Bull. Chem. Soc. Jpn., 57, 2751—2756 (1984)

Preparation and Characterization of [*S*-(2-Aminoethyl)-L-homocysteinato]-cobalt(III) Complexes with Bidentate Ligands

Masutaro Suzuki, Osamu Arisato, 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*
(Received April 4, 1984)

Three kinds of cobalt(III) complexes with *S*-(2-aminoethyl)-L-homocysteinate (L-aehc) and a bidentate ligand (glycinate, oxalate, and ethylenediamine) were prepared and chromatographically separated into the quasi-enantiomeric isomers: Δ_L-*trans(O)·mer(N)-R(S)*, Δ_L-*cis(O)·mer(N)-R(S)*, Λ_L-*cis(O)·mer(N)-S(S)*, and Λ_L-*cis(O)·fac(N)-S(S)* for the glycinato complex, Δ_L-*trans(N)-R(S)* and Λ_L-*cis(N)-S(S)* for the oxalato one, and Δ_L-*R(S)* and Λ_L-*S(S)* for the ethylenediamine one. These isomers were characterized from their electronic absorption, CD, and ^{13}C NMR spectra. The conformations of the six-membered N–S chelate ring in the L-aehc, of the chair for Δ_L-*R(S)* and of the chair or skew-boat for Λ_L-*S(S)*, were suggested on the basis of the ^{13}C NMR spectra. The CD spectra of the isomers are discussed in relation to their geometrical and absolute configurations.

CD spectra of the cobalt(III) complexes with a thioether-type terdentate ligand such as L-methioninate, *S*-methyl-L-cysteinate and their derivatives have been investigated in relation to the stereochemical properties of the coordinated sulfur donor atom.[1–8] In these works, however, the chiral sulfur atom, *R*(S) or *S*(S)[9] configuration, has been suggested to be configurationally labile.[6,10] *S*-(2-Aminoethyl)-L-homocysteinate (L-aehc) functions as a quadridentate ligand to a cobalt(III) ion and forms two five-membered (N–S and N–O) chelate rings and a six-membered (N–S) one (Fig. 1). Accordingly, the L-aehc cobalt(III) complex gives a fixed chiral sulfur atom as well as the cobalt(III) complexes with (2-aminoethylthio)acetate[11] or (2*R*)-2-(carboxymethylthio) propionate.[12] The L-aehc ligand can take two kinds of coordination modes which are mutually quasi-enantiomeric, as shown in Fig. 1. The sulfur donor atom in (a) or (c) of Fig. 1 takes only *S*(S) configuration, while two configurations, *R*(S) and *S*(S), are possible for the sulfur donor atom in (b) or (d), depending on the possible conformations, chair and skew-boat, of the six-membered N–S ring. Of the four isomers for [Co(L-aehc)(gly)]$^+$, two isomers were determined to be the Δ_L-*trans(O)·mer(N)-R*(*S*) and Δ_L-*cis(O)·mer(N)-R*(*S*) ones by the X-ray crystal structure analysis.[13–15]

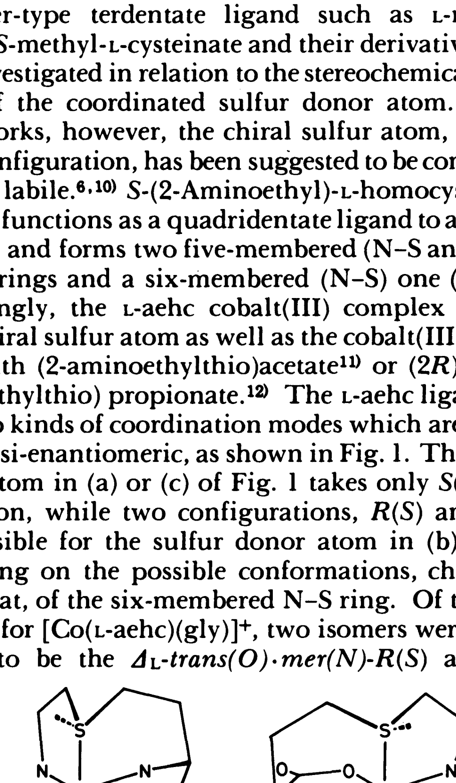

Fig. 1. Possible isomers of [Co(L-aehc)(gly)]$^+$: (a) Λ_L-*cis*(*O*)·*mer*(*N*)-*S*(*S*), (b) Δ_L-*cis*(*O*)·*mer*(*N*)-*R*(*S*), (c) Λ_L-*cis*(*O*)·*fac*(*N*)-*S*(*S*), and (d) Δ_L-*trans*(*O*)·*mer*(*N*)-*R*(*S*). Δ_L-*cis*(*O*)·*mer*(*N*)-*S*(*S*) and Δ_L-*trans*(*O*)·*mer*(*N*)-*S*(*S*) are omitted.

