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Preparation and CD Spectra of Cobalt(III) Complexes with *S*-(Carboxymethyl)-L-cysteinate and Its Analogues

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Four cobalt(III) complexes of the [Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$ type were prepared; where L-quadridentate-*N,S,O*$_2$ denotes *S*-(carboxymethyl)-L-cysteinate(L-cmc), *S*-(2-carboxyethyl)-L-cysteinate(L-cec), *S*-(carboxymethyl)-L-homocysteinate(L-cmhc), or *S*-(2-carboxyethyl)-L-homocysteinate(L-cehc). Each complex was chromatographically separated into the quasi-enantiomeric isomers; Λ_{L}-*trans*(*O*)-*S*(*S*) and Δ_{L}-*cis*(*O*)-*R*(*S*) for the L-cmc, L-cmhc, and L-cehc complexes, and Λ_{L}-*trans*(*O*)-*R*(*S*) and Δ_{L}-*cis*(*O*)-*S*(*S*) for the L-cec one. These isomers were characterized from their absorption and ^{13}C NMR spectra. The sterically strained Δ_{L}-*cis*(*O*) isomers exhibited some significant CD spectral behavior in the first d-d absorption band region. The CD spectra are discussed in relation to the sizes of the S–N and S–O chelate rings joining the chiral sulfur atom in the L-quadridentate-*N,S,O*$_2$ ligand.

In the previous papers,[1–3] we reported the stereochemical and spectrochemical properties of the cobalt(III) complexes with an L-quadridentate-*N*$_2$,*S,O* ligand, *S*-(2-aminoethyl)-L-homocysteinate (L-aehc), in which the sulfur atom is fixed by a five-membered terminal S–N and a six-membered medial S–N chelate rings. The L-quadridentate-*N,S,O*$_2$ ligand used in the present work is *S*-(carboxymethyl)-L-cysteinate (L-cmc), *S*-(2-carboxyethyl)-L-cysteinate (L-cec), *S*-(carboxymethyl)-L-homocysteinate (L-cmhc), and *S*-(2-carboxyethyl)-L-homocysteinate (L-cehc), and they are similar to L-aehc in the structure (Fig. 1). However, the L-quadridentate-*N,S,O*$_2$ ligand is different from L-aehc in the sizes of the chelate rings formed. Namely, when the L-quadridentate-*N,S,O*$_2$ ligand coordinates to the cobalt(III) ion, its terminal S–O (**A** ring in Fig. 1) and medial S–N (**B** ring) chelate rings joining the sulfur atom take the ring sizes as summarized in Table 1.

In this work, the [Co(L-quadridentate-*N,S, O*$_2$)(en)]$^+$-type complexes were prepared and chromatographically separated into two geometrical isomers, Λ_{L}-*trans(O)* and Δ_{L}-*cis(O)*. All isomers were characterized from their absorption spectra. Of these isomers the coordinated sulfur atom of Δ_{L}-*cis(O)*-[Co(L-cmhc or L-cehc)(en)]$^+$ is possible to take either configuration of *R*(*S*) and *S*(*S*), and these configurations were suggested on the basis of the ^{13}C NMR spectra. The CD spectral behaviors due to the difference in ring sizes of the chelates, S–N and S–O, were discussed in comparison with those of the L-aehc complexes.[1–3]

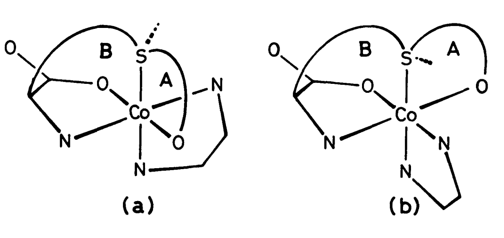

Fig. 1. Possible isomers of [Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$: (a) Λ_{L}-*trans*(*O*) and (b) Δ_{L}-*cis*(*O*).

Table 1. Chelate ring sizes of **A** and **B** rings in Fig. 1

Ligand	**A** ring[a)]	**B** ring[a)]
L-cmc	5	5
L-cec	6	5
L-cmhc	5	6
L-cehc	6	6

a) **A** and **B** rings correspond to terminal S–O and medial S–N rings, respectively.

