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Stereochemistry of Cobalt(III) Complexes with Thioethers. III.[1] Vicinal Circular Dichroism due to the Chiral Sulfur Donor Atom

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Two kinds of mixed type cobalt(III) complexes, [(2-aminoethylthio)acetato](L-methioninato)cobalt(III) chloride and [3-(2-aminoethylthio)propionato](L-methioninato)cobalt(III) chloride, have been prepared and chromatographically separated into seven and eight isomers, respectively. The characterization of isomers based on their electronic absorption and ^{1}H NMR spectra leads to the conclusion that there have been obtained four pairs of diastereomers due to the sulfur chirality of the coordinated L-methioninate. The circular dichroism spectra of isomers have been measured and discussed in relation to the absolute configurations. The vicinal CD contribution due to the chiral sulfur atom of L-methioninate has been estimated by applying an additivity rule for the three diastereomeric pairs.

A large number of investigations for the vicinal circular dichroism (CD) of asymmetric carbon[2] and nitrogen[3] atoms have been undertaken and the results have indicated that the vicinal chirality makes a relatively smaller CD contribution than the configurational one. The sulfur atom of a thioether ligand also becomes chiral by coordination to a metal ion,[4—8] leaving on itself a single lone-pair which can give a fixed configuration for the donor center at ordinary temperature. However, no optical resolution has been reported for the coordinated sulfur atom of cobalt(III) complexes with thioethers, though some examples were known for the complexes of other metals such as [Pt^{IV}Cl$_4$(NH$_2$CH$_2$CH$_2$SCH$_2$CH$_2$NH$_3$)]Cl.[9]

The present paper is concerned with the isolation of diastereomers arising from the chiral sulfur donor atom and the estimation of vicinal CD contribution due to the sulfur donor in two mixed-complex systems, [Co(terdentate-*N,S,O*)(L-met)]$^+$ [L-Hmet=L-methionine; terdentate-*N,S,O*=(2-aminoethylthio)acetic acid (Haeta), and 3-(2-aminoethylthio)propionic acid (Haetp)]. For the mixed complex six geometrical isomers, *tr.tr.tr.*, *trans(S)*, *trans(O)*, *trans(N)*, *cisciscis-I*, and *cisciscis-II*, are possible as seen in Fig. 1. As compared with [Co(terdentate-*N,S,O*)$_2$]$^+$ complexes,[1] isomer distribution is altered; *meridional* isomer becomes impossible and two *cisciscis* isomers, *cisciscis-I* and *-II*, appear in the present mixed type complexes. In addition, a pair of another type isomers are formally expected for each of the six geometrical isomers, arising from the absolute configuration (*R*) or (*S*) of the sulfur donor atom of coordinated L-methioninate ligand.

Experimental

Preparation and Separation of Isomers. *[(2-Aminoethylthio)acetato](*L*-methioninato)cobalt(III) Chloride, [Co(aeta)(*L*-met)]Cl*: To a hot solution (*ca.* 75 °C) of 9.0 g of cobalt(II) chloride hexahydrate in 60 cm^3 of water was added a mixed solution of 5.95 g of (2-aminoethylthio)acetic acid hemihydrochloride,[10] 5.65 g of L-methionine, and 0.75 g of sodium hydroxide dissolved in 80 cm^3 of water. Nine grams of lead dioxide was gradually added to the solution, and this was stirred at 70—75 °C for 40 min, whereupon the color of the solution became violet. The mixture was filtered to remove an excess of the lead dioxide after cooling to room temperature.

The filtrate was poured into a cation-exchange column of Dowex 50Wx8 (Na$^+$ form, 200—400 mesh, 4.5×40 cm). After the column had been swept with water, the adsorbed band was eluted with 0.15 M aqueous solution of sodium chloride at the rate of 1 cm^3 per min. Seven colored bands were eluted. It was confirmed from the measurements of the CD and electronic absorption spectra of these eluates, that the second eluate (brownish violet) was *tr.tr.tr.*-[Co(aeta)$_2$]$^+$, the third one (purple) *trans(S)*-[Co(L-met)$_2$]$^+$,[8] the fourth one (purple) *trans(O)*-[Co(aeta)$_2$]$^+$, and the seventh one (red) *trans(N)*-[Co(aeta)$_2$]$^+$,[1] and that the isomers of the desired complex, therefore, exist in the remaining three eluates, first, fifth, and sixth ones. It was also found that the first dark violet eluate is a single band (C-1), but the fifth and sixth reddish purple ones consist of bands more than two. The three eluates were concentrated separately in a vacuum evaporator, and then the deposit, NaCl, was filtered off. The complex in C-1 eluate was obtained by adding a large amount of ethanol to the concentrated solution and recrystallized from a small amount of water.

Each concentrated solution of the fifth and sixth eluates was again poured into a column of SP-Sephadex C-25 (K$^+$ form, 4.5×120 cm). The adsorbed band was eluted with 0.05 M aqueous solution of K$_2$[Sb$_2$(*d*-tart)$_2$]·3H$_2$O (*d*-H$_4$tart =C$_4$O$_6$H$_6$) at the rate of 0.5 cm^3/min. For the column of the fifth eluate, five colored bands, a brownish red one (C-2), a violet one which was *trans(O)*-[Co(L-met)$_2$]$^+$,[8] a reddish

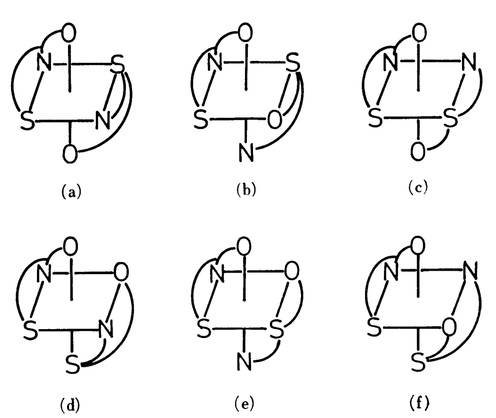

Fig. 1. Six possible geometrical isomers for the [Co(terdentate-*N,S,O*)(L-met)]$^+$ type complex: (a) *tr.tr.tr* (b) *trans(S)*, (c) *trans(O)*, (d) *trans(N)*, (e) *cisciscis-I*, and (f) *cisciscis-II*; methyl group in L-methioninate is omitted.