In this work, the [Co(L-aehc)(bidentate)]-type complexes were prepared and chromatographically separated into their possible isomers, namely, four isomers for the glycinato complex, two for the oxalato one, and two for the ethylenediamine one. The [Co(L-aehc)(NH_3)$_2$]$^{2+}$ and [Co(L-met)(NH_3)$_3$]$^{2+}$ complexes were also prepared in order to compare the CD spectra with the isomers of [Co(L-aehc)(en)]$^{2+}$. The coordination modes of L-aehc, Λ_L-*S*(*S*), Δ_L-*R*(*S*), and Δ_L-*S*(*S*), were suggested from comparisons of the CD and ^{13}C NMR spectra of the Δ_L-*trans(O)·mer(N)-R*(*S*)- and Δ_L-*cis(O)·mer(N)-R*(*S*)-[Co(L-aehc)(gly)]$^+$ isomers with those of the remaining isomers of the gly complex and of the isomers of the ox and en complexes.

Experimental

Preparation of Ligand. *S*-(2-Aminoethyl)-L-homocysteine was prepared by a procedure similar to that used for the preparation of *S*-(carboxymethyl)-L-homocysteine,[16] using 2-bromoethanamine hydrobromide instead of chloroacetic acid. The reaction mixture was neutralized with a 1 mol dm^{-3} aqueous solution of sodium hydroxide and the deposited sodium chloride was filtered off. The filtrate was poured onto a column of Dowex 50W-X8 (H$^+$ form, 5 cm×40 cm). After unreacted L-methionine had been swept with a 0.2 mol dm^{-3} sodium citrate buffer solution (pH 4.25), the desired product was eluted with a 1.0 mol dm^{-3} aqueous ammonia. The eluate was concentrated with a rotary evaporator until it became sirupy. It was neutralized with concd hydrobromic acid and to the solution was added a large amount of acetone. The crystals were collected by filtration and then washed well with acetone. Found: C, 27.59; H, 5.89; N, 10.53%. Calcd for L-Haehc·HBr=$C_6H_{14}N_2O_2S$·HBr: C, 27.57; H, 5.83; N, 10.80%.

Preparation and Separation of Complexes. 1) (S-(2-Aminoethyl)-L-homocysteinato)(glycinato)cobalt(III) Perchlorate: [*Co*(*L-aehc*)(*gly*)]*ClO*$_4$. A solution containing 4.0 g of L-Haehc·HBr and 2.0 g of glycine in 40 cm^3 of water was adjusted to pH 7 with a 1 mol dm^{-3} aqueous solution of sodium hydroxide. To this solution was added a solution containing 4.8 g of $CoCl_2·6H_2O$ in 40 cm^3 of water, 0.5 g of activated charcoal, and 8.0 g of PbO_2. The mixture was stirred at *ca.* 65 °C for 15 min and then filtered. The filtrate was poured onto a column of Dowex 50W-X8 (200—400 mesh, Na$^+$ form, 3 cm×40 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} aqueous solution of NaCl. Four colored bands; red-violet (A-1), violet (A-2), red-violet (A-3), and red (A-4), were eluted in this order. It was found from the absorption and CD spectral measurements that A-1, A-2, A-3, and A-4 eluates contained Δ_L-*trans(O)·mer(N)*, Λ_L-*cis(O)·mer(N)*, Δ_L-*cis(O)·mer(N)*, and Λ_L-*cis(O)·fac(N)* isomers, respectively. Each eluate was concentrated to a small volume with a rotary evaporator below 25 °C and the deposited NaCl was filtered off. The filtrate was passed through a column of Sephadex G-10 (3.5 cm×100 cm) by elution with water. By use of an anion-exchange column (QAE-Sephadex A-25, ClO_4^- form, 3 cm×20 cm), the chloride salt in the eluate was converted into the perchlorate one. The eluate was concentrated to a small volume again. After adding a small amount of ethanol, the solution was kept in a refrigerator for several days. The crystals which appeared were collected by filtration and recrystallized from water by addition of ethanol. Found for A-1: C, 23.44; H, 4.14; N, 10.13%. Found for A-4: C, 23.36; H, 4.16; N, 10.13%. Calcd for $[Co(L\text{-aehc})(gly)]ClO_4=CoC_8H_{17}N_3O_8SCl$: C, 23.45; H, 4.18; N, 10.25%. Found for A-2: C, 23.30; H, 4.57; N, 9.83%. Found for A-3: C, 22.48; H, 4.41; N, 9.80%. Calcd for $[Co(L\text{-aehc})(gly)]ClO_4\cdot H_2O$: C, 22.46; H, 4.49; N, 9.82%.

2) *(S-(2-Aminoethyl)-L-homocysteinato)(oxalato)cobalt(III)*: *[Co(L-aehc)(ox)]*. This complex was prepared by the same procedure as in *1)*, using oxalic acid dihydrate instead of glycine. The reaction mixture was filtered and the filtrate was passed through columns of Dowex 1-X8 (Cl^- form, 4 cm×25 cm) and Dowex 50W-X8 (Na^+ form, 4 cm×25 cm) in order to remove charged compounds. The concentrated eluate was poured onto a column of QAE-Sephadex A-25 (Cl^- form, 3.0 cm×150 cm) and eluted with water. The adsorbed band was separated into two bands, dark-violet (B-1) and purple (B-2), in this order. It was found from the absorption and CD spectral measurements that B-1 and B-2 eluates contained Δ_L-*trans(N)* and Λ_L-*cis(N)* isomers, respectively. Each eluate was concentrated to a small volume with a rotary evaporator below 25 °C and kept in a refrigerator overnight. The complex which precipitated was collected by filtration, then washed with ethanol and ether. B-1 isomer was obtained as violet needle crystals and B-2 isomer as light purple powder. Found for B-1: C, 29.42; H, 4.02; N, 8.60%. Found for B-2: C, 29.27; H, 3.98; N, 8.57%. Calcd for $[Co(L\text{-aehc})(ox)]=CoC_8H_{13}N_2O_6S$: C, 29.63; H, 4.04; N, 8.64%.

