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Preparation and Spectroscopic Studies of (Diethylenetriamine)cobalt(III) Complexes with L-Penicillaminate or Its Derivative

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The (diethylenetriamine)(L-penicillaminato)cobalt(III) complex, $[Co(L\text{-pen})(dien)]^+$, was chromatographically separated into three isomers, *trans*(N_1N), *trans*(N_1O) and *trans*(N_1S). Each of these gave a corresponding isomer of the (diethylenetriamine)(*S*-methyl-L-penicillaminato)cobalt(III) complex, $[Co(L\text{-smp})(dien)]^{2+}$, by the reaction with dimethyl sulfate. The (triammine)(*S*-methyl-L-penicillaminato)cobalt(III) complex was also derived from the corresponding L-pen complex, $[Co(L\text{-pen})(NH_3)_3]^+$. The absorption and CD spectra of the L-pen complexes were compared with those of the L-smp ones to specify the geometrical configurations. The L-pen complexes exhibited characteristic absorption behavior and CD spectra in the region of $(14—30)\times10^3$ cm^{-1}.

Cobalt(III) complexes with the thioether type terdentate-*N,S,O* ligands such as *S*-methyl-L-cysteinate and L-methioninate have been characterized on the basis of their absorption and CD spectra.[1-6] However, the absorption and CD spectral behaviors of the complexes with the thiolato type ligands have not been clarified yet.[6,7] The thiolato type complexes generate the thioether ones by the reaction with dimethyl sulfate.[6] This reaction is useful for the investigations of the spectrochemical and stereochemical properties for the thiolato type complexes.

In this work, the (diethylenetriamine)(L-penicillaminato)cobalt(III) complex, $[Co(L\text{-pen})(dien)]^+$, was prepared and chromatographically separated into three geometrical isomers, *trans*(N_1N), *trans*(N_1O), and *trans*(N_1S) (Fig. 1). Each of the L-pen isomers gave the corresponding isomer of the (diethylenetriamine)(*S*-methyl-L-penicillaminato)cobalt(III) complex, $[Co(L\text{-smp})(dien)]^{2+}$, on reaction with dimethyl sulfate. The (triammine)(*S*-methyl-L-penicillaminato)cobalt(III) complex, $[Co(L\text{-smp})(NH_3)_3]^{2+}$, was derived from the corresponding L-pen complex, $[Co(L\text{-pen})(NH_3)_3]^+$, by the same reaction as that for the dien complex. The structural assignments of the isomers for $[Co(L\text{-smp})(dien)]^{2+}$ are fairly difficult, because the three L-smp isomers which belong to a *cis(SO)*-$[Co(S)(O)(N)_4]$ type show quite similar absorption spectra. Therefore, one of $[Co(L\text{-pen})(dien)]^+$ isomers was preliminarily determined to have a *trans*(N_1N) configuration by the X-ray crystal structure analysis.[8] On the basis of the absorption and CD spectra of *trans*(N_1N)-$[Co(L\text{-pen})(dien)]^+$ and the result derived from the reaction of the *trans*(N_1N) L-pen isomer with dimethyl sulfate, the absorption and CD spectra of the L-pen and L-smp complexes will be discussed to specify their geometrical configurations.

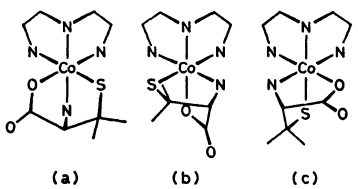

Fig. 1. Three geometrical isomers of $[Co(L\text{-pen or L-smp})(dien)]^{+ \text{ or } 2+}$; (a) *trans*($N_1N$), (b) *trans*($N_1O$), and (c) *trans*($N_1S$).