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purple one (C-3), a brownish red one (C-4), and another brownish red one which was *trans(N)*-$[Co(\text{L-met})_2]^+$,[8] were eluted in this order. On the other hand, for the column of the sixth eluate four colored bands, a brownish red one (C-2), a red one (C-5), another red one (C-6), and a violet one (C-7), were eluted in this order. CD measurements showed that each band consists of a single species. The desired eluates, C-2 to C-7, were concentrated separately in a vacuum evaporator, and the deposit, $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$, was filtered off. The concentrated eluate was poured into an anion exchange column of Dowex 1x8 (Cl^- form) and converted into the chloride salt. The desired complex was obtained by adding a large amount of ethanol to the eluate. The product was recrystallized from a minimum quantity of water by adding a small amount of ethanol and washed with ethanol and then acetone, and dried in a vacuum desiccator over $CaCl_2$. Found for C-1: C, 28.09; H, 4.79; N, 7.34%. Calcd for $[Co(aeta)(\text{L-met})]Cl = C_9H_{18}N_2S_2O_4ClCo$: C, 28.69; H, 4.82; N, 7.44%. Found for C-2: C, 27.69; H, 4.76; N, 7.09%. Calcd for $[Co(aeta)(\text{L-met})]Cl\cdot 0.5H_2O\cdot 1/10\,KCl = C_9H_{19}N_2S_2O_{4.5}ClCo\cdot 1/10\,KCl$: C, 27.49; H, 4.87; N, 7.12%. Found for C-3: C, 25.79; H, 5.30; N, 6.54%. Calcd for $[Co(aeta)(\text{L-met})]Cl\cdot 2H_2O\cdot 1/10\,KCl = C_9H_{22}N_2S_2O_6ClCo\cdot 1/10\,KCl$: C, 25.72; H, 5.28; N, 6.67%. Found for C-4: C, 26.42; H, 5.35; N, 6.60%. Calcd for $[Co(aeta)(\text{L-met})]Cl\cdot 2H_2O = C_9H_{22}N_2S_2O_6ClCo$: C, 26.17; H, 5.37; N, 6.79%. Found for C-5: C, 25.33; H, 4.89; N, 6.75%. Calcd for $[Co(aeta)(\text{L-met})]Cl\cdot 1.5H_2O\cdot 3/10\,KCl = C_9H_{21}N_2S_2O_{5.5}ClCo\cdot 3/10\,KCl$: C, 25.37; H, 4.97; N, 6.57%. Found for C-6: C, 24.99; H, 4.94; N, 6.86%. Calcd for $[Co(aeta)(\text{L-met})]Cl\cdot 1.5H_2O\cdot 3/10\,KCl = C_9H_{21}N_2S_2O_{5.5}ClCo\cdot 3/10\,KCl$: C, 25.37; H, 4.97; N, 6.57%. Found for C-7: C, 26.15; H, 5.36; N, 6.93%. Calcd for $[Co(aeta)(\text{L-met})]Cl\cdot 2H_2O = C_9H_{22}N_2S_2O_6ClCo$: C, 26.19; H, 5.37; N, 6.79%.

[3-(2-Aminoethylthio)propionato](L-methioninato)cobalt(III) Chloride, [Co(aetp)(L-met)]Cl: The preparation and separation of isomers were carried out according to the method similar to that for the corresponding [Co(aeta)(L-met)]Cl complex, by use of $Haetp\cdot HBr\cdot 0.5H_2O$[10] instead of $Haeta\cdot 0.5HCl$.

Nine colored bands were eluted. From the measurements of the electronic absorption and CD spectra, it was confirmed that the first eluate (brownish violet) is *tr.tr.tr.*-$[Co(aetp)_2]^+$, the third one (purple) *trans(S)*-$[Co(\text{L-met})_2]^+$,[8] the fourth one (purple) *trans(O)*-$[Co(aetp)_2]^+$, and the sixth one (brownish red) *trans(N)*-$[Co(aetp)_2]^+$.[1] Thus, the second eluate (dark violet, D-1), the fifth one (purple, D-2), the seventh one (reddish purple, D-3+D-4), the eighth one (purple, D-5), and the ninth one (red, D-6) were the desired isomers. These eluates were concentrated separately in a vacuum evaporator, and then the deposit, NaCl, was filtered off.