3) *(S-(2-Aminoethyl)-L-homocysteinato)(ethylenediamine)cobalt(III) Perchlorate*: *[Co(L-aehc)(en)](ClO₄)₂*. A solution containing 2.0 g of L-Haehc·HBr in 40 cm³ of water was adjusted to pH 7 with a 1 mol dm⁻³ aqueous solution of sodium hydroxide. To this solution were added 2.0 g of *trans*-$[CoCl_2(en)_2]Cl$[17] and 0.5 g of activated charcoal. The resulting mixture was stirred at *ca.* 75 °C for 15 min. The color of the solution changed from green to violet and finally to orange-red. The mixture was filtered and the filtrate was poured onto a column of Dowex 50W-X8 (200—400 mesh, Na^+ form, 3.5 cm×30 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.5 mol dm⁻³ aqueous solution of NaCl. Four colored bands: a red-violet, another red-violet, orange-red (C-1), and orange (C-2), were eluted in this order. It was found from the absorption and CD spectral measurements that C-1 and C-2 eluates contained the desired isomers, but the earlier two red-violet eluates contained a by-product; the absorption spectra of the two eluates did not show any sulfur-to-metal charge transfer band in the region of 30—35×10³ cm⁻¹.[1—4,6—8,10—12] Each of the C-1 and C-2 eluates was concentrated to a small volume with a rotary evaporator below 25 °C. The solution was passed through columns of Sephadex G-10 (3.5 cm×100 cm) and QAE-Sephadex A-25 (ClO_4^- form, 3 cm×20 cm), by elution with water as in *1)*. To the eluate concentrated again was added a small amount of methanol; this mixture was kept in a refrigerator for several days. The complex which precipitated was collected by filtration, then washed with methanol and ether. C-1 isomer was obtained as orange-red needle crystals and C-2 isomer as orange-red powder. Found for C-1: C, 18.91; H, 4.55; N, 10.88%. Calcd for $[Co(L\text{-aehc})(en)](ClO_4)_2\cdot H_2O=CoC_8H_{21}N_4O_{10}SCl_2\cdot H_2O$: C, 18.72; H, 4.53; N, 10.92%. Found for C-2: C, 18.89; H, 4.12; N, 11.12%. Calcd for $[Co(L\text{-aehc})(en)](ClO_4)_2\cdot 0.5H_2O$: C, 19.05; H, 4.20; N, 11.11%.

4) *(S-(2-Aminoethyl)-L-homocysteinato)diamminecobalt(III) Chloride*: *[Co(L-aehc)(NH₃)₂]Cl₂*. To a solution containing 2.0 g of L-Haehc·HBr in 200 cm³ of water was added 3.5 g of *cis*-$K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$.[18] To this solution was gradually added 3 mol dm⁻³ hydrochloric acid with stirring at *ca.* 45 °C until the evolution of carbon dioxide ceased. The color of the solution changed from blue-violet to dark red. The mixture was filtered and the filtrate was poured onto a column of SP-Sephadex C-25 (Na^+ form, 3 cm×90 cm). After the column had been swept with water and 0.02 mol dm⁻³ acetic acid (pH 4.5), the adsorbed band was eluted with a 0.2 mol dm⁻³ aqueous solution of NaCl. Only the red band was eluted; it was concentrated to a small volume with a rotary evaporator below 20 °C. The solution was passed through a column of Sephadex G-10 (4 cm×45 cm) and then poured onto a column of SP-Sephadex C-25 (Na^+ form, 3 cm×90 cm) again. The adsorbed band was eluted by the same conditions as described above. Four colored bands: red, red-violet, red (D-1), and another red (D-2), were eluted in this order. It was found from the comparison with the absorption and CD spectra of $[Co(L\text{-aehc})(en)]^{2+}$ isomers that D-1 and D-2 eluates contained the desired isomers. Since the yield was very poor, the desired isomers could not be isolated. The concentration of the complex cation in each eluate was evaluated by the plasma emission spectral analysis.

5) *Triammine(L-methioninato)cobalt(III) Perchlorate*: *[Co(L-met)(NH₃)₃](ClO₄)₂*. A solution containing 4.8 g of ammonium chloride and 7.2 cm³ of 25% aqueous ammonia in 40 cm³ of water were added to a solution containing 4.0 g of L-methionine in 12 cm³ of water. To this solution was added a solution containing 1.7 g of $Co(CH_3COO)_2\cdot 4H_2O$ in 40 cm³ of water and 10 g of PbO_2. The molar ratio, Co^{2+}: L-methionine: NH_3: NH_4^+, was 1:1:3:3.5. This solution was stirred at *ca.* 60 °C for 18 min, cooled to room temperature, and then filtered. The filtrate was poured onto a column of SP-Sephadex C-25 (Na^+ form, 4 cm×120 cm). After the column had been swept with water and then with a 0.03 mol dm⁻³ aqueous solution of NaCl, the adsorbed band was eluted with a 0.18 mol dm⁻³ aqueous solution of NaCl. Three colored bands: pink, orange-pink, and orange, were eluted in this order. It was found from the absorption and CD spectral measurements that the second eluate contained the desired complex. The second eluate was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. The filtrate was passed through a column of QAE-Sephadex A-25 (ClO_4^- form, 3 cm×20 cm) by elution with water. The eluate was concentrated to a small volume. The crystals which appeared were collected by filtration, then washed with ethanol and ether. Found: C, 12.25; H, 4.05; N, 11.89%. Calcd for $[Co(L\text{-met})(NH_3)_3](ClO_4)_2\cdot 0.5H_2O=CoC_5H_{19}N_4O_{10}SCl_2\cdot 0.5H_2O$: C, 12.88; H, 4.32; N, 12.02%.

