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Stereochemistry of Cobalt(III) Complexes with Sulfur-containing Amino-carboxylate. Mixed Cobalt(III) Complexes with L-Methioninate or *S*-Methyl-L-cysteinate and L- or D-Aspartate

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Four kinds of [Co(N)$_2$(O)$_3$(S)] type mixed complexes, (L- or D-aspartato)(L-methioninato), and (L- or D-aspartato) (*S*-methyl-L-cysteinato)cobalt(III) complexes have been prepared and chromatographically separated into their three geometrical isomers, *trans*(*N*), *trans*(*SO*) and *trans*(*SN*), respectively. The isomers were identified from their electronic absorption and PMR spectra. The absolute configurations of sulfur atoms in the ligands after coordination were suggested on the basis of their PMR spectra. The circular dichroism spectra of the isomers were considered in relation to their geometrical configurations.

Bis(terdentate) type Co(III) complexes containing α-amino-carboxylates have been extensively investigated during the past several years.[1-9] However, the relationship between their geometrical configurations and CD spectra remains unsolved because of the peculiarity of configurational chirality. For example, [Co(L-asp)$_2$]$^-$ (L-asp=L-aspartate) was prepared and separated into their three geometrical isomers,[1] but their configurational assignments on the basis of their CD spectra were unsuccessful.[1,10,11] As for the isomers of [Co(L-met)$_2$]$^+$ and [Co(L-smc)$_2$]$^+$ (L-met=L-methioninate and L-smc=*S*-methyl-L-cysteinate),[3,12,13] which have biochemically important functions and quite similar frameworks to those of [Co(L-asp)$_2$]$^-$, their three isomers have been assigned on the basis of their absorption spectral behavior due to the coordinated sulfur atom of the ligand, though the sulfur atom takes *R* or *S* configuration after coordination. Recently, Yamanari *et al.*[14] reported the preparation and separation of the isomers of two kinds of mixed type cobalt(III) complexes, [(2-aminoethylthio)acetato](L-methioninato) and [3-(2-aminoethylthio) propionato] (L-methioninato)cobalt(III), and suggested the vicinal CD contribution due to the chiral sulfur atom of L-methioninate by applying an additivity rule for the CD curves of their diastereomeric pairs. In these circumstances, it is significant to investigate the properties of the mixed Co(III) complexes with L- or D-aspartate and L-methioninate or *S*-methyl-L-cysteinate. In the present work, the mixed Co(III) complexes, [Co(L-asp)(L-met)], [Co(D-asp)(L-met)], [Co(L-asp)(L-smc)], and [Co(D-asp)(L-smc)], have been prepared and chromatographically separated into their three geometrical isomers, respectively. The isomers have been characterized from their electronic absorption and PMR spectra. The absolute configurations of sulfur atoms after coordination were also suggested on the basis of their PMR spectra. Their CD spectra were discussed mainly in relation to the geometrical configurations of the isomers.

Experimental

Preparation and Separation of Isomers. *(L-Aspartato)(L-methioninato)cobalt(III)*, *[Co(L-asp)(L-met)]*: A solution containing 0.9 g of L-aspartic acid and 1.1 g of L-methionine in 20 cm^3 of water was adjusted to pH 8 by the addition of sodium hydroxide aqueous solution. This was added to a a hot solution (*ca.* 65 °C) containing 1.6 g of cobalt(II) chloride hexahydrate in 30 cm^3 of water. 3.0 g of lead dioxide and 0.5 g of activated charcoal were gradually added to the solution, which was then stirred at 65 °C for 30 min, the color of the solution turning violet. The mixture was filtered in order to remove the excess of lead dioxide and charcoal after cooling to room temperature. The filtrate was passed through an anion-exchange column of Dowex 1-X8 (Cl$^-$ form, 200—400 mesh, 4.5×20 cm) and successively through a cation-exchange column of Dowex 50W-X8 (Na$^+$ form, 100—200 mesh, 4.5×20 cm) in order to obtain a solution containing the neutral species which are the isomers of [Co(L-asp)(L-met)]. The eluate was concentrated to 5—10 cm^3. Chromatographic seapration was then carried out through a cation-exchange column of Dowex 50W-X8 (Na$^+$ form, 200—400 mesh, 3.0×120 cm). The adsorbed band was eluted with water at a rate of 0.4 cm^3/min. Three colored bands, dark violet (F-1), purple (F-2) and reddish violet (F-3) were eluted in succession. Here the F-2 isomer followed closely after the F-1 isomer. The three eluates were separately concentrated to dryness in a rotary evaporator below 30 °C. The F-2 isomer was recrystallized from hot water, and the F-1 and F-3 isomers were recrystallized from as little water as possible by adding ethanol. The F-2, isomer was less soluble in water. The F-1 isomer formed needle crystals, the F-2 isomer flaky crystals and the F-3 isomer hexagonal crystals. Found for F-1: C, 28.21; H, 5.25; N, 7.31%. Calcd for [Co(L-asp)(L-met)]·2.5H$_2$O=CoC$_9$H$_{15}$N$_2$O$_6$S·2.5H$_2$O: C, 28.20; H, 5.26; N, 7.31%. Found for F-2: C, 31.57; H, 4.52; N, 8.24%. Calcd for [Co(L-asp)(L-met)]=CoC$_9$H$_{15}$N$_2$O$_6$S: C, 31.96; H, 4.42; N, 8.24%. Found for F-3: C, 30.24; H, 4.85; N, 7.85%. Calcd for [Co(L-asp)(L-met)]·H$_2$O=CoC$_9$H$_{15}$N$_2$O$_6$S·H$_2$O: C, 30.34, H, 4.81; N, 7.86%.