Each concentrated filtrate was again poured into a column containing SP-Sephadex C-25 (K^+ form, 4.5 × 120 cm). The adsorbed band was eluted with 0.05 M aqueous solution of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ at the rate of about 0.5 cm^3/min. For the column of the seventh eluate, three bands, a brownish red one (D-3), a purple one which was *trans(O)*-$[Co(\text{L-met})_2]^+$,[8] and a red one (D-4), were eluted in this order. For the other columns there was apparently a single band. However, careful CD measurements showed that D-4 and D-6 bands consist of two bands, which were designated as D-4a and D-4b for D-4 eluate, and D-6a and D-6b for D-6 one according to the elution order though the separation of the latter two isomers was insufficient. The desired eluate was concentrated in a vacuum evaporator and the deposit, $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$, was filtered off, and then converted into the chloride salt by using an anion exchange resin (Dowex 1x8, Cl^- form). To the eluate a large amount of ethanol and acetone was added. The product was recrystallized from a minimum quantity of water by adding ethanol and acetone, and washed with acetone and then diethyl ether, and dried in a vacuum desiccator over $CaCl_2$. The isomers obtained were contaminated with a small amount of potassium chloride or sodium chloride, because of the relatively lower yields of isomers as compared with those of $[Co(\text{L-met})_2]^+$ and $[Co(aetp)_2]^+$ complexes. The CD spectra of D-4a, D-4b, D-6a, and D-6b isomers were measured with the eluates, and their concentrations were calculated from the optical densities referring to that of the mixture, D-4 or D-6. Found for D-1: C, 23.88; H, 4.72; N, 5.49%. Calcd for $[Co(aetp)(\text{L-met})]Cl\cdot 2H_2O\cdot 1.4NaCl = C_{10}H_{24}N_2S_2O_6ClCo\cdot 1.4NaCl$: C, 23.61; H, 4.76; N, 5.51%. Found for D-2: C, 27.76; H, 5.36; N, 6.47%. Calcd for $[Co(aetp)(\text{L-met})]Cl\cdot 2H_2O\cdot 1/5KCl = C_{10}H_{24}N_2S_2O_6ClCo\cdot 1/5KCl$: C, 27.19; H, 5.48; N, 6.34%. Found for D-3: C, 29.38; H, 5.12; N, 6.84%. Calcd for $[Co(aetp)(\text{L-met})]Cl\cdot 0.5H_2O\cdot 0.13KCl = C_{10}H_{21}N_2S_2O_{4.5}ClCo\cdot 0.13KCl$: C, 29.33; H, 5.17; N, 6.84%. Found for D-4 (=mixture of D-4a and D-4b): C, 27.68; H, 5.61; N, 5.89%. Calcd for $[Co(aetp)(\text{L-met})]Cl\cdot 1.5H_2O\cdot CH_3OH\cdot 2/5KCl = C_{10}H_{23}N_2S_2O_{5.5}ClCo\cdot CH_3OH\cdot 2/5KCl$: C, 27.54; H, 5.67; N, 5.84%. Found for D-5: C, 28.01; H, 5.08; N, 6.56%. Calcd for $[Co(aetp)(\text{L-met})]Cl\cdot H_2O\cdot 3/10NaCl = C_{10}H_{22}N_2S_2O_5ClCo\cdot 3/10NaCl$: C, 28.17; H, 5.20; N, 6.57%. Found for D-6 (=mixture of D-6a and D-6b): C, 26.17; H, 5.23; N, 6.13%. Calcd for $[Co(aetp)(\text{L-met})]Cl\cdot 2H_2O\cdot 2/5KCl = C_{10}H_{24}N_2S_2O_6ClCo\cdot 2/5KCl$: C, 26.30; H, 5.30; N, 6.13%.

Measurements. The electronic absorption spectra were measured on a Shimadzu UV-200 spectrophotometer in aqueous solution. The CD spectra were recorded with a JASCO MOE-1 spectropolarimeter. The ^1H NMR spectra were measured in deuterium oxide on a Varian XL-100-15 spectrometer with DSS as the internal reference. All measurements were made at room temperature.

Results and Discussion

Absorption Spectra and Structural Assignments. In the $[Co(aeta)(\text{L-met})]^+$ complex, seven isomers were obtained. Their absorption spectra, are shown in Fig. 2

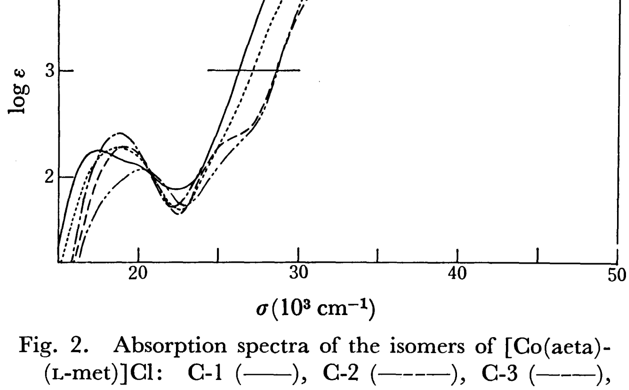

Fig. 2. Absorption spectra of the isomers of [Co(aeta)(L-met)]Cl: C-1 (——), C-2 (– – – –), C-3 (— - —), C-6 (— —), and C-7 (----); the spectra of C-4 and C-5 isomers are similar to those of C-2 and C-6 ones, respectively.

Table 1. Absorption data of isomers of $[Co(aeta)(L\text{-}met)]Cl$ and $[Co(aetp)(L\text{-}met)]Cl$

Isomer	Assignment	σ_{max}[a] $(\log \varepsilon)$		
		First d-d band	Second d-d band	Charge transfer band region
$[Co(aeta)(L\text{-}met)]Cl$				
C-1	*tr. tr. tr.*	17.5(2.25) 20.0(2.10)[b]		30.3(4.16) 44.9(4.11)
C-2	*trans*(*N*)	sh[c] 20.2(2.07)	25.5(2.10)[b]	33.5(4.16) 41.9(4.16) 47.7(4.07)
C-3	*trans*(*S*)	18.8(2.41)		30.3(4.18) 44.1(4.16)
C-4	*trans*(*N*)	sh[c] 19.9(2.07)	25.5(2.20)[b]	33.0(4.08) 42.2(4.12)
C-5	*cisciscis-I*	19.1(2.28)	25.5(2.30)[b]	34.0(4.10) 42.8(4.10)
C-6	*cisciscis-I*	19.2(2.29)	25.5(2.30)[b]	34.2(4.06) 40.3(4.14)
C-7	*trans*(*O*)	18.8(2.28) sh[c]		31.3(3.95)[b] 37.5(4.08) 41.7(4.05)[b] 48.8(4.07)
$[Co(aetp)(L\text{-}met)]Cl$				
D-1	*tr. tr. tr.*	19.2(2.26)		29.0(4.20) 46.7(4.16)
D-2	*trans*(*S*)	18.6(2.24)		29.2(4.02) 44.3(4.00)
D-3	*trans*(*N*)	18.4(1.99)[b] 20.4(2.11)	25.5(2.30)[b]	33.4(4.20) 47.5(4.08)
D-4	*cisciscis-I*	19.0(2.39)	25.5(2.40)[b]	33.0(4.13) 42.4(4.07)
D-5	*trans*(*O*)	17.9(2.37) sh[c]	sh[c]	31.9(4.04) 34.5(4.02)[b] 42.4(4.01)
D-6	*cisciscis-II*	18.8(2.39)	sh[c]	33.3(4.11) 46.3(4.05)

a) The wave numbers are given in $10^3\ cm^{-1}$ unit. b) A shoulder. c) The wave number cannot be determined.

and Table 1. The spectral behavior of the present isomers is very similar to that of $[Co(aeta)_2]^+$, and this is due to the fact that both complexes have the same chromophore $[Co(N)_2(O)_2(S)_2]$. Furthermore both complexes have the geometrical isomers of the same types. Therefore, the interpretation of the electronic absorption spectra described in the previous paper[1)] could be applied for the present isomers in the same manner.