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer and the CD spectra with a JASCO J-20 spectropolarimeter. The concentration of D-1 or D-2 isomer for $[Co(L\text{-aehc})(NH_3)_2]^{2+}$ was measured with a Jarrell-Ash model 96—975 plasma Atom Comp. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature in D_2O or 70% $DClO_4$ solvent. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference.

Results and Discussion

Structural Assignment. Two pairs of quasi-enantiomeric geometrical isomers, Λ_{L}-*cis(O)*·*mer(N)* and Δ_{L}-*cis(O)*·*mer(N)*, and Λ_{L}-*cis(O)*·*fac(N)* and Δ_{L}-*trans(O)*·*mer(N)*, are expected for [Co(L-aehc)(gly)]$^+$, regardless of the chiral sulfur atom, *R*(*S*) or *S*(*S*), in L-aehc (Fig. 1).[15] In the first absorption band region, A-1

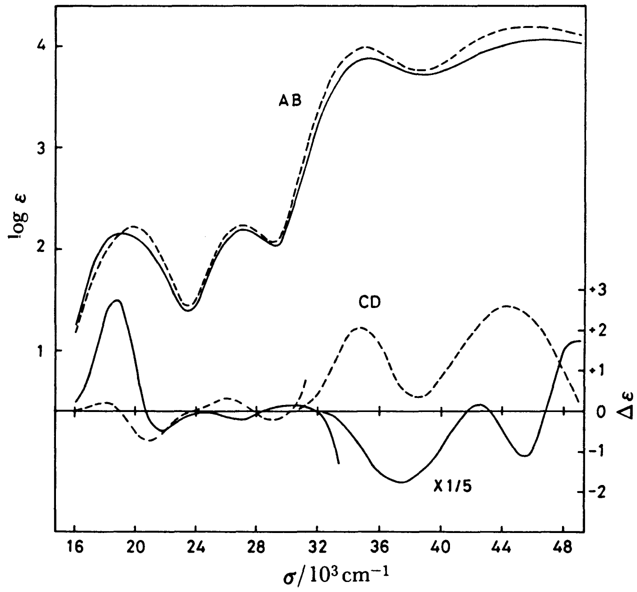

Fig. 2. Absorption and CD spectra of [Co(L-aehc)(gly)]$^+$: Λ_{L}-*cis*(*O*)·*mer*(*N*) (——) and Δ_{L}-*cis*(*O*)·*mer*(*N*) (------).

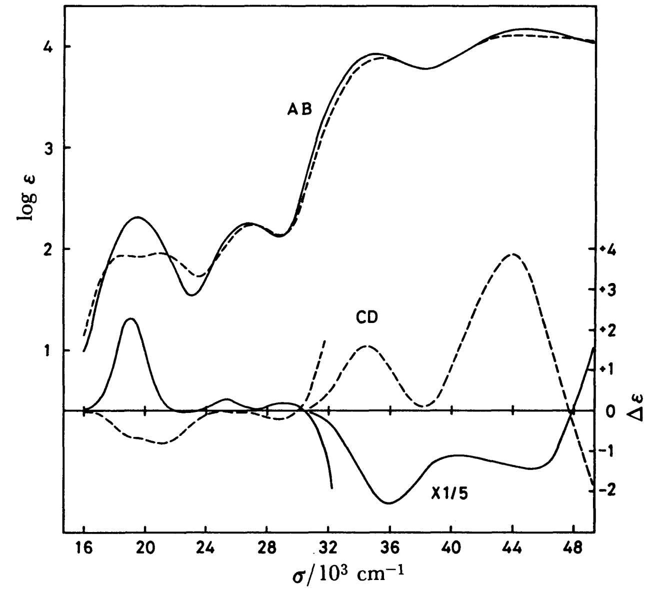

Fig. 3. Absorption and CD spectra of [Co(L-aehc)(gly)]$^+$: Λ_{L}-*cis*(*O*)·*fac*(*N*) (——) and Δ_{L}-*trans*(*O*)·*mer*(*N*) (------).