(D-Aspartato)(L-methioninato)cobalt(III), *[Co(D-asp)(L-met)]*: Preparation was carried out according to a method similar to that for [Co(L-asp)(L-met)] by using an anion-exchange column (Dowex 1-X8, Cl$^-$ form) and a cation-exchange column (Dowex 50W-X8, Na$^+$ form). Chromatographic separation was carried out through a column of QAE-Sephadex A-25 (Cl$^-$ form, 3.3×250 cm) instead of Dowex 50W-X8 (Na$^+$ form, 200—400 mesh, 3.0×120 cm). The adsorbed band was eluted with water at a rate of 0.3 cm^3/min. Three colored bands, gray-violet (G-1), reddish violet (G-2), and pink-violet (G-3) were eluted in succession. The G-2

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isomer followed colsely after the G-1 isomer. The three eluates were separately concentrated to dryness in a rotary evaporator below 30 °C. The G-1 and G-3 isomers were recrystallized from hot water and the G-2 isomer was recrystallized from as little water as possible by adding ethanol. The G-1 and G-3 isomers were sparingly soluble in water and the G-2 isomer was very soluble in water. The G-1 isomer formed needle crystals and the G-3 isomer rod crystals whereas the G-2 isomer was powdery. Found for G-1: C, 30.51; H, 4.95; N, 7.80%. Calcd for [Co(D-asp)(L-met)]·H_2O=$CoC_9H_{15}N_2O_6S\cdot H_2O$: C, 30.34; H, 4.81; N, 7.86%. Found for G-2: C, 26.78; H, 4.85; N, 6.92%. Calcd for [Co(D-asp)(L-met)]·$2H_2O\cdot 0.5NaCl$=$CoC_9H_{15}N_2O_6S\cdot 2H_2O\cdot 0.5NaCl$: C, 26.79; H, 4.75; N, 6.94%. Found for G-3: C, 28.82; H, 4.68; N, 7.49%. Calcd for [Co(D-asp)(L-met)]·$2H_2O$=$CoC_9H_{15}N_2O_6S\cdot 2H_2O$: C, 28.88; H, 5.12; N, 7.49%.

(L-Aspartato)(S-methyl-L-cysteinato)cobalt(III), [Co(L-asp)(L-smc)]: A solution containing 1.2 g of L-aspartic acid and 1.2 g of *S*-methyl-L-cysteine in 20 cm^3 of water was adjusted to pH 6 by the addition of sodium hydroxide aqueous solution. This was added to a hot solution (*ca.* 65 °C) containing 2.0 g of cobalt(II) chloride hexahydrate in 30 cm^3 of water. 3.0 g of lead dioxide and 0.5 g of activated charcoal were gradually added to the solution which was then stirred at 65 °C for 30 min, the color of the solution turning violet. After the mixture had been filtered, the filtrate was passed through an anion-exchange column and then a cation-exchange column in order to obtain a solution containing the neutral species which are the isomers of [Co(L-asp)(L-smc)]. Chromatographic separation was carried out by a method similar to that for [Co(D-asp)(L-met)], using a column of QAE-Sephadex A-25 (Cl^- form, 3.3×250 cm). Three colored bands, purple (H-1), dark violet (H-2), and light purple (H-3) were eluted in succession. The H-2 isomer followed closely after the H-1 isomer. The three eluates were separately concentrated to dryness in a rotary evaporator below 30 °C. Each crude product was recrystallized from as little water as possible by addition of ethanol. The H-3 isomer formed needle crystals whereas the H-1 and H-2 isomers were powdery. Found for H-1: C, 25.42; H, 4.69; N, 7.30%. Calcd for Co(L-asp)(L-smc)]·$3H_2O$=$CoC_8H_{13}N_2O_6S\cdot 3H_2O$: C, 25.40; H, 5.06; N, 7.41%. Found for H-2: C, 24.76; H, 4.68; N, 7.27%. Calcd for [Co(L-asp)(L-smc)]·$3.5H_2O$=$CoC_8H_{13}N_2O_6S\cdot 3.5H_2O$: C, 24.81; H, 5.20; N, 7.23%. Found for H-3: C, 26.27; H, 4.76; N, 7.64%. Calcd for [Co(L-asp)(L-smc)]·$2H_2O$=$CoC_8H_{13}N_2O_6S\cdot 2H_2O$: C, 26.67; H, 4.76; N, 7.78%.

(D-Aspartato)(S-methyl-L-cysteinato)cobalt(III), [Co(D-asp)(L-smc)]: The preparation was carried out according to a method similar to that for [Co(L-asp)(L-smc)]. Chromatographic separation was accomplished according to a method similar to that for [Co(L-asp)(L-met)], using a column of Dowex 50W-X8 (Na^+ form, 200—400 mesh, 3.0×120 cm). Three colored bands, purple (I-1), gray-violet (I-2), and light purple (I-3) were eluted in succession. The I-2 isomer followed closely after the I-1 isomer. The three eluates were separately concentrated to dryness in a rotary evaporator below 30 °C. The I-2 and I-3 isomers were recrystallized from hot water and the I-1 isomer was recrystallized from as litlte water as possible by adding ethanol. The I-2 isomer was sparingly soluble in water. The I-2 isomer formed needle crystals and the I-3 isomer cubic crystals whereas the I-1 isomer was powdery. The yields of the I-1 and I-2 isomers were rather small. Found for I-1: C, 26.50; H, 4.90; N, 7.72%. Calcd for [Co(D-asp)(L-smc)]·$2H_2O$=$CoC_8H_{13}N_2O_6S\cdot 2H_2O$: C, 26.67; H, 4.76; N, 7.78%. Found for I-2: C, 29.31; H, 4.08; N, 8.57%. Calcd for [Co(D-asp)(L-smc)]=$CoC_8H_{13}N_2O_6S$: C, 29.64; H, 4.04; N, 8.64%. Found for I-3: C, 27.78; H, 4.58; N, 8.22%. Calcd for [Co(D-asp)(L-smc)]·H_2O=$CoC_8H_{13}N_2O_6S\cdot H_2O$: C, 28.08; H, 4.42; N, 8.19%.

Measurements. Electronic absorption spectra were measured with a JASCO UVIDEC-1 spectrophotometer in aqueous solution. CD spectra were recorded with a JASCO J-20 spectropolarimeter. Proton magnetic resonance spectra were recorded in deuterium oxide or trifluoroacetic acid (CF_3COOH) on a JEOL JUM-MH-100 NMR spectrometer with DSS as an internal reference. All measurements were carried out at room temperature.