Of seven isomers, the long wavelength thioether charge transfer bands for C-1 ($30300\ cm^{-1}$, $\log \varepsilon = 4.16$) and C-3 ($30300\ cm^{-1}$, $\log \varepsilon = 4.18$) locate at lower energy side than those for the other five isomers. This indicates that the former two isomers have two ligating sulfur atoms in *trans* positions and the latter five in *cis* positions. The isomers C-1 shows a broad first absorption band with a shoulder at high energy side, while C-3 shows a sharp peak. Therefore, C-1 and C-3 can be assigned to *tr.tr.tr.* and *trans*(*S*) structures, respectively.

On the other hand, of the latter five isomers, C-2 and C-4 show a shoulder at low energy side of the major peak at 20200 and $19900\ cm^{-1}$, respectively, and C-7 shows a band at $18800\ cm^{-1}$ with a vague shoulder at high energy side, while C-5 and C-6 apparently a sharp peak at 19100 and $19200\ cm^{-1}$, respectively. From these absorption patterns it was affirmed that C-2 and C-4 isomers are *trans*(*N*), C-5 and C-6 *cisciscis*, and C-7 *trans*(*O*). As shown in Fig. 1, there exists the only one geometrical isomer for the *trans*(*N*) geometry. Accordingly, C-2 and C-4 isomers with *trans*(*N*) structure should be diastereomers due to the sulfur atom chirality (*R*) or (*S*) of the coordinated L-methioninate. For the *cisciscis* form, two geometrical isomers, *cisciscis-I* and *cisciscis-II*, are expected, but it is impossible to decide the configuration of C-5 and C-6 isomers from their electronic absorption spectra. In order to achieve the assignments, NMR spectra of C-5 and C-6 isomers were measured in D_2O by adding a small amount of DCl; the spectra are entirely similar to each other all over the measured region. Furthermore, in the region of amine protons, there are four peaks at 6.35, 5.85, 5.18, and 4.48 ppm from DSS for both isomers. These results indicate that both isomers have either *cisciscis-I* or *cisciscis-II* structure. The C-5 and C-6 isomers, therefore, are diastereomers due to the sulfur atom chirality (*R*) or (*S*) of the coordinated L-methioninate. Referring to the characterization of *cisciscis-I* and *cisciscis-II* isomers for the $[Co(aetp)(L\text{-}met)]^+$ complex, which will be described below, the C-5 and C-6 isomers are assigned finally to have the *cisciscis-I* structure (see Figs. 1 (e) and (f)).

In the $[Co(aetp)(L\text{-}met)]^+$ complex, eight isomers were obtained chromatographically and their absorption spectra are shown in Fig. 3 and Table 1. These isomers can be assigned in the same manner described above; D-1 is *tr.tr.tr.*, D-2 *trans*(*S*), D-3 *trans*(*N*), D-4a and D-4b *cisciscis*, D-5 *trans*(*O*), and D-6a and D-6b *cisciscis*. It is reasonable from their chromatographic behavior to consider that D-4a and D-4b (or D-6a and D-6b) have the same geometrical structure.

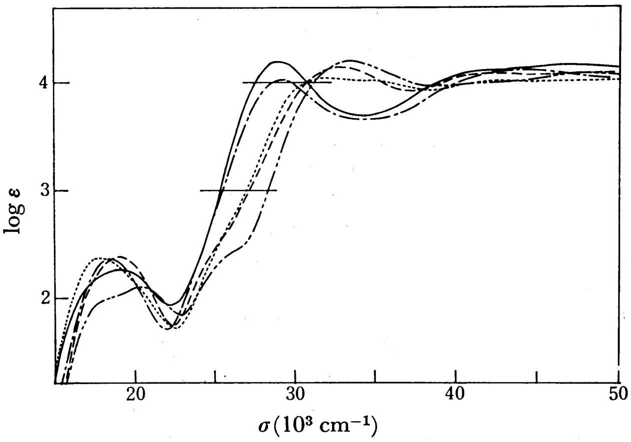

Fig. 3. Absorption spectra of the isomers of $[Co(aetp)(L\text{-}met)]Cl$: D-1 (——), D-2 (——), D-3 (———), D-4a (——), and D-5 (----); the spectra of D-4b, D-6a, and D-6b isomers are similar to that of D-4a one.

The assignment of *cisciscis-I* and *cisciscis-II* was made on the basis of ^{1}H NMR spectra. D-4 complex which is a mixture of D-4a and D-4b isomers, showed a methine signal at 3.91 ppm from DSS, and D-6 one which is a mixture of D-6a and D-6b, showed at 3.45 ppm. This very large difference of the chemical shift between D-4 and D-6 isomers is explained on the basis of C–O deshielding effect[11] as follows; in the *cisciscis-I* structure, the methine proton is located just above a line drawn down the C–O bond of the other ligand and will be deshielded by the anisotropy associated with the C–O bond, while in the *cisciscis-II* form, this effect does not occur. From these reasons, D-4 and D-6 isomers can be assigned to the *cisciscis-I* and *cisciscis-II* structures, respectively. In addition, in the region of the amine protons, D-4 isomer showed three peaks at 4.31, 5.03, and 6.19 ppm, whereas D-6 isomer one peak at 5.97 ppm from DSS. Since the *cisciscis-I* structure has each of two amine groups in the deshielded and shielded positions and the *cisciscis-II* one has two amine groups in the shielded positions, it is also expected that D-4 isomer is *cisciscis-I* and D-6 one *cisciscis-II*. The similar consideration was applied for the assignment of *cisciscis-I* structure of the C-5 and C-6 isomers of [Co(aeta)(L-met)]$^+$. Thus, four diastereomeric pairs, C-2 and C-4, C-5 and C-6, D-4a and D-4b, and D-6a and D-6b, are discovered, which are arising from the chiral sulfur donor atom of the coordinated L-methioninate.