Table 1. Absorption and CD spectral data of [Co(L-aehc)(L)] (L=gly, ox, en, and $(NH_3)_2$), and [Co(L-met)$(NH_3)_3]^{2+}$

Complex	Absorption $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)	CD $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\Delta\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)
Δ_{L}-*trans(O)*·*mer(N)*-[Co(L-aehc)(gly)]$^+$	18.52 (1.93)	19.23 (−0.66)
	21.14 (1.96)	21.20 (−0.81)
	27.03 (2.24)	28.57 (−0.21)
	35.34 (3.88)	34.56 (+7.83)
	44.64 (4.11)	44.21 (+18.8)
Λ_{L}-*cis(O)*·*mer(N)*-[Co(L-aehc)(gly)]$^+$	18.94 (2.16)	18.67 (+2.75)
	27.03 (2.23)	21.74 (−0.51)
	36.36 (3.89)	26.89 (−0.21)
	46.95 (4.08)	30.12 (+0.14)
		37.60 (−0.75)
		42.55 (+0.79)
		45.45 (−5.56)
Δ_{L}-*cis(O)*·*mer(N)*-[Co(L-aehc)(gly)]$^+$	18.90 (2.22)	17.80 (+0.19)
	27.03 (2.23)	20.83 (−0.77)
	34.97 (3.99)	25.97 (+0.28)
	45.45 (4.19)	28.96 (−0.22)
		34.60 (+10.1)
		44.44 (+13.0)
Λ_{L}-*cis(O)*·*fac(N)*-[Co(L-aehc)(gly)]$^+$	19.53 (2.32)	19.05 (+2.35)
	26.81 (2.26)	22.58 (−0.02)
	36.36 (3.92)	25.32 (+0.31)
	44.64 (4.18)	28.90 (+0.23)
		35.59 (−11.5)
		45.05 (−7.09)
Δ_{L}-*trans(N)*-[Co(L-aehc)(ox)]	19.53 (2.10)	16.61 (+0.17)
	26.25 (2.27)	19.69 (−0.87)
	34.72 (3.92)	25.45 (+0.11)
	42.92 (4.11)	28.01 (−0.42)
		34.13 (+11.3)
		38.17 (−2.39)
		45.05 (+15.3)

Table 1. Continued

Complex	Absorption $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)	CD $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\Delta\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)
Λ_{L}-*cis(N)*-	18.73 (2.20)	18.15 (+1.86)
[Co(L-aehc)(ox)]	26.18 (2.19)	20.79 (−0.27)
	34.60 (3.88)	23.98 (+0.03)
	43.67 (4.09)	26.25 (−0.12)
		28.57 (+0.03)
		36.76 (−5.24)
		42.92 (+6.16)
		46.95 (−4.33)
Δ_{L}-$[\mathrm{Co(L\text{-}aehc)(en)}]^{2+}$	20.58 (2.10)	19.96 (−1.04)
	27.93 (2.23)	28.41 (−0.39)
	35.56 (3.96)	35.09 (+6.07)
	46.30 (4.18)	43.29 (+15.4)
Λ_{L}-$[\mathrm{Co(L\text{-}aehc)(en)}]^{2+}$	19.92 (2.21)	19.16 (+3.30)
	27.78 (2.28)	22.08 (−0.91)
	35.56 (3.89)	26.45 (+0.12)
	44.64 (4.09)	29.32 (+0.42)
		31.85 (+0.48)
		36.90 (−12.7)
		44.44 (−5.68)
Δ_{L}-$[\mathrm{Co(L\text{-}aehc)(NH_3)_2}]^{2+}$	19.92 (2.29)	20.20 (−1.43)
	27.78 (2.4 sh[a])	25.32 (+0.14)
	34.84 (3.95)	28.41 (−0.55)
	46.73 (4.11)	33.56 (+9.87)
		42.55 (+10.4)
Λ_{L}-$[\mathrm{Co(L\text{-}aehc)(NH_3)_2}]^{2+}$	19.88 (2.34)	18.90 (+1.73)
	27.78 (2.46 sh)	21.51 (−0.48)
	34.97 (3.96)	25.19 (+0.12)
	45.66 (4.36)	27.25 (−0.08)
		28.99 (+0.05)
		35.71 (−6.58)
		46.30 (−4.17)
$[\mathrm{Co(L\text{-}met)(NH_3)_3}]^{2+}$	20.00 (2.03)	20.00 (+0.50)
	27.03 (2.2 sh)	27.47 (−0.16)
	34.36 (3.94)	30.58 (+0.06)
	47.62 (4.22)	35.84 (−5.64)
		46.30 (+6.87)

a) sh denotes a shoulder.

isomer of $[\mathrm{Co(L\text{-}aehc)(gly)}]^+$ exhibits well separated two absorption components, A-2 and A-3 isomers exhibit a broad band, and A-4 isomer exhibits a sharp band (Figs. 2 and 3, and Table 1). These splittings of the first absorption bands agree well with the splitting patterns which can be expected from the semiempirical calculation[19] on the basis of the ligand field strength, N>S>O.[1–4,6–8,10–13] Of these isomers, A-1 and A-3 isomers were determined to be Δ_{L}-*trans(O)·mer(N)*[13] and Δ_{L}-*cis(O)·mer(N)*,[14] respectively, by the X-ray crystal structure analysis and then A-2 isomer was assigned to Λ_{L}-*cis(O)·mer(N)* from a comparison of the absorption and CD spectra with those of A-3 one.[14] Thus A-4 isomer is Λ_{L}-*cis(O)·fac(N)*. For the [Co(L-aehc)(ox)] complex, the isomers are regulated to a pair of quasi-enantiomeric isomers, Δ_{L}-*trans(N)* and Λ_{L}-*cis(N)* (Fig. 1). In the first absorption band region, B-1 isomer of [Co(L-aehc)(ox)] exhibits a band with an explicit shoulder on the lower energy side and B-2 isomer exhibits a sharp band (Fig. 4 and Table 1). These spectral patterns suggest that B-1 isomer is Δ_{L}-*trans(N)* and B-2 one Λ_{L}-*cis(N)*. Similarly, the two isomers, Δ_{L} and Λ_{L}, are possible for the ethylenediamine complex, $[\mathrm{Co(L\text{-}aehc)(en)}]^{2+}$. In this case, however, it is