Experimental

Preparation of Ligands. *1) S-(Carboxymethyl)-L-homocysteine and S-(2-Carboxyethyl)-L-homocysteine*: *L-H$_2$cmhc and L-H$_2$cehc.* These ligands were prepared by the method of Armstrong and Lewis.[4)] Anal. for L-H$_2$cmhc ($C_6H_{11}NO_4S$) C, H, N. Anal. for L-H$_2$cehc ($C_7H_{13}NO_4S$) C, H, N. $[\alpha]_D^{24}=+34.9°$ for L-H$_2$cmhc and $[\alpha]_D^{24}=+44.4°$ for L-H$_2$cehc (*c* 1.0, 1 mol dm^{-3} HCl).

2) S-(2-Carboxyethyl)-L-cysteine: *L-H$_2$cec.* This ligand was prepared by a procedure similar to that used for (*R*)-2-(carboxymethylthio)propionic acid.[5)] Anal. ($C_6H_{11}NO_4S$) C, H, N. $[\alpha]_D^{24}=-14.8°$ (*c* 1.0, 1 mol dm^{-3} HCl).

3) S-(Carboxymethyl)-L-cysteine: *L-H$_2$cmc.* This ligand was supplied by the Aldrich Chemical Co. Ltd., and used without purification.

Preparation and Separation of Complexes. *4)* {*S-(Carboxymethyl)-L-homocysteinato*}*(ethylenediamine)cobalt(III) Chlolide*: *[Co(L-cmhc)(en)]Cl.* A solution containing 2.0 g of L-H$_2$cmhc 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 were added a solution containing 2.0 g of *trans*-[Co(Cl)$_2$(en)$_2$]Cl[6)] in 10 cm^3 of water and 0.5 g of activated charcoal. The mixture was stirred at *ca.* 75 °C for 15 min, while the color of the solution changed from green to purple. After the solution had been cooled to room temperature, it was filtered and the filtrate was poured onto a column of Dowex 50W-X8 (200—400 mesh, Na$^+$ form, 2.0 cm×50 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.05 mol dm^{-3} aqueous solution of NaCl. Two colored bands, red-violet (A-1) and red (A-2), were eluted in this order. It was found, from the absorption spectral measurements, that eluates A-1 and A-2 contained *trans(O)*- and *cis(O)*-[Co(L-cmhc)(en)]$^+$, 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

(2.0 cm×150 cm) by elution with water and the eluate was concentrated again. After adding a small amount of ethanol, the solution was kept in a refrigerator. The crystals appeared were collected by filtration, and washed with ethanol and then ether. Isomer A-1 was obtained as flaky red-violet crystals and isomer A-2 as red needle ones. Found for A-1: C, 27.54; H, 5.07; N, 12.13%. Calcd for [Co(L-cmhc)(en)]Cl·0.25H$_2$O=CoC$_8$H$_{17}$N$_3$O$_4$SCl·0.25H$_2$O: C, 27.44; H, 5.04; N, 12.00%. Found for A-2: C, 26.54; H, 5.27; N, 11.68%. Calcd for [Co(L-cmhc)(en)]Cl·H$_2$O: C, 26.42; H, 5.27; N, 11.55%.

5) {S-(2-Carboxyethyl)-L-homocysteinato}(ethylenediamine)cobalt(III) Chloride: [Co(L-cehc)(en)]Cl. This complex was prepared and the isomers were chromatographically separated by the same procedure as for *4)*, using L-H$_2$cehc instead of L-H$_2$cmhc. Two colored bands, red-violet (B-1) and red (B-2), were eluted in this order, and eluates B-1 and B-2 contained *trans(O)*- and *cis(O)*-[Co(L-cehc)(en)]$^+$, respectively. Isomers B-1 and B-2 were obtained as red-violet flaky and red needle crystals, respectively. Found for B-1: C, 28.80; H, 5.47; N, 11.44%. Calcd for [Co(L-cehc)(en)]Cl·0.5H$_2$O=CoC$_9$H$_{19}$N$_3$O$_4$SCl·0.5H$_2$O: C, 29.31; H, 5.47; N, 11.48%. Found for B-2: C, 28.78; H, 5.65; N, 11.43%. Calcd for [Co(L-cehc)(en)]Cl·H$_2$O: C, 28.61; H, 5.61; N, 11.13%.