Results and Discussion

Absorption Spectra and Configurational Assignment. Three geometrical isomers are possible for the present $[Co(N)_2(O)_3(S)]$ type complex because of the stereospecific regulation by the coordinated terdentate ligands. The three isomers for each of [Co(L-asp)(L-met)], [Co(D-asp)(L-met)], [Co(L-asp)(L-smc)], and [Co(D-asp)(L-smc)] are shown in Fig. 1. The isomers are designated as *trans*(*N*), *trans*(*SO*), and *trans*(*SN*) with respect to the coordinated atoms, N, O, and S. The absorption spectra of the isomers of [Co(L- or D-asp)(L-met)] are shown in Fig. 2 and their data are summarized in Table 1. For all the isomers the first absorption bands are located at around 19000 cm^{-1} and the charge transfer bands due to the coordinated sulfur atoms at around 33000 cm^{-1}. The second absorption bands appear as shoulders on the lower energy side of the thioether charge transfer bands. The shape of the first absorption band for each of the isomers can be expected from the semi-empirical calculation[15] on the basis of the ligand field order N>S>O.[16–18] The first absorption band of the *trans*(*N*) isomer is expected to show a well separated minor component on the lower energy side of the major one, that of the *trans*(*SN*) isomer a broad band, and the *trans*(*SO*) isomer a sharp band. As seen in Fig. 2 and Table 1, the F-1 isomer of [Co(L-asp)(L-met)] shows an explicit shoulder on the lower energy side of the major peak (19600 cm^{-1}), and the G-1 isomer of [Co(D-asp)(L-met)] a peak on the lower energy side of the major one (19600 cm^{-1}). Thus F-1 and G-1 isomers are assigned to *trans*(*N*) form. The similar splitting pattern was also observed for the *trans*(*N*) isomers of $[Co(L\text{-}met)_2]^+$,[3] $[Co(L\text{-}smc)_2]^+$,[12] and $[Co(L\text{-}asp)_2]^-$.[1] The F-2 isomer of [Co(L-asp)(L-met)] shows a broad band and the G-2 isomer of [Co(D-asp)(L-met)] a broad band with a vague shoulder on the higher energy side, while the F-3 isomer of [Co(L-asp)(L-met)] and the G-3 isomer of [Co(D-asp)(L-met)] show apparently a sharp band. These absorption patterns indicate that the F-2 and G-2 isomers are *trans*(*SN*) form and the F-3 and G-3 ones *trans*(*SO*) form in accordance with the expected splittings which were estimated semiempirically.[15] A similar treatment was successfully applied to the isomers of bis[(2-aminoethylthio)acetato]cobalt(III) complex.[18] The present assignment is in line with that based on the PMR spectra (*vide post*). The absorption spectra of the isomers of [Co(L- or D-asp)(L-smc)] are shown in Fig. 3 and their

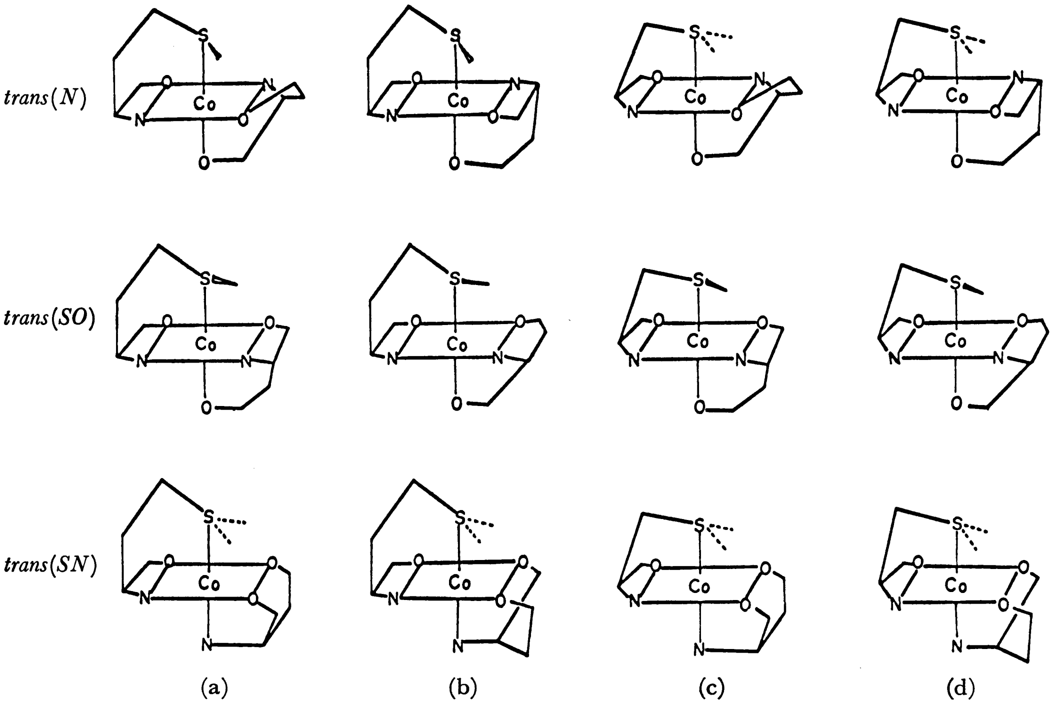

Fig. 1. Three geometrical isomers of [Co(L-asp)(L-met)] (a), [Co(D-asp)(L-met)] (b), [Co(L-asp)(L-smc)] (c) and [Co(D-asp)(L-smc)] (d).

Table 1. Absorption data of isomers of [Co(L- or D-asp)(L-met)] and [Co(L- or D-asp)(L-smc)]
Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.