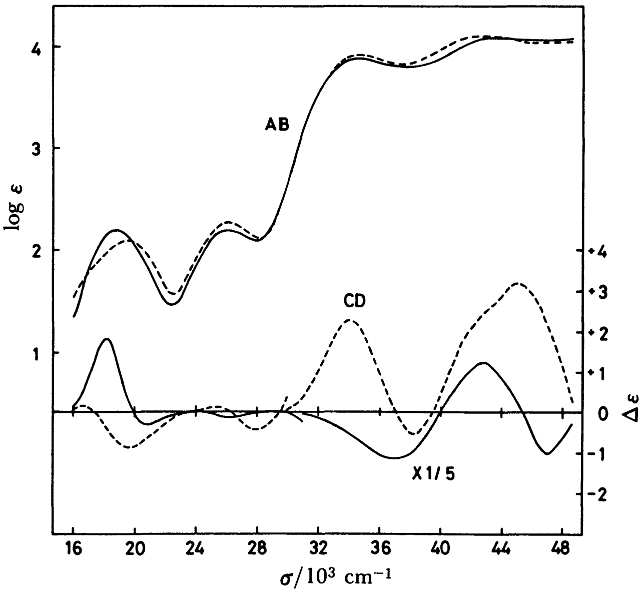

Fig. 4. Absorption and CD spectra of [Co(L-aehc)-(ox)]: Λ_{L}-*cis*(*N*) (——) and Δ_{L}-*trans*(*N*) (------).

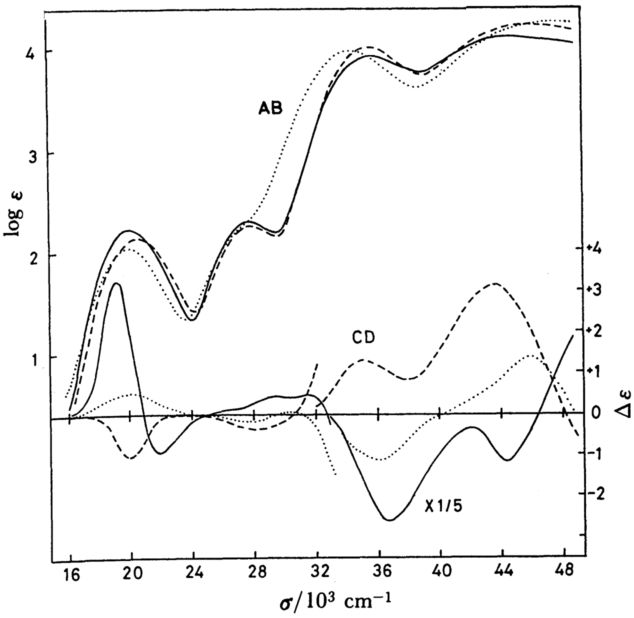

Fig. 5. Absorption and CD spectra of [Co(L-aehc)-(en)]$^{2+}$: Λ_L (——) and Δ_L (------), and [Co(L-met)-$(NH_3)_3$]$^{2+}$ (......).

difficult to assign the structure of the two isomers on the basis of their first absorption bands (Fig. 5), so their ^{13}C NMR spectra were measured.

The ^{13}C NMR spectra of the six isomers of the gly and ox complexes can be classified into two groups according to the distribution of the chemical shifts due to the β-methylene carbon atom of L-aehc (Fig. 6). One group, the Δ_L isomers, exhibits the resonance line in the range of 40—43 ppm (A-1, A-3, and B-1 isomers), while the other, the Λ_L isomers, exhibits the line in the range of 34—37 ppm (A-2, A-4, and B-2 isomers). The same trend was observed for the ^{13}C NMR spectra of the two isomers of [Co(L-aehc)(en)]$^{2+}$, namely, the resonance line for the β-methylene carbon atom of C-1 isomer (34.51 ppm) appears at a higher field than that of C-2 one (40.25 ppm) (Fig. 6). Stereomodel examination reveals that the interligand interaction between the six-membered N-S chelate ring containing the β-methylene and the five-membered N-S chelate ring of L-aehc is more remarkable for the Λ_L isomer than for the Δ_L one. Taking the classification based on the ^{13}C NMR spectral behavior of the β-methylene carbon and the steric effects of the chemical shift of carbon[19,20] into consideration, the C-1 isomer of [Co(L-aehc)(en)]$^{2+}$ is tentatively assigned to Λ_L and the C-2 isomer to Δ_L. This assignment is consistent with that from their CD spectra (*vide infra*).