Experimental

1) (Diethylenetriamine)(L-penicillaminato)cobalt(III) Chloride. [Co(L-pen)(dien)]Cl: This complex was prepared and separated into three isomers by the method described in the previous paper.[8] Dark-brown needle crystals were obtained from the first eluate (A-1) of the three brown bands eluted, A-1, A-2, and A-3. The A-1 isomer was determined to have a *trans*(N_1N) isomer by the X-ray crystal structure analysis.[8] Found for A-1: C, 30.51; H, 6.73; N, 15.12%. Found for A-2: C, 30.04; H, 6.67; N, 15.56%. Calcd for $[Co(L\text{-pen})(dien)]Cl\cdot H_2O = CoC_9H_{22}N_4O_2SCl\cdot H_2O$: C, 29.80; H, 6.69; N, 15.44%. Found for A-3: C, 30.37; H, 6.28; N, 16.00%. Calcd for $[Co(L\text{-pen})(dien)]Cl\cdot 0.25H_2O$: C, 30.95; H, 6.49; N, 16.04%.

2) (Diethylenetriamine)(S-methyl-L-penicillaminato)cobalt(III) Chloride. [Co(L-smp)(dien)]Cl$_2$: This complex was prepared by the reaction of $[Co(L\text{-pen})(dien)]^+$ obtained in 1) with dimethyl sulfate. About 10 cm^3 of dimethyl sulfate was added drop by drop to a solution containing 0.5 g of the A-1 isomer of $[Co(L\text{-pen})(dien)]^+$ in 10 cm^3 of water and the mixture was mechanically stirred for a few minutes. When the mixture had been allowed to stand at room temperature for a while, it separated into two layers: a brown (upper) layer and a cloudy colorless (lower) layer. The former changed gradually from brown to reddish orange. After being allowed to stand at room temperature for about 5 h, the reddish orange solution was separated and poured onto a column of SP-Sephadex C-25 (Na^+ form, 3×40 cm). After the column was swept with water, the adsorbed reddish orange band was eluted with a 0.15 mol dm^{-3} aqueous solution of sodium chloride. Only one reddish orange band was eluted and fractionated. It was found, from the absorption and CD spectra of the fractionated eluates, that the eluate contained only one isomer (B-1). Then the fractions were combined and concentrated to a small volume with a rotary evaporator at about 20 °C. The deposited sodium chloride was filtered off. After a large amount of ethanol was added to the filtrate, the solution was kept in a refrigerator overnight. The B-1 isomer obtained was recrystallized from a small amount of water by the addition of acetone. Similarly, the B-2 and B-3 isomers were derived from the A-2 and A-3 isomers by a reaction with dimethyl

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sulfate. Found for B-1: C, 29.82; H, 6.46; N, 13.68%. Calcd for $[Co(L\text{-}smp)(dien)]Cl_2 \cdot 0.5H_2O = CoC_{10}H_{25}N_4O_2SCl_2 \cdot 0.5H_2O$: C, 29.71; H, 6.48; N, 13.86%. Found for B-2: C, 28.00; H, 6.62; N, 13.31%. Calcd for $[Co(L\text{-}smp)(dien)]Cl_2 \cdot 1.5H_2O$: C, 28.44; H, 6.68; N, 13.27%. Found for B-3: C, 26.92; H, 6.82; N, 12.95%. Calcd for $[Co(L\text{-}smp)(dien)]Cl_2 \cdot 2.5H_2O$: C, 27.28; H, 6.87; N, 12.73%.