6) {S-(2-Carboxyethyl)-L-cysteinato}(ethylenediamine)cobalt(III) Chloride: [Co(L-cec)(en)]Cl. This complex was prepared and the isomers were chromatographically separated by the same procedure as for *4)*, using L-H$_2$cec instead of L-H$_2$cmhc. Two colored bands, red-violet (C-1) and red (C-2), were eluted in this order, and eluates C-1 and C-2 contained *trans(O)*- and *cis(O)*-[Co(L-cec)(en)]$^+$, respectively. Isomers C-1 and C-2 were also obtained as red-violet flaky and red needle crystals, respectively. Found for C-1: C, 26.50; H, 5.18; N, 11.75%. Calcd for [Co(L-cec)(en)]Cl·0.75H$_2$O=CoC$_8$H$_{17}$N$_3$O$_4$SCl·0.75H$_2$O: C, 26.75; H, 5.19; N, 11.70%. Found for C-2: C, 25.08; H, 5.48; N, 11.21%. Calcd for [Co(L-cec)(en)]Cl·1.75H$_2$O: C, 25.47; H, 5.48; N, 11.14%.

7) {S-(Carboxymethyl)-L-cysteinato}(ethylenediamine)cobalt(III) Chloride: [Co(L-cmc)(en)]Cl. This complex was also prepared and the isomers were chromatographically separated by the same procedure as for *4)*, using L-H$_2$cmc instead of L-H$_2$cmhc, except for adding activated charcoal. Two colored bands, red-violet (D-1) and red (D-2), were eluted in this order, and eluates D-1 and D-2 contained *trans(O)*- and *cis(O)*-[Co(L-cmc)(en)]$^+$, respectively. The yield of the slower eluted isomer (D-2) was very poor and this was obtained by repeating the preparation several times. Isomers D-1 and D-2 were also obtained as red-violet flaky and red needle crystals, respectively. Found for D-1: C, 24.07; H, 4.77; N, 12.24%. Calcd for [Co(L-cmc)(en)]Cl·0.75H$_2$O=CoC$_7$H$_{15}$N$_3$O$_4$SCl·0.75H$_2$O: C, 24.36; H, 4.82; N, 12.17%. Found for D-2: C, 24.83; H, 4.71; N, 12.52%. Calcd for [Co(L-cmc)(en)]Cl·0.25H$_2$O: C, 25.01; H, 4.65; N, 12.50%.

Measurements. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and UVIDEC-610 spectrophotometers, and the CD spectra with a JASCO J-20 spectropolarimeter. All the measurements were carried out at room temperature.

The ^{13}C NMR spectra were recorded with a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference.

Results and Discussion

Two quasi-enantiomeric geometrical isomers, Δ_L-*trans(O)* and Δ_L-*cis(O)*, are possible for the present [Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$-type complexes with L-cmc, L-cec, L-cmhc, and L-cehc (Fig. 1).[7] The Δ_L-*trans(O)* isomers take the facial coordination with respect to the terminal S–O and medial S–N chelate rings joining the sulfur atom, while the Δ_L-*cis(O)* isomers take the meridional one, where the terminal S–O and medial S–N chelate rings correspond to rings **A** and **B** in Fig. 1, respectively. The representative absorption spectra of [Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$ are shown in Fig. 2, and the data are summarized in Table 2. The eight isomers are classified into two groups based on the splittings of their first d-d absorption bands. One exhibits an explicit shoulder on the higher energy side of the major peak at 18.2—18.5×10^3 cm^{-1}, and the other a sharp band at 19.3—19.6×10^3 cm^{-1}. Referring to the splitting of the first d-d absorption band of the [Co(N)$_3$(S)(O)$_2$]-type complexes,[1–3,8] the former group can be assigned as Δ_L-*trans(O)* and the latter as Δ_L-*cis(O)*. This assignment is consistent with that based on their ^{13}C NMR and CD spectra (*vide infra*). The terminal S–O and medial S–N chelate rings in [Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$ take the ring sizes as summarized in Table 1. As the ring size increases, the sulfur to metal charge transfer band at *ca.* 36×10^3 cm^{-1} for each of the Δ_L-*trans(O)* and Δ_L-*cis(O)* isomers shifts to lower energy in the following order: L-cmc>L-cmhc>L-cec>L-cehc (Table 2).

