CoC_6H_{22}N_7O_8Se$, $M.W.=458.2$, monoclinic, space group $P2_1$, $a=9.572(4)$, $b=10.410(3)$, $c=8.838(5)$ Å, $\beta=115.35(3)°$, $V=795.9(6)$ Å^3, $D_m=1.90$ g cm^{-3} (by the flotation), $D_x=1.91$ g cm^{-3}, and $Z=2$.

The intensity data were collected by the ω-2θ scan technique with a scan rate of 3 ° min^{-1}. During the course

of the data collection, three reflections were monitored every 40 reflections. The intensity data were converted to the Fo data in the usual manner. Absorption corrections were not applied. A total of 2603 reflections up to $2\theta = 60°$ was collected, of which 2358 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as 'observed' and used for the structure analysis.

Determination of the Crystal Structure

1) Solution and Refinement of 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 atoms. 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, as modified by H. Horiuchi, was used). The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.[13] The final residual values were $R = 0.036$ and $R_w = 0.049$, respectively.

2) Determination of the Absolute Configuration. The absolute configuration was determined by the anomalous scattering technique. The anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for all the non-hydrogen atoms were taken from the literature.[13] When the refinements were carried out by the use of a set of the atomic parameters containing the Δ configuration of the complex cation, the residual values converged to $R = 0.035$ and $R_w = 0.046$, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the Λ configuration) resulted in the residual values of $R = 0.041$ and $R_w = 0.055$, respectively. These facts indicate that the former is probably the correct choice, namely, the complex cation has the Δ configuration. A similar relationship between the residual values and the absolute configuration was observed for the determination of the crystal structure of cobalt(III) complexes with the *S*-(2-aminoethyl)-L-homocysteinate.[14,15] The crystal, which was used for this X-ray intensity measurement, showed the enantiomeric CD curve for that of the $(+)^{CD}_{500}$-[Co(aesei)(en)$_2$]$^{2+}$ isomer derived from the $(+)^{CD}_{500}$-[Co(aes)(en)$_2$]$^{2+}$ one. This is in line with the result that the $(+)^{CD}_{500}$ aesei isomer has been assigned to the Δ configuration from the comparison with the CD spectrum of the Λ-[Co(mea)(en)$_2$]$^{3+}$ isomer mea; 2-(methylthio)ethylamine).[9,11]

The final atomic parameters with their estimated standard deviations are given in Table 1. A list of structure factors and anisotropic thermal parameters of the non-hydrogen atoms is kept at the Chemical Society of Japan as Document No. 8416.

TABLE 1. POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Co	0.25167(6)	0.0	0.11276(7)	1.81
Se	-0.06427(5)	0.04554(8)	0.15590(6)	2.39
O1	0.0520(4)	-0.0458(4)	0.0985(4)	2.29
O2	-0.0878(5)	0.1826(4)	0.0473(5)	3.04
N1	0.1851(5)	0.1665(4)	-0.0006(5)	2.54
N2	0.1715(5)	-0.0733(4)	-0.1139(5)	2.47
N3	0.3147(5)	-0.1705(5)	0.2097(5)	2.60
N4	0.3256(5)	0.0842(5)	0.3356(5)	2.92
N5	0.4619(5)	0.0146(5)	0.1258(6)	3.03
C1	0.0851(7)	0.1023(7)	0.3766(6)	2.99
C2	0.2217(7)	0.1724(6)	0.3701(7)	3.15
C3	0.1390(8)	0.1502(6)	-0.1835(7)	3.47
C4	0.0607(7)	0.0220(6)	-0.2290(6)	3.23
C5	0.4603(7)	-0.2055(7)	0.1979(9)	3.63
C6	0.5582(7)	-0.0888(8)	0.2409(9)	3.99
N11	0.4785(7)	-0.5686(6)	0.2448(8)	3.84
N21	0.7421(6)	-0.7714(6)	0.4177(7)	3.42
O11	0.5894(6)	-0.5020(6)	0.2682(7)	4.72
O12	0.4169(8)	-0.6259(9)	0.1023(8)	7.22
O13	0.4301(13)	-0.5822(13)	0.3464(12)	11.39
O21	0.7180(6)	-0.8041(7)	0.2720(7)	5.14
O22	0.6499(9)	-0.8119(11)	0.4731(8)	9.27
O23	0.8529(6)	-0.7038(6)	0.5012(7)	5.33

a) B_{eq} is the equivalent isotropic temperature factor defined by Hamilton.[24]