3) (Triammine)(L-penicillaminato)cobalt(III) Ion. *[Co(L-pen)(NH$_3$)$_3$]$^+$*: A hot solution (*ca.* 40 °C) containing 4.5 g of $[Co(NH_3)_6]Cl_3$[9] in 50 cm^3 was adjusted to pH *ca.* 2.5 by the addition of 15% hydrochloric acid. To this solution were added 2 g of L-penicillamine and a small amount of activated charcoal. The mixture was mechanically stirred at 40 °C for 15 min. The resultant mixture was filtered in order to remove the activated charcoal, after cooling to room temperature. The filtrate was poured onto a column of SP-Sephadex C-25 (Na^+ form, 5×40 cm). After the column was swept with water, the adsorbed brown band was eluted with a 0.075 mol dm^{-3} aqueous solution of sodium perchlorate. Two colored bands, a large amount of the brown band and a small amount of the yellow one, were eluted in this order. Of the two eluates, the yellow eluate was found to contain a by-product without the coordinated sulfur atom, because the absorption spectrum of this eluate did not show the charge transfer band in the region of (30—35)×10^3 cm^{-1}. The absorption spectrum of the brown eluate was similar to that of *trans(N$_1$N)*-[Co(L-pen)(dien)]$^+$[8] in the whole region and showed the charge transfer band at 34.7×10^3 cm^{-1}. As described in 4), furthermore, the brown eluate gave $[Co(L\text{-}smp)(NH_3)_3]^{2+}$ after treatment with dimethyl sulfate. These facts suggest that the brown eluate contained only $[Co(L\text{-}pen)(NH_3)_3]^+$. However, the complex was so unstable that it could not be isolated in solid state. The absorption and CD spectra of $[Co(L\text{-}pen)(NH_3)_3]^+$ were measured with a solution passed through a cation exchange column; they are illustrated with an arbitrary scale in Fig. 5.

4) (Triammine)(S-methyl-L-penicillaminato)cobalt(III) Perchlorate. *[Co(L-smp)(NH$_3$)$_3$](ClO$_4$)$_2$*: This complex was prepared by the same procedure as in 2), using the brown eluate obtained in 3) instead of $[Co(L\text{-}pen)(dien)]^+$. The complex treated with dimethyl sulfate was chromatographed on the column (SP-Sephadex C-25, Na^+ form) as in 2). Only one reddish orange band was eluted. It was found, from the comparison of the absorption spectrum of the brown eluate to those of $[Co(L\text{-}smp)(dien)]^{2+}$ isomers in 2), that the eluate contained only $[Co(L\text{-}smp)(NH_3)_3]^{2+}$. The eluate was concentrated to a small volume with a rotary evaporator at about 20 °C. The deposited sodium perchlorate was filtered off and to the filtrate was added a small amount of ethanol. The complex which precipitated was collected and recrystallized from as little water as possible by the addition of acetone. The pure complex was washed with ethanol and ether, and then dried in a vacuum desiccator over $CaCl_2$. Found: C, 15.08; H, 4.50; N, 11.66%. Calcd for $[Co(L\text{-}smp)(NH_3)_3](ClO_4)_2 \cdot 0.25H_2O = CoC_6H_{21}N_4O_{10}SCl_2 \cdot 0.25H_2O$: C, 15.15; H, 4.56; N, 11.78%.

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra with JASCO J-20 and J-500 spectropolarimeters. All measurements were carried out in aqueous solution at room temperature.

The ^{1}H NMR spectra were recorded in deuterium oxide on 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

Structural Assignment. For $[Co(L\text{-}pen)(dien)]^+$ and for $[Co(L\text{-}smp)(dien)]^{2+}$, three geometrical isomers are possible. These isomers are designated as *trans(N$_1$N)*, *trans(N$_1$O)*, and *trans(N$_1$S)* with respect to the coordinated atoms as shown in Fig. 1, where N_1 denotes the imino nitrogen atom of the coordinated dien. The three isomers, B-1, B-2, and B-3, of $[Co(L\text{-}smp)(dien)]^{2+}$ were derived from the A-1, A-2, and A-3 isomers of $[Co(L\text{-}pen)(dien)]^+$ by the reaction with dimethyl sulfate. Of the three L-pen isomers, the A-1 isomer was preliminarily determined to have a *trans(N$_1$N)* configuration by the X-ray crystal structure analysis[8] which is a basis of the present work. As shown in Figs. 2—4 and Table 1, the absorption spectra of the three L-smp isomers resemble one another