The structural assignments described above were able to be made mainly on the basis of electronic absorption spectra. This indicates that the absorption spectral behavior in the mixed type complexes is similar on the whole to that of the bis(terdentate-*N*,*S*,*O*) type complexes. However, there appear some interesting differences in details. Firstly, two *trans*(*N*) isomers of [Co(aeta)$_2$]$^+$ and [Co(aetp)$_2$]$^+$ show no splitting in the first absorption band region, but four *trans*(*N*) isomers of the present mixed type complexes and of the [Co(L-met)$_2$]$^+$ complex exhibit an explicit shoulder at low energy side of the major peak. Two bis(terdentate) type *trans*(*O*) isomers show more explicit shoulder at high energy side of the major peak than the *trans*(*O*) isomers of the mixed type and [Co(L-met)$_2$]$^+$ complex. These differences indicate that the sulfur atom in the linear terdentate-*N*,*S*,*O* ligands has a strong ligand field strength than that in L-methioninate. Secondly, the thioether charge transfer band positions of the mixed type *trans*(*O*) isomers apparently differ from those of the bis type *trans*(*O*) isomers: 31300 cm^{-1} for [Co(aeta)(L-met)]$^+$ (C-7); 31900 cm^{-1} for [Co(aetp)(L-met)]$^+$ (D-5); 35100 cm^{-1} for [Co(aeta)$_2$]$^+$; 34200 cm^{-1} for [Co(aetp)$_2$]$^+$. The present mixed complexes have two kinds of sulfur atoms, one in the ligand aeta$^-$ or aetp$^-$ and the other in L-met$^-$. The *trans*(*O*) isomer of [Co(L-met)$_2$]$^+$ shows the thioether charge transfer band at 32700 cm^{-1}, a considerably lower energy position than that of [Co(aeta)$_2$]$^+$ or [Co(aetp)$_2$]$^+$. Therefore, the thioether charge transfer bands due to two kinds of sulfur atoms appear separately in this case. In fact, C-7 isomer shows another intense band at 37500 cm^{-1} and D-5 one at 34500 cm^{-1} (sh), which correspond roughly to the positions of the bis type complexes.

CD Spectra. CD spectra of fifteen mixed type complexes are shown in Figs. 4—9 and Table 2. The CD patterns hardly change with the substitution of the aetp ligand for the aeta one, especially in the first absorption band region. This suggests that the difference in size of the *S*-carboxylate chelate ring has not large effect on the CD spectra as in the case of the bis(terdentate-*N*,*S*,*O*) type complexes.[1] In contrast to this, drastic changes were reported for the cobalt(III) complexes of bis(terdentate-*O*,*N*,*O*) type.[12]

The *tr.tr.tr.* isomers show two CD bands in the first absorption band region; the low energy band has a positive sign and the high energy negative (Fig. 4). This is good agreement with the fact that both isomers have *Λ* configurations[13] according to the ring pairing method.[14]

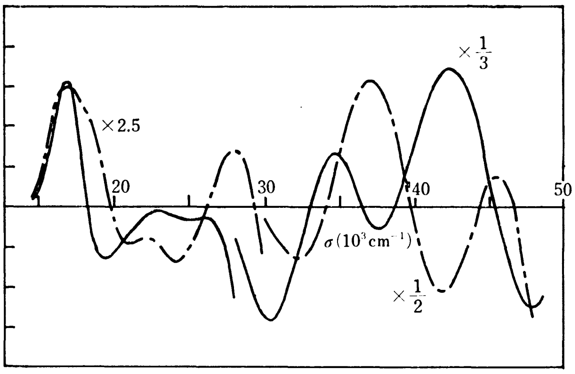

Fig. 4. CD spectra of *tr.tr.tr.* complexes: [Co(aeta)(L-met)]Cl (——) and [Co(aetp)(L-met)]Cl (– – –).

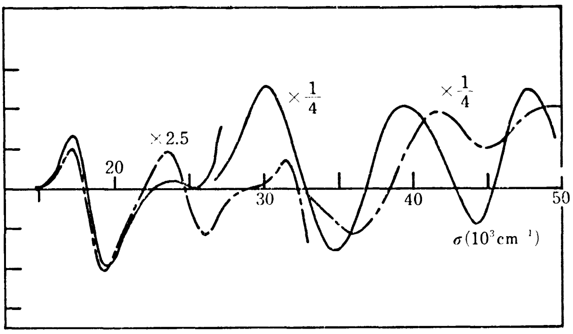

Fig. 5. CD spectra of *trans(S)* complexes: [Co(aeta)(L-met)]Cl (——) and [Co(aetp)(L-met)]Cl (– – –).

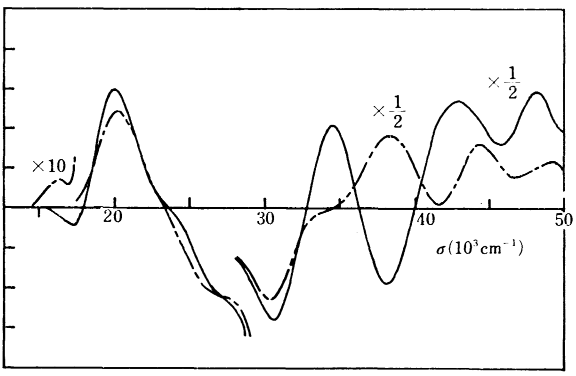

Fig. 6. CD spectra of *trans(O)* complexes: [Co(aeta)(L-met)]Cl (——) and [Co(aetp)(L-met)]Cl (– – –).