Results and Discussion

Description of the Structure. Perspective drawing of the complex cation obtained is given in Fig. 1 and its packing mode is illustrated in Fig. 2. The bond lengths and angles with their estimated standard deviations in the complex are summerized in Table 2. The coordination geometry around the cobalt atom is approximately octahedral. The 2-aminoethaneseleninate coordinates to cobalt atom with the nitrogen and oxygen atoms instead of the nitrogen and selenium ones in the starting complex, [Co(SeCH$_2$CH$_2$NH$_2$)(en)$_2$]$^{2+}$ [3] in contrast to the case of the related sulfinato complex whose coordinated atoms remain intact during the oxidation process.[2] This suggests that the treatment of the selenolato complex with excess hydrogen peroxide is accompanied by linkage isomerization and the *O*-bonded seleninato complex is obtained. The asymmetric selenium atom in the Δ-$(-)^{CD}_{500}$-[Co(aesei-N,O)(en)$_2$]$^{2+}$ takes the *S* configuration as shown in Fig. 1.

The bond lengths and angles are similar to those for the [Co(en)$_2$(L)] type complexes, where L denotes the selenium- or sulfur-containing bidentate ligands.[1-5,8,14,15] The selenium–oxygen bond lengths,

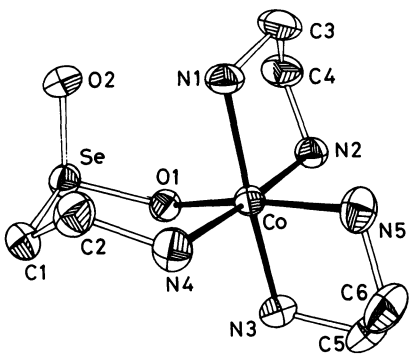

Fig. 1. A perspective drawing of Δ-$(-)^{CD}_{500}$-[Co(aesei-N,O)(en)$_2$]$^{2+}$ with the numbering scheme of atoms.

Se-O1 and Se-O2, are 1.698(4) and 1.680(4) Å, respectively. They are longer than those of the sulfur-oxygen ones (1.456 and 1.476 Å) in the [Co(aesi-N,S)-(en)$_2$](ClO$_4$)·(NO$_3$).[2] The bond angle of O1-Co-N4 for the six-membered chelate ring is 95.6(2)°, which is consistent with that of the cobalt(III) complexes containing amino carboxylate.[16,17] The bond angles around the selenium atom are about 100°, and this value seems tobe reasonable for the selenium atom whose tetragonal positions are occupied by the three bonding pairs and a lone pair.[18]

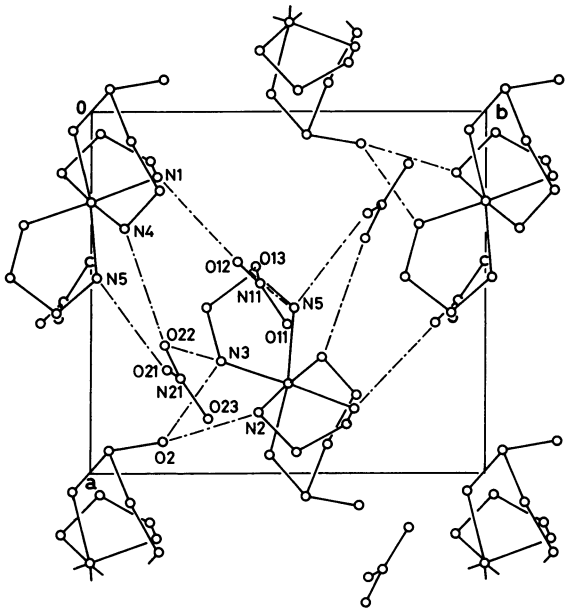

Fig. 2. A projection of the crystal packing viewed along the c axis. The hydrogen bonds are represented by the lines (-·-·-); O2-N2′, 2.802(7); O2-N3′, 2.827(6); O12-N1, 2.948(10); O12-N5′, 3.091(11); O21-N5, 2.920(8); O22-N4, 3.009(10); and O22-N3′, 3.054(10) Å.

Table 2. Intermolecular distances and bond angles (with e.s.d. 's)