As shown in Fig. 3, the ^{13}C NMR spectra for [Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$ exhibit the resonance lines less than or equal to the numbers of the carbon

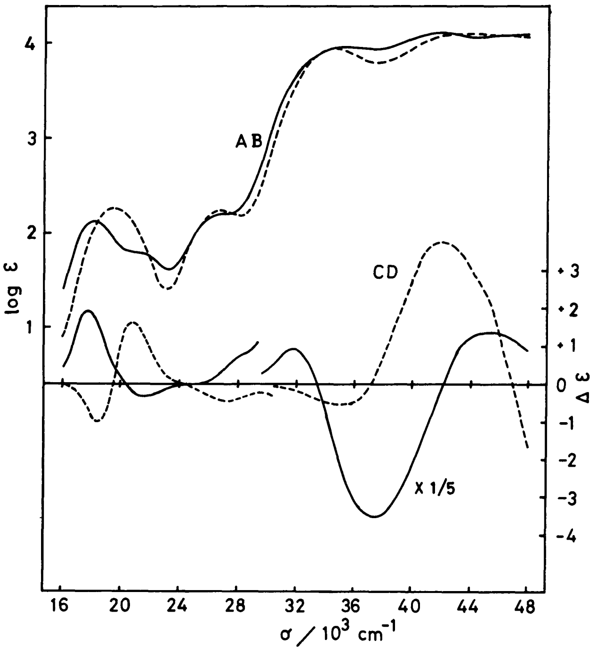

Fig. 2. Absorption and CD spectra of [Co(L-cehc)(en)]$^+$: Δ_L-*trans(O)* (——) and Δ_L-*cis(O)* (----).

Table 2. Absorption and CD spectral data of [Co(quadridentate-*N,S,O*$_2$)(en)]$^+$

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)*-[Co(L-cmc)(en)]$^+$	18.51 (2.10)	17.68 (+5.88)
	20.65 (1.86sh)$^{a)}$	21.04 (−3.24)
	27.66 (2.28)	26.05 (+0.50)
	36.82 (3.87)	28.64 (+2.40)
	42.73 (4.13)	33.92 (+2.50)
	47.84 (4.10)	41.30 (−18.2)
		50.07 (−11.1)
Δ_{L}-*cis(O)*-[Co(L-cmc)(en)]$^+$	19.31 (2.20)	17.52 (−0.14)
	27.03 (2.31)	19.13 (+0.33)
	36.80 (3.87)	21.37 (−0.12)
	44.42 (4.14)	25.55 (+0.10)
		28.80 (−0.43)
		35.71 (−17.1)
		44.39 (+25.2)
Δ_{L}-*trans(O)*-[Co(L-cmhc)(en)]$^+$	18.52 (2.14)	17.66 (+4.05)
	21.05 (1.82sh)	20.74 (−1.36)
	27.12 (2.28)	28.45 (+1.32)
	36.46 (3.88)	33.07 (+4.65)
	43.17 (4.09)	39.25 (−2.09)
Δ_{L}-*cis(O)*-[Co(L-cmhc)(en)]$^+$	19.63 (2.16)	18.80 (−1.75)
	27.24 (2.24)	21.18 (+0.92)
	35.66 (4.00)	28.63 (−0.55)
	44.10 (4.21)	36.45 (+3.70)
		43.79 (+3.41)
Δ_{L}-*trans(O)*-[Co(L-cec)(en)]$^+$	18.34 (2.13)	17.65 (+2.92)
	20.75 (1.87sh)	21.46 (−1.65)
	26.71 (2.17)	28.18 (+1.07)
	36.08 (3.86)	31.90 (+0.15)
	42.90 (4.06)	35.73 (−0.75)
	48.35 (4.01)	41.87 (−14.0)
Δ_{L}-*cis(O)*-[Co(L-cec)(en)]$^+$	19.50 (2.32)	17.14 (−0.06)
	26.83 (2.26)	19.87 (+0.54)
	35.74 (3.93)	25.74 (+0.32)
	43.18 (3.98sh)	35.10 (−14.0)
	47.24 (4.11)	42.01 (+18.4)
		44.79 (+16.8)
Δ_{L}-*trans(O)*-[Co(L-cehc)(en)]$^+$	18.19 (2.13)	17.78 (+1.99)
	21.18 (1.79sh)	21.40 (−0.34)
	26.84 (2.21)	28.25 (+0.72)
	35.36 (3.95)	31.89 (+4.76)
	42.01 (4.10)	37.23 (−17.2)
		45.38 (+6.96)
Δ_{L}-*cis(O)*-[Co(L-cehc)(en)]$^+$	19.42 (2.28)	18.47 (−1.04)
	26.85 (2.25)	20.79 (+1.68)
	34.49 (3.94)	27.14 (−0.43)
	43.56 (4.11)	35.23 (+2.69)
		42.02 (+18.5)