Table 2. CD data of isomers of [Co(aeta)(L-met)]Cl and [Co(aetp)(L-met)]Cl

Isomer	σ_{ext} a) ($\Delta\varepsilon$) First d-d band region	Second d-d band region	Charge transfer band region
[Co(aeta)(L-met)]Cl			
tr. tr. tr. (C-1)	16.9(+3.16) 19.5(−1.28)	24.9(−0.33)	30.5(−8.48) 34.8(+3.98) 37.6(−1.51) 42.4(+10.5) 48.0(−7.55)
trans(N) (C-2)	18.0(−1.19) 20.7(+2.14)	25.6(+0.96)	30.4(+0.36) 35.3(−9.99) 42.1(−11.8) 47.6(+19.1)
trans(S) (C-3)	17.2(+1.31) 19.5(−1.96)	23.7(+0.20)	30.1(+10.2) 34.8(−6.42) 39.5(+8.23) 44.3(−3.73) 47.8(+9.99)
trans(N) (C-4)	17.9(+1.31) 20.7(−3.29)	27.4(+2.54)	31.6(+6.74) 35.3(−4.09) 44.3(+3.20)
cisciscis-I (C-5)	18.5(+0.53) 23.6(+0.17)	26.4(−0.69)	29.9(+0.22) 32.4(−0.70) 34.4(+0.11) 37.7(−2.64) 42.1(+9.11) 46.4(−3.38)
cisciscis-I (C-6)	17.8(−0.84) 20.1(+0.69)	26.0(−0.45)	33.3(+2.04) 39.5(+5.36) 44.5(−3.65)
trans(O) (C-7)	17.2(−0.89) 20.0(+6.01)	27.0(−4.30) b)	30.6(−11.2) 34.5(+8.33) 38.1(−7.59) 42.8(+10.8) 48.3(+11.8)

Isomer	σ_{ext} a) ($\Delta\varepsilon$) First d-d band region	Second d-d band region	Charge transfer band region
[Co(aetp)(L-met)]Cl			
tr. tr. tr. (D-1)	16.8(+1.22) 17.3(+0.97) b) 21.1(−0.35)	24.2(−0.55)	28.2(+0.58) 32.3(−2.56) 37.1(+6.40) 41.9(−4.29) 45.3(+1.54)
trans(S) (D-2)	17.2(+0.39) 19.2(−0.83)	23.5(+0.38) 26.1(−0.49)	31.5(+0.27) 36.0(−4.56) 41.7(+7.68) 49.1(+8.39)
trans(N) (D-3)	16.5(+0.03) 17.7(−0.05) 20.6(+2.06)	25.8(+0.87)	30.8(+3.61) 35.9(−18.9) 46.3(+15.3)
cisciscis-I (D-4)	17.0(+0.08) 18.3(+0.12) 20.6(−0.44)		31.5(+2.30) 35.9(−0.90) 40.3(−0.42) 44.8(+0.32)
cisciscis-I c) (D-4a)	17.8(+1.30) 20.7(−0.88)	26.9(+0.59)	32.5(−7.11) 37.7(+2.05) 40.8(−0.24) 43.6(+1.94) 47.7(−3.99)
cisciscis-I c) (D-4b)	17.7(−1.13) 20.5(+0.11)	24.3(−0.17)	31.9(+11.9) 36.8(−3.65) 43.5(−1.26) 46.7(+3.28)
trans(O) (D-5)	16.1(+0.14) 20.2(+4.89)	27.0(−4.40) b)	30.4(−9.17) 38.3(+7.37) 44.4(+6.60) 49.3(+4.86)
cisciscis-II (D-6)	17.2(−0.17) 19.3(+0.14)	25.7(−0.48)	37.0(+7.04) 45.0(−4.73)
cisciscis-II c) (D-6a)	15.6(+0.04) 17.3(−0.07) 20.5(−0.21)	25.5(−0.29)	36.8(+7.47) 44.4(−5.63)
cisciscis-II c) (D-6b)	16.0(+0.05) b) 19.5(+0.64)	26.2(−0.28)	37.9(+5.31) 45.5(−2.09)

a) The wave numbers are given in 10^3 cm^{-1} unit. b) A shoulder. c) CD spectra were measured for the eluates.

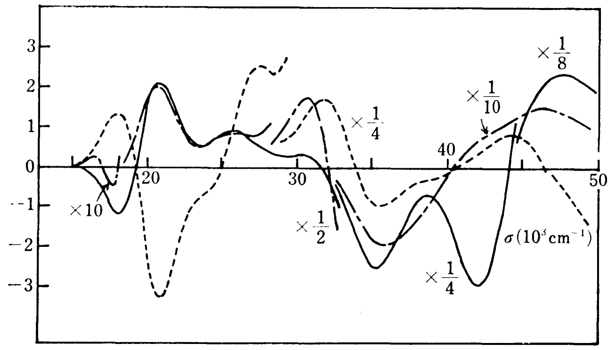

Fig. 7. CD spectra of *trans(N)* complexes: [Co(aeta)-(L-met)]Cl, C-2 (——) and C-4 (----); [Co(aetp)-(L-met)]Cl (———).

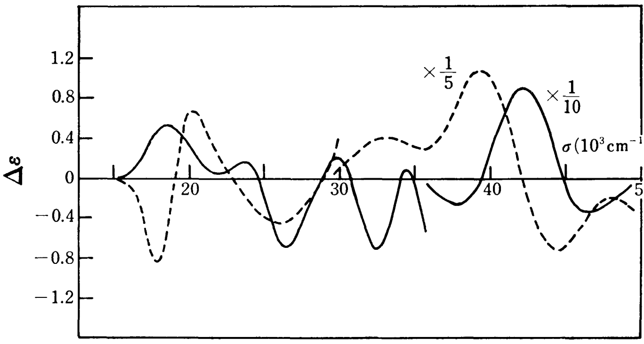

Fig. 8. CD spectra of *cisciscis-I*-[Co(aeta)(L-met)]Cl, C-5 (——) and C-6 (----).