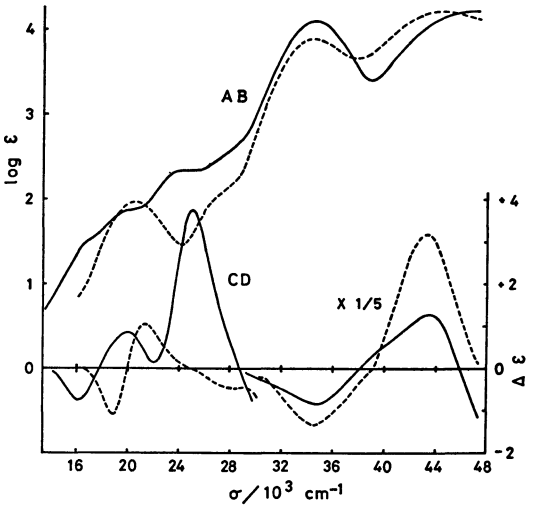

Fig. 2. Absorption and CD spectra of *trans(N$_1$N)*-$[Co(L\text{-}pen)(dien)]^+$ (——) and *trans(N$_1$N)*-$[Co(L\text{-}smp)(dien)]^{2+}$ (----).

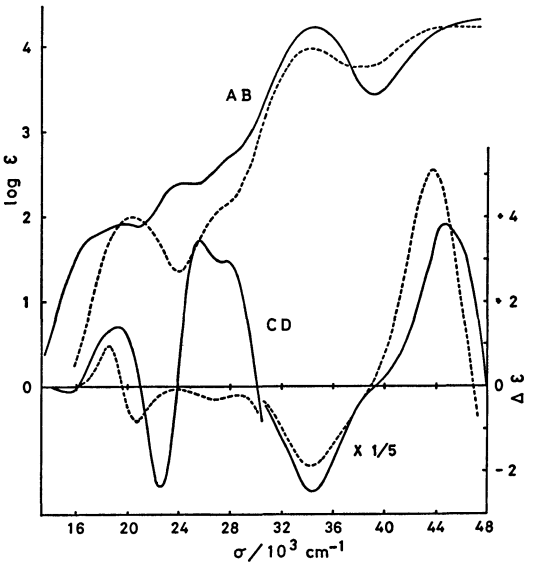

Fig. 3. Absorption and CD spectra of *trans(N$_1$O)*-$[Co(L\text{-}pen)(dien)]^+$ (——) and *trans(N$_1$O)*-$[Co(L\text{-}smp)(dien)]^{2+}$ (----).

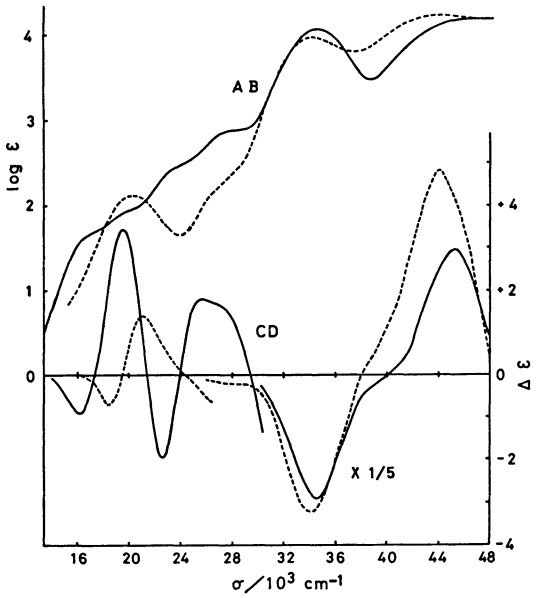

Fig. 4. Absorption and CD spectra of *trans*(N_1S)-[Co(L-pen)(dien)]$^{+}$ (——) and *trans*(N_1S)-[Co(L-smp)-(dien)]$^{2+}$ (----).

in the whole region, because these isomers belong to a *cis(SO)*-[Co(S)(O)$(N)_4$] type having a thioether group. The absorption spectra of the three L-pen isomers, which have a thiolato instead of a thioether group, differ remarkably from those of the L-smp isomers in the region of $(14—30)\times10^3$ cm^{-1}. A difference in absorption spectral behavior is also observed between the triammine complexes, [Co(L-pen)$(NH_3)_3$]$^{+}$ and [Co(L-smp)$(NH_3)_3$]$^{2+}$, as shown in Fig. 5 and Table 1.