a) Sh denotes a shoulder.

atoms in the L-quadridentate-*N,S,O*$_2$ and en ligands. When the complexes take only *R(S)* or *S(S)* configuration[7] with respect to the chiral sulfur atom, the ^{13}C NMR spectra can be expected to show seven resonance lines for the L-cmc complex, eight ones for the L-cec and L-cmhc complexes, and nine ones for the L-cehc complex. While, when the complexes are a mixture of the *R(S)* and *S(S)* isomers and/or the other species such as [Co(L-cmc)(en)(H$_2$O)]$^+$ more multiple peaks can be expected for their ^{13}C NMR spectra. The present result suggests that each of the complexes takes either *R(S)* or *S(S)* configuration. According to the model constructions, the coordinated sulfur atoms of Δ_{L}-*cis(O)*-[Co(L-cmc)(en)]$^+$ and Δ_{L}-*trans(O)*-[Co(L-cec)(en)]$^+$ are limited to *R(S)* configuration, whereas those of Δ_{L}-*trans(O)*-[Co(L-cmc)(en)]$^+$, Δ_{L}-*cis(O)*-[Co(L-cec)(en)]$^+$, Δ_{L}-*trans(O)*-[Co(L-cmhc)(en)]$^+$, and Δ_{L}-*trans(O)*-[Co(L-cehc)(en)]$^+$ to *S(S)* configuration. In contrast to the above isomers, the coordinated sulfur atom of Δ_{L}-*cis(O)*-[Co(L-cmhc or L-cehc)(en)]$^+$ can take either configuration of *R(S)* and *S(S)*, depending on the conformation of the medial S–N chelate ring,[9] as in the case of the L-aehc complexes.[1–3] The Δ_{L}-*S(S)*- and Δ_{L}-*R(S)*-[Co(L-aehc)(en)]$^{2+}$ isomers exhibited a well defined

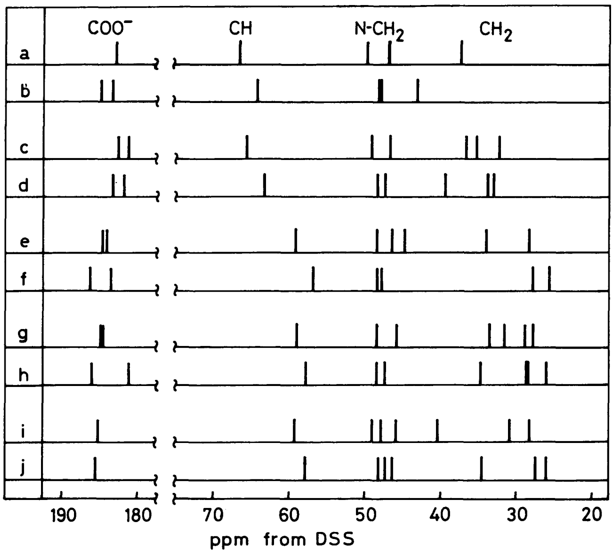

Fig. 3. The distribution of ^{13}C NMR chemical shifts of [Co(L)(en)]: L=L-cmc, a and b; L=L-cec, c and d; L=L-cmhc, e and f; L=L-cehc, g and h; and L=L-aehc, i and j. a, c, e, and g are $\Delta_{\rm L}$-*cis(O)* isomers, b, d, f, and h are $\Lambda_{\rm L}$-*trans(O)* isomers, i is $\Delta_{\rm L}$ isomer, and j is $\Lambda_{\rm L}$ isomer.