Bond distance	l/Å	Bond distance	l/Å
Co-O1	1.922(4)	Co-N1	1.966(4)
Co-N2	1.967(5)	Co-N3	1.950(5)
Co-N4	1.988(5)	Co-N5	1.972(5)
Se-O1	1.698(4)	Se-O2	1.680(4)
N1-C3	1.491(8)	N2-C4	1.490(7)
N3-C5	1.487(9)	N4-C2	1.479(9)
N5-C6	1.497(8)	C1-Se	1.952(5)
C1-C2	1.520(10)	C3-C4	1.500(9)
C5-C6	1.481(10)	N11-O11	1.209(8)
N11-O12	1.286(9)	N11-O13	1.183(16)
N21-O21	1.255(9)	N21-O22	1.251(12)
N21-O23	1.223(7)		
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
O1-Co-N1	95.1(2)	O1-Co-N2	83.9(2)
O1-Co-N3	85.1(2)	O1-Co-N4	95.6(2)
O1-Co-N5	170.0(2)	N1-Co-N2	85.6(2)
N1-Co-N3	175.9(2)	N1-Co-N4	90.9(2)
N1-Co-N5	93.5(2)	N2-Co-N3	90.4(2)
N2-Co-N4	176.4(2)	N2-Co-N5	91.9(2)
N3-Co-N4	93.1(2)	N3-Co-N5	85.9(2)
N4-Co-N5	89.2(2)	O1-Se-O2	104.5(2)
O1-Se-Cl	100.1(2)	O2-Se-Cl	100.1(2)
Co-O1-Se	127.0(2)	Co-N1-C3	109.5(4)
Co-N2-C4	106.9(3)	Co-N3-C5	108.4(4)
Co-N4-C2	119.5(3)	Co-N5-C6	107.5(4)
Se-C1-C2	112.4(4)	N4-C2-C1	112.0(5)
N1-C3-C4	105.9(5)	N2-C4-C3	106.4(4)
N3-C5-C6	106.8(6)	N5-C6-C5	106.1(4)
O11-N11-O12	115.8(8)	O11-N11-O13	122.6(8)
O12-N11-O13	121.6(8)	O21-N21-O22	117.4(6)
O21-N21-O23	120.4(7)	O22-N21-O23	122.2(7)

In the present complex cation, the two gauche conformations, δ and λ, are possible for each of the two ethylenediamine chelate rings.[1-5,8,17] As shown in Fig. 1 and Table 3, both of the ethylenediamine chelate rings in the Δ-$(-)^{CD}_{500}$-[Co(aesei-N,O)(en)$_2$]$^{2+}$ isomer take up the reasonable λ gauche conformation. The six-membered chelate ring (O1-Se-C1-C2-N4) of the coordinated aesei ligand takes up a chair conformation (Table 3) and dihedral angle for the two-planes, O1-Co-N4 and Se-C1-C2, is 24.5°. This suggests that the six-membered chelate ring is distorted from the normal chair conformation, because the bond lengths and angles around the selenium atom are larger than those around the carbon atom (Table 2).

The crystal structure consists of the complex cations and nitrate anions, and the distance between the two nitrate anions is 3.140(8) Å. The O2-N2 and O2-N3 distances between adjacent complex cations are

Table 3. Displacements of atoms from the least-squares plane (d/Å)

Diamine chelate ring				
Plane 1; $0.9929X+0.1190Y-0.0007Z-1.9677=0$				
Co	0.0000	N1 0.0000	N2 0.0000	C3 −0.2292
C4	0.5024			
Plane 2; $0.0791X-0.3897Y-0.9175Z+0.6695=0$				
Co	0.0000	N3 0.0000	N5 0.0000	C5 0.3421
C6	−0.3855			
Six-membered chelate ring				
Plane 3; $0.1970X-0.8736Y+0.4451Z-0.7914=0$				
Co	0.0000	O1 0.0000	N4 0.0000	Se 0.8888
C1	0.5029	C2 0.9017		

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

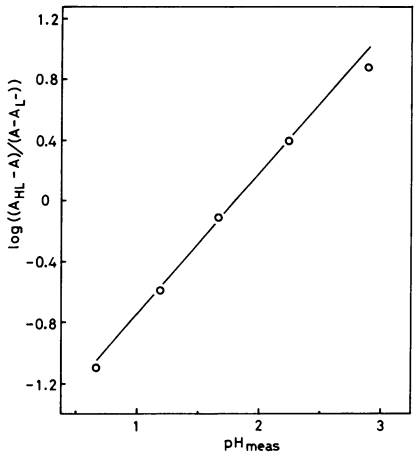

Fig. 3. Relation between pH_{meas} and $\log\{(A_{HL}-A)/(A-A_{L^-})\}$. μ=1.0 mol dm^{-3} ($NaClO_4$), 25°C, and absorbance at 304 nm.

TABLE 4. ABSORPTION AND CD SPECTRAL DATA

Complex ion	Absorption maxima $\sigma/10^3\,cm^{-1}$ ($\log\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$)	CD extrema $\sigma/10^3\,cm^{-1}$ ($\Delta\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$)
$(+)^{CD}_{500}$-[Co(aesei-N, O)$(en)_2]^{2+}$	19.23(2.02) 33.00(3.61) 47.17(4.19)	17.15(+ 1.90) 27.17(− 0.52) 32.26(− 1.25) 45.5 (−21.8)
$(+)^{CD}_{500}$-[Co(aesi-N, S)$(en)_2]^{2+}$	23.07(2.37) 34.48(4.16) 47.06(4.18)	21.05(+ 1.46) 24.21(− 0.48) 28.65(+ 0.39) 34.97(− 4.18) 47.2 (−22.0)
[Co(aesi-N, O)$(en)_2]^{2+}$ [a]	19.53(2.13) 30.67(3.61)	

a) Ref. 6).