Isomer	First absorption band	Second absorption band	Charge transfer band
trans(*N*)-[Co(L-asp)(L-met)]	16.8 (1.60)[a)] 19.6 (1.93)	26.3 (2.13)[a)]	33.0 (3.94) 41.7 (4.03)[a)] 46.9 (4.11)
trans(*N*)-[Co(D-asp)(L-met)]	16.7 (1.76) 19.6 (1.97)	26.3 (2.23)[a)]	32.5 (3.98) 42.6 (4.13)[a)] 46.5 (4.18)
trans(*N*)-[Co(L-asp)(L-smc)]	16.7 (1.73)[a)] 19.6 (1.99)	26.3 (2.09)[a)]	33.9 (3.93) 41.7 (4.04)[a)] 47.6 (4.11)
trans(*N*)-[Co(D-asp)(L-smc)]	16.4 (1.67) 19.6 (1.93)	26.3 (1.99)[a)]	33.3 (3.93) 43.5 (4.05)[a)] 47.2 (4.08)
trans(*SN*)-[Co(L-asp)(L-met)]	18.9 (2.15)	26.7 (2.34)[a)]	33.6 (3.95) 43.5 (4.08)[a)] 45.5 (4.09)
trans(*SN*)-[Co(D-asp)(L-met)]	18.2 (2.00)	26.3 (2.27)[a)]	33.3 (3.95) 43.5 (4.10)[a)] 45.2 (4.11)
trans(*SN*)-[Co(L-asp)(L-smc)]	19.2 (2.22)	26.7 (2.33)[a)]	34.5 (3.93) 43.5 (4.10)[a)] 46.7 (4.17)
trans(*SN*)-[Co(D-asp)(L-smc)]	18.5 (2.14)	26.3 (2.26)[a)]	33.9 (3.94) 42.6 (4.13)[a)] 47.8 (4.16)
trans(*SO*)-[Co(L-asp)(L-met)]	18.5 (2.15)	26.3 (2.07)[a)]	32.9 (4.02) 45.5 (4.18)
trans(*SO*)-[Co(D-asp)(L-met)]	18.9 (2.28)	26.3 (2.14)[a)]	33.2 (4.02) 45.2 (4.13)
trans(*SO*)-[Co(L-asp)(L-smc)]	18.2 (2.22)	26.3 (2.06)[a)]	33.1 (3.95) 45.7 (3.95)
trans(*SO*)-[Co(D-asp)(L-smc)]	18.7 (2.29)	26.7 (2.05)[a)]	33.6 (3.93) 45.0 (4.10)

a) A shoulder.

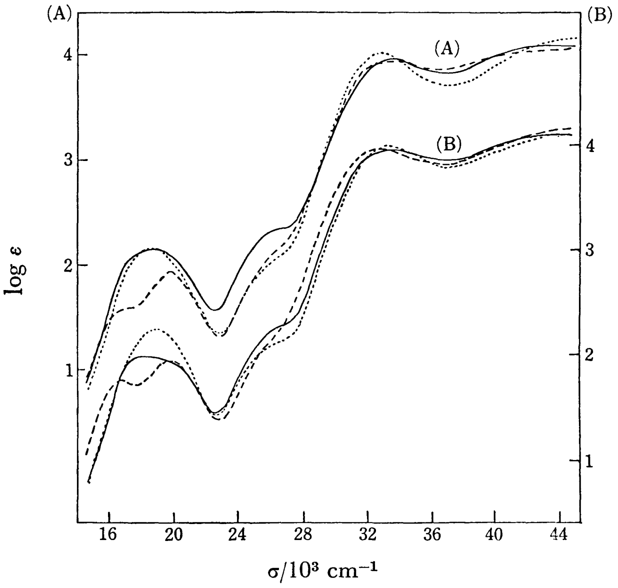

Fig. 2. Absorption spectra for the isomers of [Co(L-asp)(L-met)] (A); F-1 (——), F-2 (-----), and F-3 (······) and [Co(D-asp)(L-met)] (B); G-1 (——), G-2 (-----), and G-3 (······).

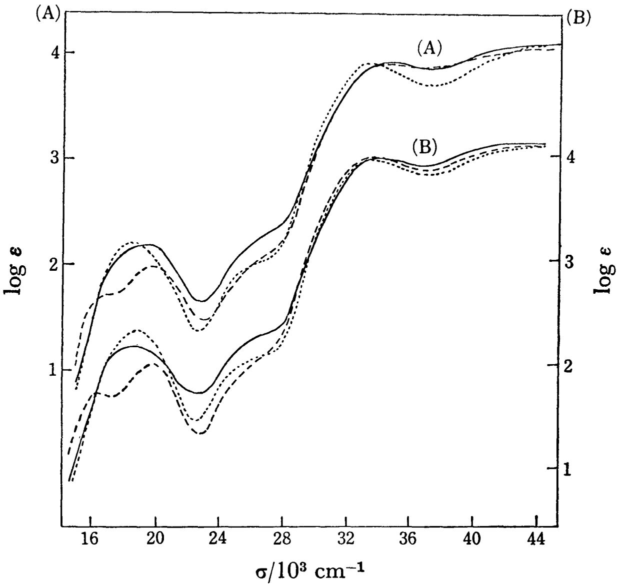

Fig. 3. Absorption spectra for the isomers of [Co(L-asp)(L-smc)] (A); H-1 (——), H-2 (-----) and H-3 (······) and [Co(D-asp)(L-smc)] (B); I-1 (——), I-2 (-----), and I-3 (······).

data are summarized in Table 1. The splitting behavior of their first absorption bands is very similar to that of the corresponding isomers of L-methioninato complex. Thus the H-1, H-2, and H-3 isomers of [Co(L-asp)(L-smc)] are assigned to *trans*(*SN*), *trans*(*N*), and *trans*(*SO*) forms, respectively. As for the [Co(D-asp)(L-smc)], the I-1, I-2, and I-3 isomers are assigned to *trans*(*SN*), *trans*(*N*), and *trans*(*SO*) forms, respectively.