^{13}C NMR spectral relationship with regard to their β-methylene and the other carbon atom regions.[3] A similar relationship is also observed for the ^{13}C NMR spectra of the $\Lambda_{\rm L}$-*trans(O)* and $\Delta_{\rm L}$-*cis(O)* isomers of each complex in the present work, especially in the methine carbon atom region (Fig. 3); namely, $\Lambda_{\rm L}$-*trans(O)-S(S)* and $\Delta_{\rm L}$-*cis(O)-R(S)* for the L-cmc complex, $\Lambda_{\rm L}$-*trans(O)-R(S)* and $\Delta_{\rm L}$-*cis(O)-S(S)* for the L-cec one, and $\Lambda_{\rm L}$-*trans(O)-S(S)* and $\Delta_{\rm L}$-*cis(O)-R(S)* or *-S(S)* for the L-cmhc and L-cehc ones. Taking account of the shielding effect due to the two carboxyl groups[10,11] and the steric effect due to the interaction between the terminal S–O and medial S–N chelate rings, as in the L-aehc complexes,[3] the distribution of the chemical shifts for each of the methine, *N*-methylene, and carboxylate carbons in the L-quadridentate-N,S,O_2 and en ligands seems to depend on the direction of the terminal S–O chelate ring regardless of its chelate ring size. Thus, it is assumed that the $\Delta_{\rm L}$-*cis(O)* isomers of the L-cmhc and L-cehc complexes may take *R(S)* configuration.

Figure 2 shows the representative CD curves for [Co(L-quadridentate-N,S,O_2)(en)]$^+$, and the CD data are summarized in Table 2. The overall CD patterns for the L-cehc isomers are almost enantiomeric, although some deviations are observed in the region of 30—48×10^3 cm^{-1} (Fig. 2). A similar trend was also observed for the CD spectra of the isomers of each of the L-cmc, L-cec, and L-cmhc complexes (Table 2). In the first d-d absorption band region, the *trans(O)* and *cis(O)* isomers of the present complexes exhibit similar CD patterns to those of the $\Lambda_{\rm L}$-*S(S)* and $\Delta_{\rm L}$-*R(S)* isomers of [Co(L-aehc)(L)] (L; ox, gly, en, and (NH$_3$)$_2$), respectively, whose CD patterns depend mainly on the coordination mode of the L-quadridentate-N_2,S,O ligand, L-aehc, regardless of the kind of ligand coordinating to the two remaining coordination sites.[1–3] These facts indicate that the *trans(O)* isomers take $\Lambda_{\rm L}$ coordination with respect to the configurational chirality of the coordinated L-quadridentate-N,S,O_2 ligand and the *cis(O)* isomers take $\Delta_{\rm L}$ one, namely, $\Lambda_{\rm L}$-*trans(O)* and $\Delta_{\rm L}$-*cis(O)*.

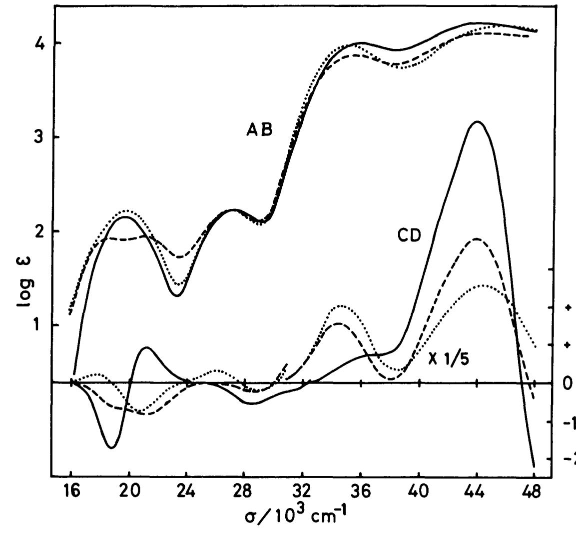

Fig. 4. Absorption and CD spectra of $\Delta_{\rm L}$-*cis(O)*-[Co(L-cmhc)(en)]$^+$ (——), $\Delta_{\rm L}$-*cis(O)·mer(N)*-[Co(L-aehc)(gly)]$^+$ (······), and $\Lambda_{\rm L}$-*trans(O)·mer(N)*-[Co(L-aehc)(gly)]$^+$ (----).