According to the model constructions, the coordinated sulfur atom of the Λ_L isomer is limited to *S*(*S*) configuration, whereas that of the Δ_L isomer is able to take *R*(*S*) and *S*(*S*) configurations which depend on the conformation of the six-membered N-S chelate ring in L-aehc, namely, the *R*(*S*) coordination takes with a chair-formed N-S chelate ring and the *S*(*S*) coordination with a skew-boat one. In fact, Δ_L-*trans(O)*·*mer(N)*-[Co(L-aehc)(gly)]$^+$ (A-1) has the *R*(*S*) configuration and the six-membered N-S chelate ring in the chair form,[13] and the Δ_L-*cis(O)*·*mer(N)* isomer (A-3) also has *R*(*S*) with the chair-formed N-S chelate ring.[14] These two glycinato isomers show similar ^{13}C NMR spectral behavior on the carbon atoms of L-aehc to those of the Δ_L-*trans(N)*-[Co(L-aehc)(ox)] and Δ_L-[Co(L-aehc)(en)]$^{2+}$ ones (Fig. 6). The distribution of the chemical shifts for each carbon atom of L-aehc seems to be related with the interligand interaction between the six-membered N-S chelate ring and the five-membered N-S chelate ring, as in the case of the chemical shift for the β-methylene carbon mentioned above. Thus it is suggested that the six-membered N-S chelate ring for the ox and en complexes takes a chair conformation (simultaneously *R*(*S*) configuration) in the Δ_L isomers.

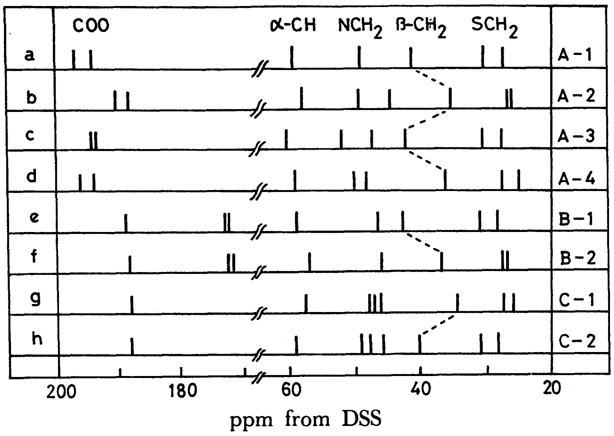

Fig. 6. The distribution of ^{13}C NMR chemical shifts of [Co(L-aehc)(L)].
a—d: L=gly; e and f: L=ox; g and h; L=en.

Two isomers, Δ_L and Λ_L, are possible for [Co(L-aehc)$(NH_3)_2$]$^{2+}$ as well as the ethylenediamine complex. The absorption spectra of D-1 and D-2 isomers of the diammine complex are quite similar to those of the [Co(L-aehc)(en)]$^{2+}$ and [Co(L-met)$(NH_3)_3$]$^{2+}$ complexes over the whole region (Figs. 5 and 7). Furthermore, the CD spectral patterns of D-1 and D-2 isomers also agree well with those of [Co(L-aehc)(en)]$^{2+}$ isomers (*vide infra*).

CD Spectra. The CD spectra of the L-aehc complexes are shown in Figs. 2—5 and 7, and their data are summarized in Table 1. Three pairs of quasi-enantiomeric geometrical isomers for the gly and ox complexes exhibit approximately enantiomeric CD patterns, respectively, though some deviations are observed in the first absorption band region (Figs. 2—4). This enantiomeric CD spectral relationship can be applied for the assignment of the two isomers of [Co(L-aehc)(en)]$^{2+}$, namely, Λ_L for C-1 isomer and Δ_L for C-2 one (Fig. 5). This assignment agrees with that based on their ^{13}C NMR spectra mentioned above. Similarly, D-1 and D-2 isomers of [Co(L-aehc)$(NH_3)_2$]$^{2+}$ correspond to Δ_L- and Λ_L-[Co(L-aehc)(en)]$^{2+}$, respectively, as shown in Fig. 7. Here, it should be noted that Δ_L-[Co(L-aehc)$(NH_3)_2$]$^{2+}$ (D-1) isomerized gradually to Λ_L one (D-2) in aqueous solution, while Λ_L isomer did not. This trend in isomerization agrees with the suggestion from the stereomodel examination that L-aehc prefers Λ_L coordination to Δ_L one, because of more strained *R*(*S*) caused by the Δ_L coordination of L-aehc. Further study is being undertaken to investigate the isomerization

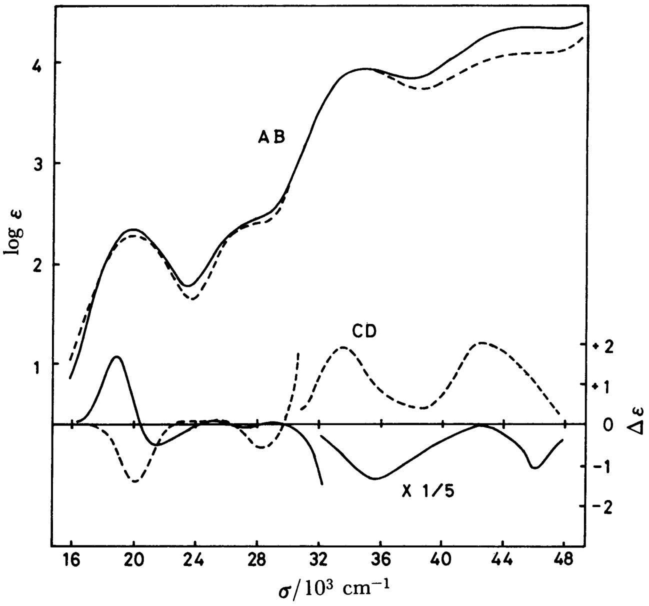

Fig. 7. Absorption and CD spectra of [Co(L-aehc)-$(NH_3)_2]^{2+}$: Λ_{L} (——) and Δ_{L} (------).

in detail.