Proton Magnetic Resonance Spectra. Proton magnetic resonance spectra of the isomers isolated were measured in D_2O or trifluoroacetic acid. Representative spectra are shown in Fig. 4. The sulfur atom of a thioether

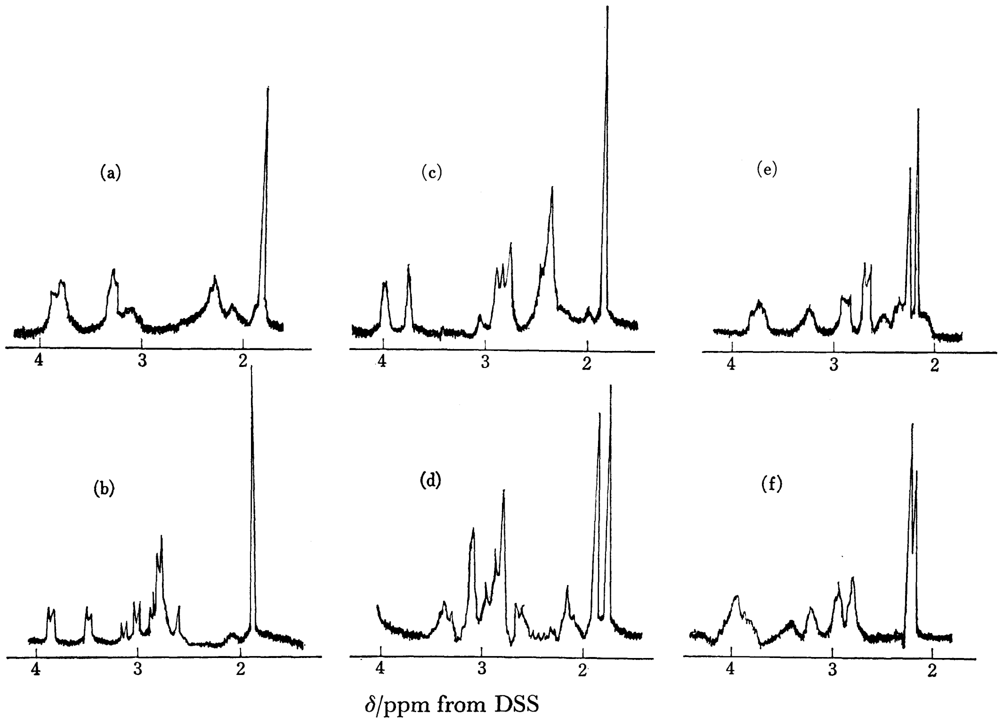

Fig. 4. The representative PMR spectra for the isomers of [Co(L- or D-asp)(L-met)] and [Co(L- or D-asp)(L-smc)]: (a) *trans*(*SO*)-[Co(L-asp)(L-met)] in CF_3COOH, (b) *trans*(*SO*)-[Co(L-asp)(L-smc)] in D_2O, (c) *trans*(*N*)-[Co(L-asp)(L-met)] in D_2O, (d) *trans*(*N*)-[Co(L-asp)(L-smc)] in D_2O, (e) *trans*(*SN*)-[Co(D-asp)(L-met)] in D_2O and (f) *trans*(*SN*)-[Co(D-asp)(L-smc)] in D_2O.

ligand becomes chiral by coordination, leaving on itself a single lone-pair which can give a fixed configuration for the donor center at ordinary temperature.[14] The sulfur atom of L-methioninate or *S*-methyl-L-cysteinate should take *R* or *S* configuration after coordination. Taking the chiral sulfur atom into consideration, two isomers of another type are expected for each of the three geometrical isomers. Each reacted solution was separated chromatographically into three bands (*trans*(*N*), *trans*(*SN*), and *trans*(*SO*) isomers), the detailed fractions of each separated band showing similar CD spectra. This suggests that the isomers due to the configuration *R* or *S* of the chiral sulfur atom are not separable from each other by the present procedure or the sulfur atom is coordinated stereoselectively. As seen in Figs. 4 and 5, the F-3, G-3, H-3, and I-3 isomers assigned to *trans*(*SO*) from their absorption spectra show a single peak (1.87[1.88] ppm for F-3, [2.00] ppm for G-3, 1.90 ppm for H-3 and 1.98 ppm for I-3. Chemical shifts in trifluoroacetic acid are shown in the brackets) in the *S*-methyl proton region, respectively. It seems that sulfur atoms of these isomers selectively take either *R* or *S* configuration. Molecular model constructions indicate that the *S*-methyl group of *trans*(*SO*) isomer has a significant steric interaction with the amino group of L- or D-aspartate chelate when the sulfur atom takes *R* configuration, while no interaction arises for *S* configuration. A similar result was obtained for the sulfur atoms of *trans*(*S*)-$[Co(L\text{-}smc)_2]^+$ [12,13] which has a similar framework to the present *trans*(*SO*) isomers. On the other hand, the F-2, G-2, H-1, and I-1 isomers assigned to *trans*(*SN*) show two peaks (2.27, 2.16 ppm for F-2; 2.13, 2.25 ppm for G-2; 2.19, 2.33 ppm for H-1, and 2.21, 2.26 ppm for I-1) in the *S*-methyl proton region, respectively (Figs. 4 and 5). The results indicate that each of the isomers contains the sulfur atoms of both *R* and *S* configurations. Molecular models reveal that the sulfur atoms of *trans*(*SN*) isomers can easily coordinate in both configurations *R* and *S* (Fig. 1). The F-1 and G-1 isomers assigned to *trans*(*N*) show a single peak (1.82 ppm for F-1 and 1.79 ppm for G-1) due to the *S*-methyl protons of L-methioninate, respectively. These *trans*(*N*) isomers seem to take *R* configuration, since the *S*-methyl group is *S* configuration interacts with the amino group of L- or D-aspartate (Fig. 1). However, the H-2 and I-2 isomers assigned similarly to *trans*(*N*) show two peaks (1.91, 1.80 ppm for H-2 and 1.90, 1.78 ppm for I-2) due to the *S*-methyl protons of *S*-methyl-L-cysteinate, respectively (Figs. 4 and 5). This indicates that both of the isomers contain the sulfur atoms of both *R* and *S* configurations. The difference between the *trans*(*N*)-L-methioninato and *S*-methyl-L-cysteinato isomers is attributed to the situation in which the steric interaction between the *S*-methyl group in *S*-configuration and the adjacent amino group of aspartate is more serious in orientation of *S*-methyl group for the six-membered chelate ring of L-methioninato isomers than for the five-membered ring of *S*-methyl-L-cysteinato isomers (Fig. 1). The consideration on the basis of their PMR spectra and molecular model constructions is in line with the structural arguments from their first absorption band patterns.