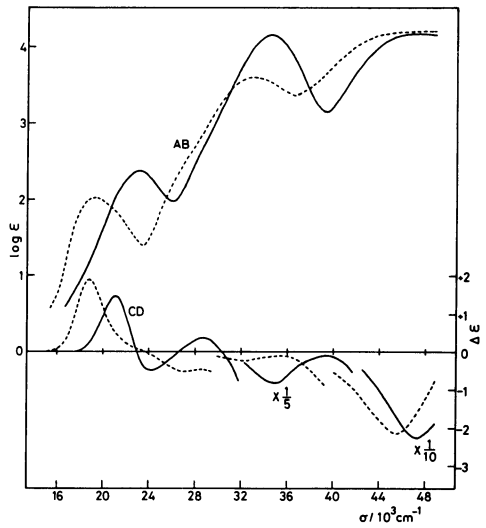

Fig. 4. Absorption and CD spectra of $(+)^{CD}_{500}$-[Co(aesei-N,S)$(en)_2]^{2+}$ (------) and $(+)^{CD}_{500}$-[Co(aesi-N,S)$(en)_2]^{2+}$ (——).

2.802(7) and 2.827(6) Å, respectively. In addition, the distances between the nitrogen atoms of the complex cation and the oxygen atoms of the nitrate anions are from 2.948 Å to 3.091 Å, as shown in Fig. 2. These distances suggest that they are hydrogen bonds.

Protonation Constant. The absorption spectral changes were reversible and an acid-base equilibrium is indicated. The value of the protonation constant (pK_a) is calculated from the following equation.

$$pK_a = -\log\gamma_H + pH_{meas} - \log\{(A_{HL}-A)/(A-A_{L^-})\},$$

where A_{HL} and A_{L^-} are the absorbances of acid and base, respectively, and A is the absorbance containing both of them. The γ_H is the activity coefficient of hydrogen ion and the value, $-\log\gamma_H = 0.13$, is calculated by the Debye-Hückel equation.[19] The value of pH_{meas} at $-\log\{(A_{HL}-A)/(A-A_{L^-})\}=0$ is determined to 1.78 ± 0.05 by least-squares treatment from Fig. 3. As a result, the value of pK_a can be determined to be 1.91 ± 0.05. The corresponding sulfinato complex, [Co(aesi-N,O)$(en)_2]^{2+}$, gave a pK_a of -0.7 (8 mol dm^{-3} ($NaClO_4$) uncorrected for H^+ activity coefficient changes).[6] This is consistent with the conclusion that the selenium atom is more "basic or soft" than the sulfur atom.[20]

Electronic Absorption and CD Spectra. The electronic absorption and CD spectra of the *A*-$(+)^{CD}_{500}$-[Co(aesei-N,O)$(en)_2]^{2+}$ isomer are shown in Fig. 4 and their data are summarized in Table 4, together with the related sulfinato complex, $(+)^{CD}_{500}$-[Co(aesi-N,S)$(en)_2]^{2+}$. This aesei isomer, which belongs to the [Co(O)$(N)_5$] type, exhibits a broad band with a vague shoulder on the higher energy side in the first absorption band region. This absorption behavior agrees well with those for the [Co(amino-carboxylato)$(en)_2$] type complexes.[21-23] The intense absorption band at *ca.* $33\times10^3\,cm^{-1}$ is weaker than that of the *Se*-bonded or *S*-bonded cobalt(III) complexes (Fig. 3 and Table 4) [2,3,5-11] Since the seleninate moiety can still interact with a cobalt center (Fig. 1), this absorption band seems to be a new charge transfer band from the seleninato chromophore to the cobalt atom. A similar absorption spectral trend was also observed for the photoproduct of the [Co(aesi-N,S)-$(en)_2]^{2+}$ complex.[6,7]

The CD spectrum shows a positive band in the first absorption band region (Fig. 4). This CD spectral behavior is consistent with those of the *A*-[Co(amino-carboxylato)$(en)_2$] type complexes.[21-23] These facts suggest that the asymmetric selenium atom contributes little to the CD band in this region. The $(+)^{CD}_{500}$-[Co(aesi-N,S)$(en)_2]^{2+}$ isomer exhibits a similar CD spectrum to that of *A*-$(+)^{CD}_{500}$-[Co(aesei-N,O)$(en)_2]^{2+}$ over the whole region, although the absorption and CD spectra of the latter shift to lower energy than those of the former. This seems to suggest that the $(+)^{CD}_{500}$ aesi isomer is also in the *A* configuration.

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