In order to estimate the CD contribution due to the L-methionine moiety of L-aehc, the triammine(L-methioninato)cobalt(III) complex, $[Co(L\text{-met})(NH_3)_3]^{2+}$, was prepared. The ^{1}H NMR spectrum of the triammine complex exhibits a peak (2.34 ppm) with a shoulder at lower field due to the *S*-methyl protons, suggesting the coexistence of *R*(*S*) and *S*(*S*) isomers. This result suggests that the CD spectrum of $[Co(L\text{-met})(NH_3)_3]^{2+}$ is mainly due to *S*(*C*) of the L-met (Fig. 5). In contrast to the triammine complex, $[Co(L\text{-aehc})(NH_3)_2]^{2+}$ and $[Co(L\text{-aehc})(en)]^{2+}$ have two additional CD contributions besides that due to *S*(*C*) of L-aehc, namely, one from the configurational chirality due to the skew pair of chelate rings of L-aehc and the other the chirality due to the sulfur donor atom, though the two contributions can not be separated. As shown in Fig. 5, the CD curves of $[Co(L\text{-aehc})(en)]^{2+}$ isomers in the region of 24—48×10³ cm⁻¹ are almost enantiomeric, taking into account that the CD curve of $[Co(L\text{-met})(NH_3)_3]^{2+}$ is subtracted from that of Δ_{L}- or Λ_{L}-$[Co(L\text{-aehc})(en)]^{2+}$, while their CD patterns in the first absorption band region deviate significantly from the enantiomeric relation. The same situation holds for each of the quasi-enantiomeric pairs of the other L-aehc complexes (Figs. 2—4). The Λ_{L} isomers of all the L-aehc complexes exhibit a similar CD pattern ((+) and (−) from lower energy) in the first absorption band region, regardless of the geometrical configurations with respect to the coordinated atoms, while the patterns of Δ_{L} isomers depend remarkably on their geometrical configurations. These CD spectral behaviors of Δ_{L} and Λ_{L} isomers in the first absorption band region are also observed for the CD spectra of the *S*-(carboxymethyl)-L-homocysteinato and *S*-(2-carboxyethyl)-L-homocysteinato complexes.[22] These deviations in the first absorption band region seem to be attributed to the difference of configurational chiralities due to the coordinated L-aehc, Δ_{L}-*R*(*S*) and Λ_{L}-*S*(*S*), rather than the chiral sulfur atom, taking account of the fact that the CD patterns of *R*(*S*)- and *S*(*S*)-$[Co(R\text{-cmtp or }R\text{-cetp})(NH_3)_3]^+$, which are mainly contributed to the chirality due to the sulfur donor atom, are almost enantiomeric in the first absorption band region (where *R*-cmtp and *R*-cetp denote (2*R*)-2-(carboxymethylthio)propionate and (2*R*)-2-(2-carboxyethylthio)propionate).[12]

References

1) J. Hidaka, S. Yamada, and Y. Shimura, *Chem. Lett.*, **1974**, 1487.

2) K. Yamanari, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 2451 (1977).

3) T. Isago, K. Igi, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **52**, 407 (1979).

4) K. Okamoto, K. Wakayama, H. Einaga, S. Yamada, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 165 (1983).

5) R. J. Magee, W. Mazurek, M. J. O'Conner, and A. T. Philip, *Aust. J. Chem.*, **27**, 1629 (1974).

6) K. Okamoto, T. Isago, M. Ohmasa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **55**, 1077 (1982).

7) T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 2631 (1983).

8) K. Okamoto, H. Maki, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **57**, 595 (1984).

9) The symbols, *R*(*S*), *S*(*S*), and *S*(*C*), denote the absolute configurations of the chiral sulfur donor atom and the carbon atom, respectively.

10) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **17**, 2165 (1978).

11) K. Yamanari, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 2299, 2643 (1977).

12) M. Suzuki, K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **55**, 3929 (1982).

13) K. Okamoto, M. Suzuki, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 3505 (1983).

14) K. Okamoto, M. Suzuki, and J. Hidaka, *Chem. Lett.*, **1983**, 401.

15) The symbols, Δ_{L} and Λ_{L}, are designed on the basis of the configurational chirality due to the skew pair of the chelate rings of the L-aehc (Fig. 1). In former papers,[13,14] Δ and Λ correspond to Δ_{L} and Λ_{L}, respectively.

16) M. D. Armstrong and J. D. Lewis, *J. Org. Chem.*, **16**, 749 (1951).

17) J. C. Bailar, Jr., *Inorg. Synth.*, **2**, 222 (1946).

18) M. Shibata, *Nippon Kagaku Zasshi*, **87**, 771 (1966).

19) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

20) C. A. Chang and B. E. Douglas, *J. Coord. Chem.*, **9**, 93 (1979).

21) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967).

22) The present authors, to be published.