Trans(N_1N*)*-[Co(L-pen)(dien)]$^{+}$ (A-1 isomer) did not isomerize in aqueous solution and gave only one isomer (B-1) of [Co(L-smp)(dien)]$^{2+}$ by the reaction with dimethyl sulfate. In a previous paper,[6] the reaction of the coordinated thiolato donor atoms of *trans(N)*- or *trans(O)*-[Co(D-pen)$_2$]$^{-}$ with dimethyl sulfate was accompanied by the geometrical isomerization and the three isomers of [Co(D-smp)$_2$]$^{+}$, *trans(N)*, *trans(O)*, and *trans(S)*, were obtained. Similar isomerization in aqueous solution was also observed for the cobalt(III) complexes with the tripod-like terdentate ligands such as *S*-methyl-L-cysteinate, L-histidinate, and L- or D-aspartate.[6,10–12] When these facts are taken into account, the present result suggests that the reaction of the A-1 isomer with dimethyl sulfate proceeded with retention of the *trans(*N_1N*)* configuration, namely, the B-1 isomer of [Co(L-smp)-(dien)]$^{2+}$ held the *trans(*N_1N*)* configuration because of the rigidity of the coordinated dien.[13] Each of the remaining two L-pen isomers (B-2 and B-3) also gave only one isomer of the L-smp complex by the reaction with dimethyl sulfate, respectively. Namely, the B-2 isomer of [Co(L-smp)(dien)]$^{2+}$ was derived from the A-2 isomer of [Co(L-pen)(dien)]$^{+}$ and the B-3 L-smp isomer from the A-3 L-pen one. The consideration used for the *trans(*N_1N*)* isomers suggests that the B-2 and B-3 isomers retain the geometrical configurations of the A-2 and A-3 ones.

Table 1. Absorption and CD spectral data of [Co(L-pen or L-smp)(dien)]$^{+ \text{ or } 2+}$ and [Co(L-pen or L-smp)$(NH_3)_3$]$^{+ \text{ or } 2+}$

Complex	Absorption $\sigma/10^3$ cm^{-1} (ε/mol^{-1} dm^3 cm^{-1})	CD $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
trans(N_1N)-[Co(L-pen)(dien)]$^{+}$	16.69(1.5 sh[a])	16.23(−0.75)
	20.20(1.9 sh)	20.00(+0.85)
	24.27(2.35)	25.00(+3.75)
	28.01(2.6 sh)	34.84(−4.14)
	34.48(4.10)	43.29(+6.40)
trans(N_1O)-[Co(L-pen)(dien)]$^{+}$	17.30(1.8 sh)	15.48(−0.14)
	19.80(1.93)	19.31(+1.43)
	24.39(2.41)	22.60(−2.35)
	28.01(2.7 sh)	25.55(+3.47)
	34.48(4.23)	27.78(+2.98)
		34.48(−12.3)
		44.64(+19.2)
trans(N_1S)-[Co(L-pen)(dien)]$^{+}$	16.89(1.7 sh)	16.13(−0.87)
	19.42(1.9 sh)	19.53(+3.45)
	23.47(2.45 sh)	22.52(−1.90)
	28.01(2.7 sh)	25.64(+1.82)
	34.72(4.07)	34.60(−14.5)
		45.25(+14.8)
trans(N_1N)-[Co(L-smp)(dien)]$^{2+}$	20.62(1.97)	18·87(−1.08)
	27.10(2.06 sh)	21.37(+1.06)
	34.30(3.88)	28.17(−0.45)
	44.44(4.20)	34.42(−6.65)
		43.48(+15.9)
trans(N_1O)-[Co(L-smp)(dien)]$^{2+}$	20.37(2.01)	18.52(+0.98)
	27.78(2.1 sh)	20.76(−0.79)
	34.25(3.96)	26.88(−0.27)
	44.84(4.20)	34.25(−9.28)
		43.68(+25.6)
trans(N_1S)-[Co(L-smp)(dien)]$^{2+}$	20.37(2.12)	18.52(−0.71)
	26.25(2.1 sh)	21.05(+1.42)
	34.25(3.96)	33.78(−16.0)
	44.25(4.23)	44.05(+24.1)
[Co(L-pen)$(NH_3)_3$]$^{+}$	16.9 (sh)	15.64(−)
	20.0 (sh)	18.01(+)
	24.6 (sh)	21.82(−)
	27.8 (sh)	24.78(+)
	34.68	34.85(−)
		45.24(+)
[Co(L-smp)$(NH_3)_3$]$^{2+}$	20.06(2.02)	18.35(−0.28)
	27.78(2.2 sh)	20.79(+0.96)
	34.48(3.82)	27.78(−0.53 sh)
	45.87(4.14)	34.25(−10.8)
		45.25(+12.4)