The absorption and CD spectra of $\Delta_{\rm L}$-*cis(O)-R(S)*-[Co(L-cmhc)(en)]$^+$, which has a quite similar framework and steric environment to the L-aehc complexes, are shown in Fig. 4, together with those of $\Delta_{\rm L}$-*cis(O)·mer(N)-R(S)*- and $\Delta_{\rm L}$-*trans(O)·mer(N)-R(S)*-[Co(L-aehc)(gly)]$^+$.[3] The $\Delta_{\rm L}$-*cis(O)-R(S)* L-cmhc isomer exhibits a more sharp first d-d absorption band than $\Delta_{\rm L}$-*cis(O)·mer(N)-R(S)*-[Co(L-aehc)(gly)]$^+$, indicating the *fac(N)* form (Fig. 4).[3] The $\Delta_{\rm L}$-*cis(O)-R(S)* L-cmhc isomer exhibits a different CD pattern in the first d-d absorption band region from $\Delta_{\rm L}$-*cis(O)·mer(N)-R(S)*- and $\Delta_{\rm L}$-*trans(O)·mer(N)-R(S)*-[Co(L-aehc)(gly)]$^+$, while $\Lambda_{\rm L}$-*trans (O)-S(S)*-[Co(L-cmhc](en)]$^+$ and $\Lambda_{\rm L}$-*cis(O)·mer(N)-S(S)*- and $\Lambda_{\rm L}$-*cis(O)·fac(N)-S(S)*-[Co(L-aehc)(gly)]$^+$ exhibit similar CD patterns, (+) and (−) CD bands from lower energy.[1–3] These indicate that the CD pattern of the $\Delta_{\rm L}$-*cis(O)-R(S)*-[Co(L-cmhc)(en)]$^+$ isomer depends remarkably on the geometrical configuration with respect to the coordinated atom as in the case of the L-aehc complexes.[3] In the region of 32—48×10^3 cm^{-1}, it should be noted that the $\Delta_{\rm L}$-*R(S)* isomers commonly exhibit positive CD bands, suggesting that the configurational chirality due to the L-quadridentate ligand, $\Delta_{\rm L}$-*R(S)*, is mainly responsible for the CD pattern in this region, as in $\Delta_{\rm L}$-*R(S)*-[Co(L-aehc)(L)] (L; ox, gly, en, and (NH$_3$)$_2$).

The four $\Lambda_{\rm L}$-*trans(O)* isomers of [Co(L-quadridentate-N,S,O_2)(en)]$^+$ exhibit some notable differences in CD intensity in the first d-d absorption band region. As shown in Fig. 5, the order of their CD intensities is L-

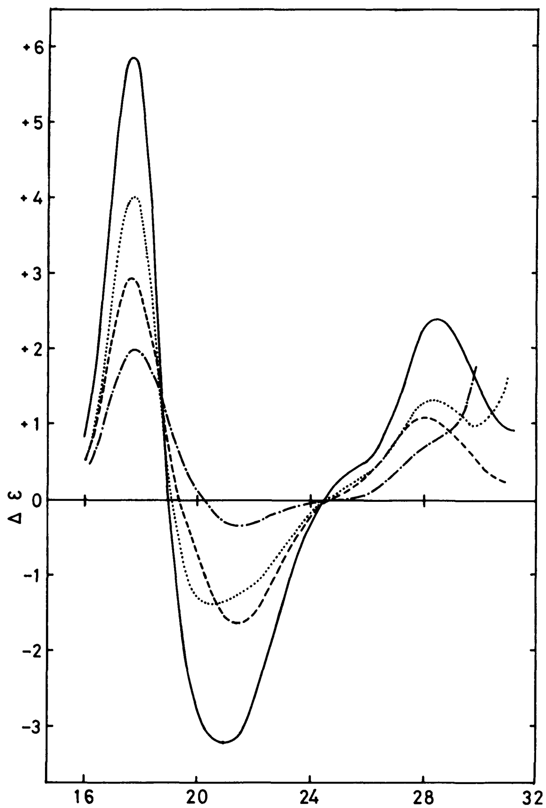

Fig. 5. CD spectra of Λ_{L}-*trans(O)*-[Co(L)(en)]$^+$: L=L-cmc (——), L-cmhc (······), L-cec (----), and L-cehc (-·-·-·-).