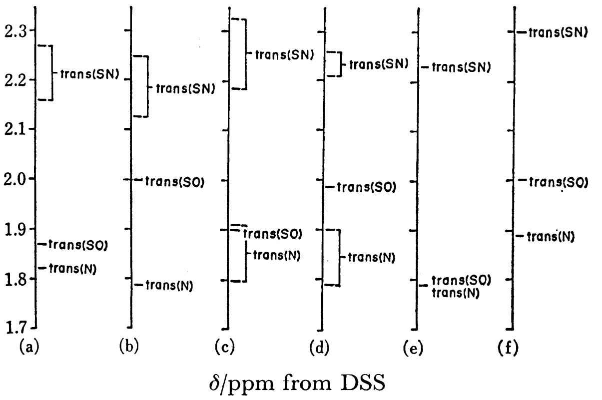

Fig. 5. The distribution of the *S*-methyl protons' chemical shifts: (a) [Co(L-asp)(L-met)], (b) [Co(D-asp)(L-met)], (c) [Co(L-asp)(L-smc)], (d) [Co(D-asp)(L-smc)], (e) [Co(ida)(L-met)], and (f) [Co(ida)(L-smc)].

The chemical shifts of *S*-methyl protons of the twelve isomers isolated are summarized in Fig. 5 with those of six isomers of (iminodiacetato)(L-methioninato) and (iminodiacetato)(*S*-methyl-L-cysteinato)cobalt(III).[20] The PMR spectra were measured in D_2O except for *trans*(*SO*)-[Co(D-asp)(L-met)] which was measured in trifluoroacetic acid because of its low solubility in D_2O. The values can be arranged in order in accordance with their geometries (Figs. 1 and 5). The chemical shifts of the *trans*(*N*) isomers (F-1, G-1, H-2, and I-2) and *trans*(*SO*) isomers (F-3, G-3, H-3, and I-3) appear in a higher magnetic field (1.7—2.0 ppm) than those of the *trans*(*SN*) isomers (F-2, G-2, H-1, and I-1) (2.1—2.4 ppm). The chemical shifts of *trans*(*SO*) isomers are similar to those of *trans*(*N*) ones, though the former has a tendency to a slightly lower field (Fig. 5). This is understandable from the fact that the oxygen atom occupies the trans position to the sulfur atom for the *trans*(*N*) and *trans*(*SO*) isomers, whereas the nitrogen

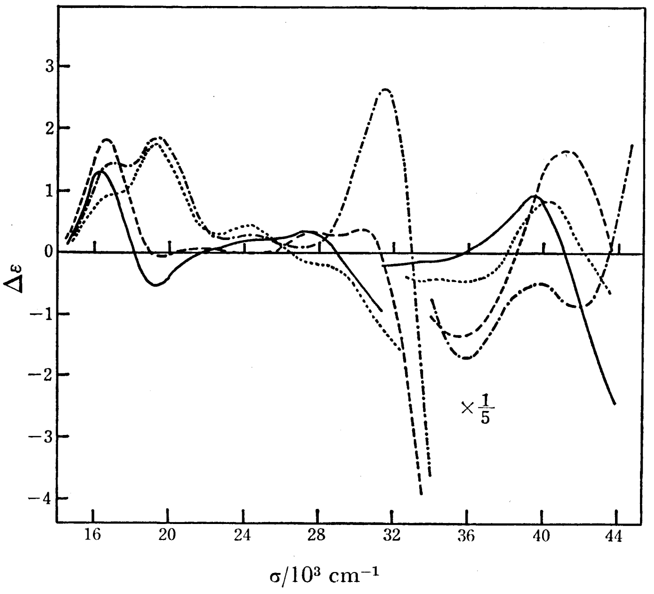

Fig. 6. CD spectra of *trans*(*N*) complexes: [Co(L-asp)(L-met)](-•-•-), [Co(D-asp)(L-met)](------), [Co(L-asp)(L-smc)](······), and [Co(D-asp)(L-smc)] (——).

Table 2. CD data of isomers of [Co(L- or D-asp)(L-met)] and [Co(L- or D-asp)(L-smc)]
Wave numbers and Δε values (in parenthese) are given in 10^3 $\mathrm{cm^{-1}}$ and $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$, respectively.

Isomer	First absorption band	Second absorption band	Charge transfer band
trans(*N*)-[Co(L-asp)(L-met)]	16.9(+1.47) 19.4(+1.90)	24.4(+0.29)	31.3(+2.65) 35.7(−8.54) 42.0(−0.46) 45.9(+12.7)
trans(*N*)-[Co(D-asp)(L-met)]	16.6(+1.86) 19.5(−0.07) 21.3(+0.07)	27.8(+0.33)	29.9(+0.38) 35.7(−6.67) 41.2(+8.26)
trans(*N*)-[Co(L-asp)(L-smc)]	16.9(+0.93)a) 19.2(+1.75)	24.1(+0.44)	35.5(−2.33) 40.0(+4.15)
trans(*N*)-[Co(D-asp)(L-smc)]	16.4(+1.25) 19.2(−0.52)	25.0(+0.18) 27.2(+0.31)	31.5(−0.98) 39.2(+4.35) 47.2(−2.97)
trans(*SN*)-[Co(L-asp)(L-met)]	16.5(+0.66) 18.3(−1.55) 20.5(+0.78)	26.2(+0.66)	31.1(+1.44) 35.7(−5.74) 44.4(+19.5)
trans(*SN*)-[Co(D-asp)(L-met)]	17.8(−1.29) 20.5(+0.90)	25.0(+0.34)	30.3(+0.53) 34.5(−6.20) 39.2(+5.72)
trans(*SN*)-[Co(L-asp)(L-smc)]	16.5(+0.15) 18.0(−0.20) 20.0(+1.04)	26.7(+0.44)	34.5(−5.83) 43.9(+14.2)
trans(*SN*)-[Co(D-asp)(L-smc)]	17.2(−1.44) 20.5(+0.98)	25.5(+0.24)	34.4(−6.75) 40.0(+8.41) 47.6(−8.41)
trans(*SO*)-[Co(L-asp)(L-met)]	17.6(+1.48) 20.6(−0.46)	26.3(−0.73)	38.5(+1.22) 45.0(+12.5)
trans(*SO*)-[Co(D-asp)(L-met)]	17.3(+0.43) 20.2(−0.83)	26.8(−0.59)	34.5(−1.90) 44.1(+13.1)
trans(*SO*)-[Co(L-asp)(L-smc)]	17.5(+2.52) 20.4(−0.70)	25.1(−1.05)	32.8(−13.0) 42.9(+17.1)
trans(*SO*)-[Co(D-asp)(L-smc)]	17.3(+1.36) 20.2(−0.83)	24.5(−0.89)	33.3(−13.5) 42.9(+18.6)