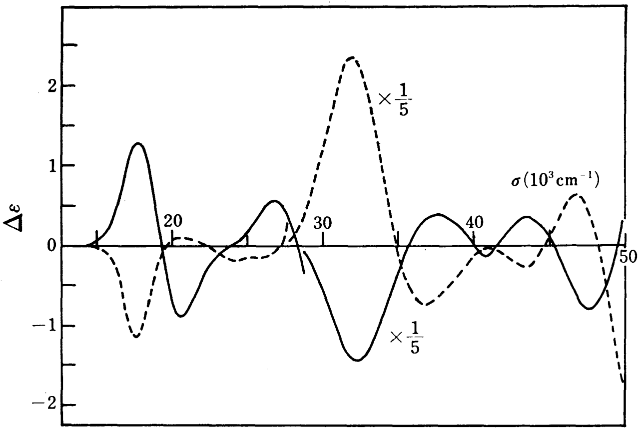

Fig. 9. CD spectra of *cisciscis-I*-[Co(aetp)(L-met)]$^+$, D-4a (——) and D-4b (----).

The two *trans*(*S*) isomers (Fig. 5) exhibit the same pattern as that of the *tr.tr.tr.* isomers in the first absorption band region. Since both *trans*(*S*) isomers also have Λ absolute configuration but the $^1A \rightarrow {}^1A + {}^1B_b(C_2)$ transition should be in higher energy for this geometry, this result indicates that CD spectral pattern cannot be always related to the ring pairing method for the complexes containing L-methioninate. A similar case has been reported for another system.[15)]

Both *trans*(*O*) isomers exhibit a major positive CD band at high energy side, though a weak positive or negative band occurs in low energy (Fig. 6). This may suggest that the high energy positive band represents a composite transition $^1A \rightarrow {}^1B_a + {}^1B_b(C_2)$. However, these mixed *trans*(*O*) isomers have formally no configurational chirality according to the ring pairing method. Thus it may be more reasonable to consider that the CD contributions due to the chiral sulfur donor atoms become dominant.

For the *trans*(*N*) isomers, this viewpoint becomes more important; two *trans*(*N*) isomers of the aeta complex, C-2 and C-4, exhibit completely enantiomeric CD patterns in the first absorption band region (Fig. 7), which can be attributed mainly to the enantiomeric configurations of chiral sulfur atom of the coordinated L-methioninate. In the case of the aetp complex, the only one *trans*(*N*) isomer was obtained. Its CD spectral pattern is similar to that of C-2 isomer and its structure is considered to be same as that of C-2. The D-4a *cisciscis-I* isomer shows the CD spectrum almost enantiomeric to the D-4b *cisciscis-I* isomer (Fig. 9).

Of the fifteen mixed type complexes, eight ones which are classified into diastereomeric pairs, C-2 and C-4, C-5 and C-6, D-4a and D-4b, and D-6a and D-6b, have of course a definite configuration, (*R*) or (*S*), with respect to the chiral sulfur donor atom of L-methioninate. Furthermore, the remaining five isomers except two *tr.tr.tr.* ones take also a definite configuration of the chiral sulfur atom of L-methioninate on the basis of the following reasons; firstly, all fractions of each isomer on the chromatographic separation shows the same CD spectra. Secondly, ^{1}H NMR spectra of these isomers showed a single peak in the *S*-methyl proton region (Fig. 10). Thirdly, corresponding geometrical isomers of the mixed aeta and aetp complexes show very similar CD spectra, and stereomodel examination reveals that the isomers except *tr.tr.tr.* one prefer (*S*) configuration, since the S-CH$_3$ group in (*R*) configuration interacts with the chelate ring of the other ligand.

For the present mixed type complexes, there are two kinds of chiral sulfur atoms, one in the ligand aeta$^-$ or aetp$^-$, and the other in L-met$^-$. Therefore, the CD signs in the thioether charge transfer band region cannot

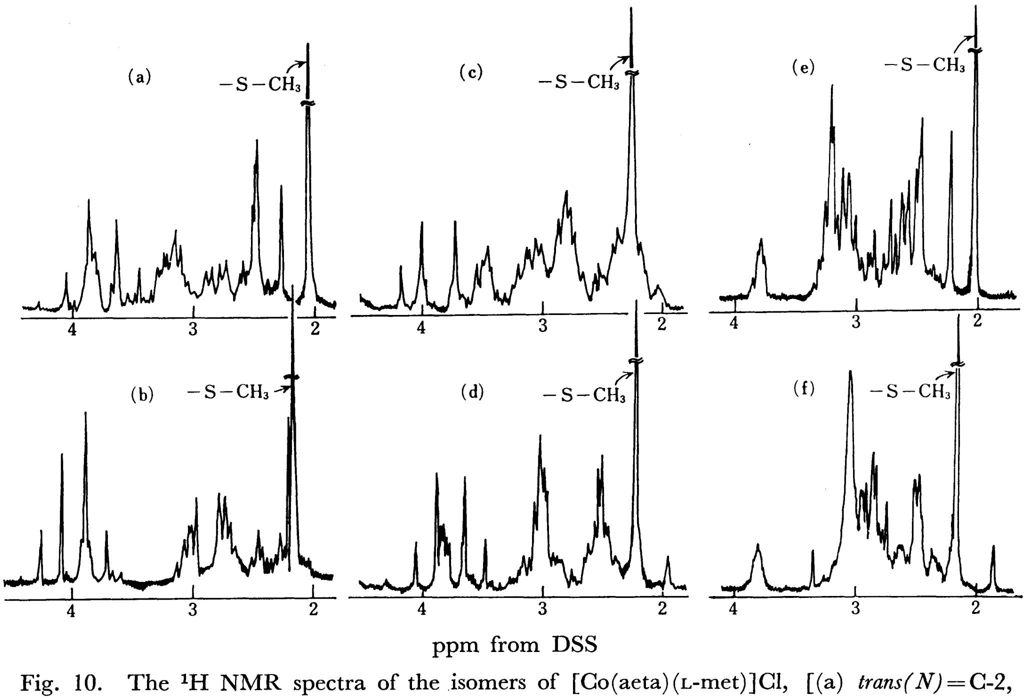

Fig. 10. The ^{1}H NMR spectra of the isomers of [Co(aeta)(L-met)]Cl, [(a) *trans(N)*=C-2, (b) *trans(N)*=C-4, (c) *trans(S)*, and (d) *trans(O)*] and [Co(aetp)(L-met)]Cl [(e) *trans(N)* and (f) *trans(O)*].

be simply related to the absolute configurations. However, some correlations are found for the *trans*(*S*) and *trans*(*N*) isomers. Namely, both *trans*(*S*) isomers show two CD bands, (+) and (−) from low energy side, and both *trans*(*N*) isomers (C-2 and D-3) also two CD bands of opposite signs (Table 2).