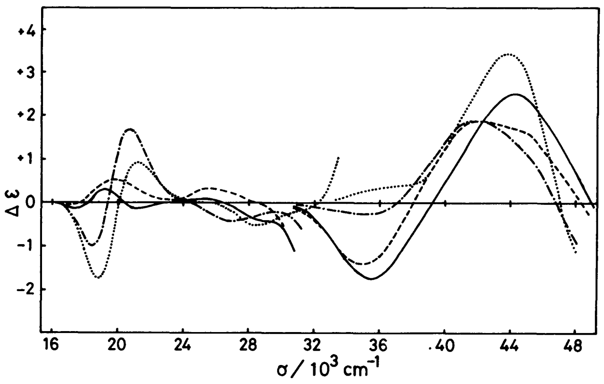

Fig. 6. CD spectra of Δ_{L}-*cis(O)*-[Co(L)(en)]$^+$: L=L-cmc (——), L-cmhc (······), L-cec (----), and L-cehc (-·-·-·-).

cmc>L-cmhc>L-cec>L-cehc. This seems to be related to the ring sizes of the terminal S–O and medial S–N chelates. Namely, the L-cec and L-cehc isomers with the six-membered S–O chelate ring exhibit much weaker CD bands than the L-cmc and L-cmhc isomers with the five-membered one (Table 1). The L-cehc isomer taking the six-membered S–N chelate ring also exhibits more weak CD bands than the L-cec isomer taking the five-membered one (Table 1). A similar relationship was also observed for the L-cmc and L-cmhc isomers. The CD spectral change in intensity will be attributable to the rigidity of the chelate rings joining the chiral sulfur atom. In contrast to the Λ_{L}-*trans(O)* isomers, two types of the CD patterns are observed for the Δ_{L}-*cis(O)* isomers in the first d-d absorption band region (Fig. 6), namely, one is Δ_{L}-*cis(O)*-[Co(L-cmc or L-cec)(en)]$^+$ taking the medial five-membered S–N chelate ring and the other Δ_{L}-*cis(O)*-[Co(L-cmhc or L-cehc)(en)]$^+$ taking the six-membered one. The Δ_{L}-*cis(O)* isomer of [Co(L-cmhc or L-cehc)(en)]$^+$ exhibits an almost enantiomeric CD pattern to that of the corresponding Λ_{L}-*trans(O)* one, while the CD pattern for the Δ_{L}-*cis(O)* isomer of [Co(L-cmc or L-cec)(en)]$^+$ deviates significantly from that for the corresponding Λ_{L}-*trans(O)* one, as seen in Fig. 6. Of the four Δ_{L}-*cis(O)* isomers, the L-cmhc and L-cehc isomers are possible to take either configuration of *R(S)* or *S(S)* depending on the conformations (chair and skew-boat)[9] of the medial six-membered S–N chelate ring because of the flexible methioninate moiety.[1–3] From the good enantiomeric correspondence of the CD patterns of the two Δ_{L}-*cis(O)* isomers to the common CD pattern for the four Λ_{L}-*trans(O)*-[Co(L-quadridentate-*N,S,O*$_2$)(en)]$^+$ isomers, it is tentatively assigned that the Δ_{L}-*cis(O)* isomer of [Co(L-cmhc or L-cehc)(en)]$^+$ takes *R(S)* configuration in accordance with the assignment based on their ^{13}C NMR spectra. In the Δ_{L}-*cis(O)* isomer of [Co(L-cmc or L-cec)(en)]$^+$, on the other hand, the terminal S–O chelate ring is strongly strained because of the rigid cysteinate moiety. From this viewpoint, it may be assumed that the deviation in the CD pattern in the first d-d absorption band region is related to the flexibility around the chiral sulfur atom in the L-quadridentate-*N,S,O*$_2$ ligand.

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