a) A shoulder.

atom occupies the trans position for the *trans*(*SN*) isomers. The results are in line with the PMR spectra for the isomers of (L- or D-aspartato)(L-2,4-diaminobutyrato)cobalt(III) complexes.19) In these complexes, the carbon proton adjacent to the coordinated nitrogen atom resonates at a higher magnetic field when oxygen atom occupies trans position to the nitrogen atom than when nitrogen atom occupies the same position.

Circular Dichroism Spectra. The CD curves of *trans*(*N*)-[Co(L- or D-asp)(L-met)] and [Co(L- or D-asp)(L-smc)] are shown in Fig. 6 and their data are summarized in Table 2. In the first absorption band region, the two L-aspartato complexes, [Co(L-asp)(L-met)] and [Co(L-asp)(L-smc)], show two positive CD bands which correspond to their absorption components (Table 1). This CD pattern is similar to that of *trans*(*N*)-$[\mathrm{Co(L\text{-}asp)_2}]^-$ 1) and of *trans*(*N*)-$[\mathrm{Co(L\text{-}met)_2}]^+$ 3) The replacement of the ligand L-aspartate by D-aspartate reveals a negative CD component at the higher energy side, though the positive CD band at the lower energy side remains unchanged. A similar CD behavior was observed for the curves of *trans*(*SN*) isomers (Fig. 7 and Table 2). In this isomer, however, the replacement of the D-aspartate to L-aspartate reveals a positive CD component at the lower energy side in contrast with the case of *trans*(*N*) isomers, the CD band at the higher energy side remaining unchanged. The CD curves of *trans*(*SO*) isomers show a similar CD pattern (+ and − from the lower energy) to each other in the corresponding region,

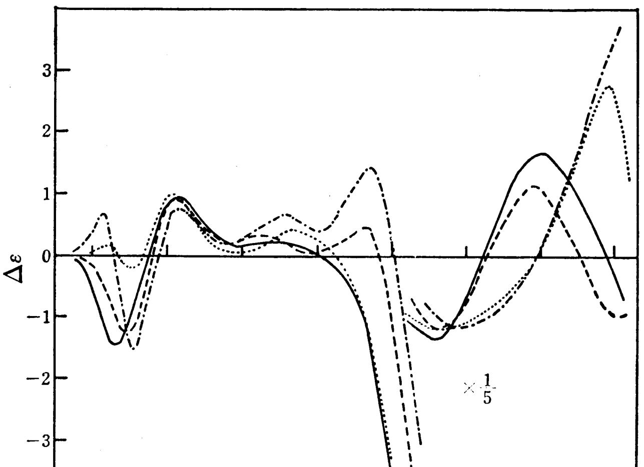

Fig. 7. CD spectra of *trans*(*SN*) complexes: [Co(L-asp)(L-met)](-•-•-), [Co(D-asp)(L-met)](——), [Co(L-asp)(L-smc)](······), and [Co(D-asp)(L-smc)] (——).

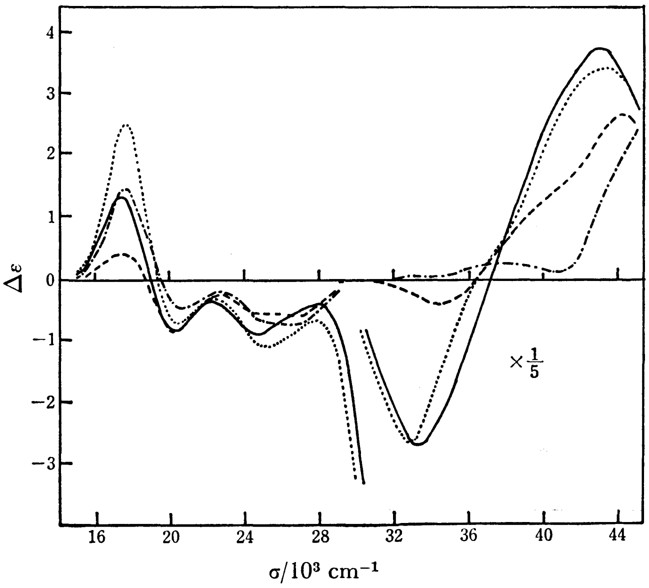

Fig. 8. CD spectra of *trans*(*SO*) complexes: [Co(L-asp)(L-met)](-·-·-), [Co(D-asp)(L-met)](-----), [Co(L-asp)(L-smc)](······), and [Co(D-asp)(L-smc)](——).

though the positive CD band intensities significantly differ from each other (Fig. 8 and Table 2). This pattern might be related to the situation where the first absorption components of *trans*(*SO*) isomer are close to each other. These observations approximately suggest that the LL mixed or DL mixed type complexes of each of three isomers show a similar CD pattern regardless of L-methioninate coordination or *S*-methyl-L-cysteinate one, the CD pattern depending mainly on the L- or D-aspartate coordination in the first absorption band region.