CD Contribution due to the Chiral Sulfur Donor Atom. In order to estimate the vicinal CD contribution of the chiral sulfur donor atom of L-methioninate, an additivity rule was applied to the CD spectra of the diastereomeric pairs C-2 and C-4, C-5 and C-6, and D-4a and D-4b isomers; the chiral sulfur contribution can be obtained by subtracting the observed CD of one isomer from that of the counterpart, while the overall CD contribution due to the remaining factors such as the chiral carbon atom of L-methininate and the chiral sulfur atom of the terdentate-*N*,*S*,*O* ligand and/or the configurational chirality due to the skew pair of chelate rings can be obtained by summing up the two observed CD curves. The calculated CD curves are shown in Figs. 11—13.

In the case of *trans*(*N*)-[Co(aeta)(L-met)]$^+$ (Fig. 11), the CD contribution of the chiral sulfur donor atom of L-methioninate is very large in the first absorption band region ($\Delta\varepsilon = -1.24$ at 18000 cm^{-1} and $\Delta\varepsilon = +2.72$ at 20700 cm^{-1}). Similarly, for the *cisciscis*-*I*-[Co(aeta)(L-met)]$^+$ and -[Co(aetp)(L-met)]$^+$ complexes (Figs. 12 and 13), their L-methioninate sulfur vicinal CD are dominant in the first absorption band region. It is interesting to note that the observed CD curve of the D-4 mixture is very similar to the calculated contribution of chiralities other than the sulfur atom chirality of L-methioninate. This indicates that the D-4 complex is composed of equal amounts of D-4a and D-4b isomers.

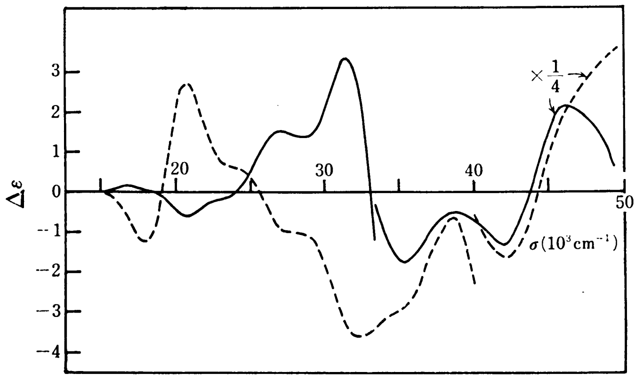

Fig. 11. Curve analysis of *trans(N)*-[Co(aeta)(L-met)]Cl complexes: $1/2 \times \{\Delta\varepsilon(\text{C-2}) + \Delta\varepsilon(\text{C-4})\}$ (——) and $1/2 \times \{\Delta\varepsilon(\text{C-2}) - \Delta\varepsilon(\text{C-4})\}$ (----).

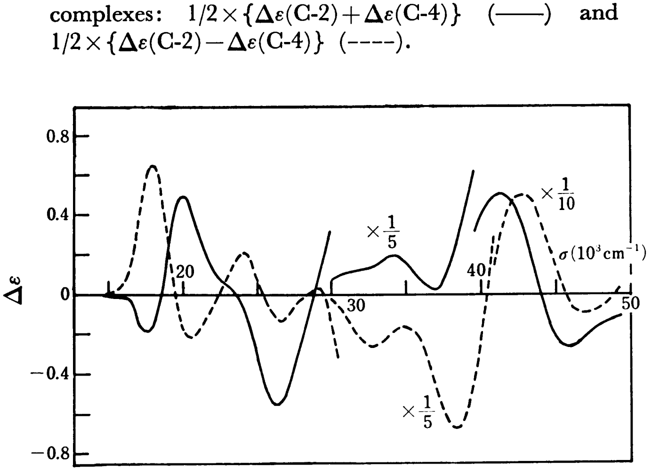

Fig. 12. Curve analysis of *cisciscis*-*I*-[Co(aeta)(L-met)]Cl complexes: $1/2 \times \{\Delta\varepsilon(\text{C-5}) + \Delta\varepsilon(\text{C-6})\}$ (——) and $1/2 \times \{\Delta\varepsilon(\text{C-5}) - \Delta\varepsilon(\text{C-6})\}$ (----).

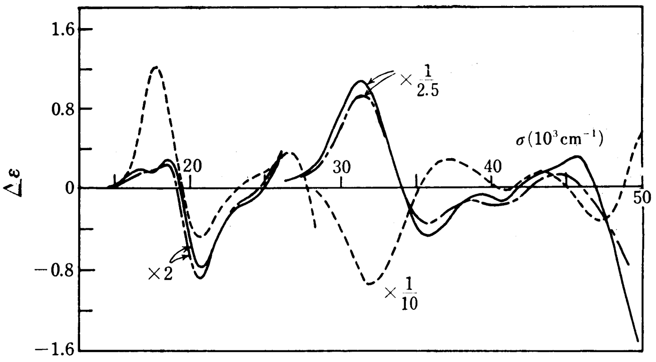

Fig. 13. Curve analysis of *cisciscis*-*I*-[Co(aetp)(L-met)]$^+$ complexes: $1/2 \times \{\Delta\varepsilon(\text{D-4a}) + \Delta\varepsilon(\text{D-4b})\}$ (——), $1/2 \times \{\Delta\varepsilon(\text{D-4a}) - \Delta\varepsilon(\text{D-4b})\}$ (----), and D-4 mixture of diastereomers (———).

In conclusion, the sulfur chirality of the coordinated L-methioninate has large vicinal CD contribution even in the first absorption band region. In this respect, there are some differences between the chiral sulfur and nitrogen[3] donor atoms. Therefore, care must be taken in relating the CD spectra to the absolute configurations of the complexes containing L-methioninate ligand.

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