The three isomers of [Co(L-asp)(L-met)] are very similar in framework to the corresponding isomers of $[Co(L\text{-}asp)_2]^-$ or $[Co(L\text{-}met)_2]^+$. As an example, the *trans*(*N*) isomer of the mixed complex corresponds to *trans*(*N*)-$[Co(L\text{-}asp)_2]^-$, the *trans*(*SN*) isomer to *trans*(O_5)-$[Co(L\text{-}asp)_2]^-$ and the *trans*(*SO*) isomer to *trans*(O_6)-$[Co(L\text{-}asp)_2]^-$, respectively. The *trans*(*SN*) and *trans*(*SO*) isomers of [Co(L-asp)(L-met)] are quasiantipodal in framework as in the case of the *trans*(O_5) and *trans*(O_6) isomers of $[Co(L\text{-}asp)_2]^-$. In fact, the CD curves of the *trans*(*SN*) and *trans*(*SO*) isomers reflect their antipodal relationship in the first and second absorption band region, though the *trans*(*SN*) isomer shows a positive CD band (16500 cm^{-1}), which suggests a lowering of molecular symmetry or the vicinal CD contributions (Fig. 9). A similar consideration is also applicable to each pair of the *trans*(*SO*) and *trans*(*SN*) isomers of [Co(D-asp)(L-met)] or [Co(L- or D-asp)(L-smc)] (Figs. 7 and 8). The quasiantipodal relationship in framework and CD curve is better for the DL mixed complexes than for the LL mixed ones, being especially good for the *trans*(*SO*) and *trans*(*SN*) isomers of [Co(D-asp)(L-met)]. From these observations in the first and second absorption band regions, it seems that the CD patterns of the complexes are understandable in relation to their frameworks so far as the present terdentate ligands are concerned. It was suggested that the sulfur chirality of the coordinated L-methioninate has large vicinal CD contribution in the first absorption band region.[14] In the present case, however, the CD curves of *trans*(*N*)-[Co(L-asp)(L-met)], in which the coordinated sulfur atom is assigned to *R* configuration, are similar to those of *trans*(*N*)-[Co(L-asp)(L-smc)] which contains two kinds of chiral sulfur atoms, *R* and *S* configurations (Fig. 4 and Table 2). It seems that in the present mixed complexes the framework of isomer determines dominantly the CD pattern in the first absorption band region. In the thioether charge transfer band region (30000—35000 cm^{-1}), the CD curves of the twelve isomers are classified apparently into two groups. L-Methioninato complexes show a positive CD band regardless of L- or D-aspartate coordination, though it is only a trend for the *trans*(*SO*) isomers. In contrast, no CD band appears for the *S*-methyl-L-cysteinato complexes (Figs. 6—8). The sulfur atoms of *trans*(*N*)-L-methioninato complexes take *R* configuration and *trans*(*N*)-*S*-methyl-L-cysteinato one contain two kinds of chiral sulfur atoms, *R* and *S* configurations. The *trans*(*SN*) isomers contain the sulfur atom of both *R* and *S* configurations for both the L-methioninato and *S*-methyl-L-cysteinato complexes. The *trans*(*SO*) isomers take only *S* configuration. From the information on their PMR spectra, it is assumed that the CD spectra in this region apparently depend mainly on L-methioninate coordination or *S*-methyl-L-cysteinate one, though the influence of the CD bands in the highest energy region (35000—44000 cm^{-1}) should be taken into consideration.

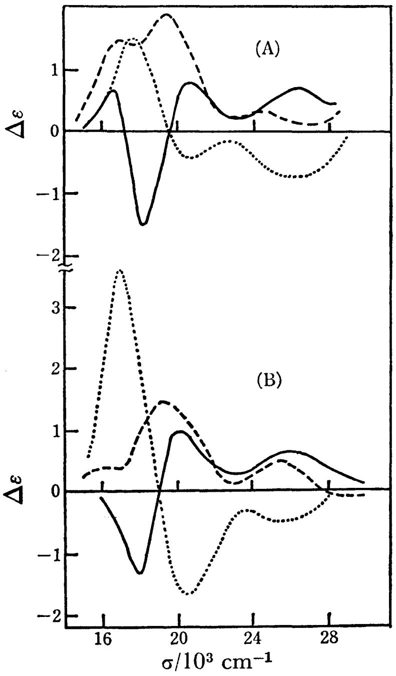

Fig. 9. The CD spectra for isomers of [Co(L-asp)(L-met)] (A), [*trans*(*N*)(-----), *trans*(*SN*)(——), and *trans*(*SO*)(······)] and $[Co(L\text{-}asp)_2]^-$ (B), [*trans*(*N*)(-----), *cis*(*N*)-*trans*(O_5)(——), and *cis*(*N*)*trans*(O_6)(······)].

References

1) S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem.*,

10, 2187 (1971).

2) K. Hosaka, H. Nishikawa, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **42**, 277 (1969).

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

4) L. J. Zompa, *Chem. Commun.*, **1969**, 783.

5) S. Bagger, K. Gibson, and C. S. Sorensen, *Acta Chem. Scand.*, **26**, 2503 (1972).

6) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

7) C. F. Liu and J. A. Ibers, *Inorg. Chem.*, **8**, 1911 (1969).

8) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **9**, 1191 (1970).

9) Y. Nakayama, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **49**, 151 (1976).

10) I. Oonishi, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 1318 (1975).

11) J. I. Legg and J. A. Neal, *Inorg. Chem.*, **12**, 1805 (1973).

12) J. Hidaka and Y. Shimura, presented at the XVI I.C.C.C., Dublin, Ireland (1974), Paper 1.7a.

13) P. de Meester and D. J. Hodgson, *J. Chem. Soc. Dalton. Trans.*, **1976**, 618.

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

16) G. H. Searle and E. Larsen, *Acta Chem. Scand.*, **A30**, 143 (1976).

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

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

19) M. Watabe, K. Onuki, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **48**, 687 (1975).

20) To be submitted.