a) sh denotes a shoulder.

In the first absorption band region, the B-1, B-2, and B-3 isomers of the L-smp complex commonly show a sharp band at around 20×10^3 cm^{-1} (Figs. 2—4 and Table 1), as in the isomers of [Co(ida)(dien)]$^{+}$ (ida; iminodiacetate),[14] [Co(L-alama)(dien)]$^{+}$ (L-alama; *N*-

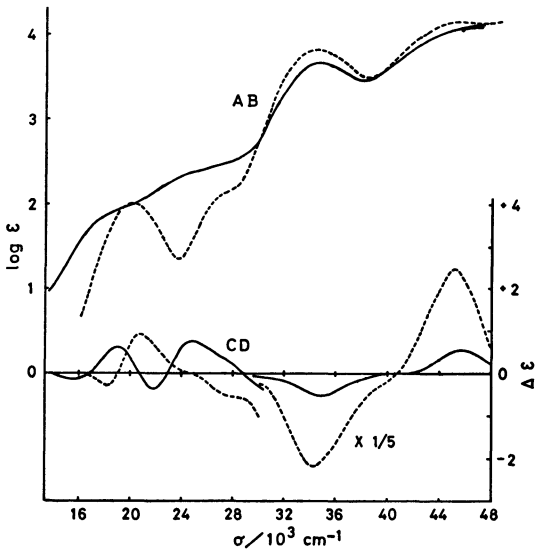

Fig. 5. Absorption and CD spectra of [Co(L-pen)-$(NH_3)_3]^+$ (——) and [Co(L-smp)$(NH_3)_3]^{2+}$ (----). The L-pen complex is illustrated with arbitrary scale.

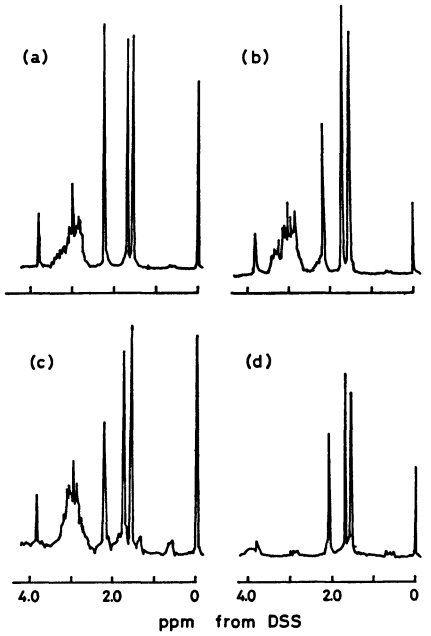

Fig. 6. ^1H NMR spectra of the L-smp complexes; (a) *trans*(N_1N), (b) *trans*(N_1O), and (c) *trans*(N_1S) for [Co(L-smp)(dien)]$^{2+}$, and (d) [Co(L-smp)$(NH_3)_3]^{2+}$.

(carboxylatomethyl)-L-alaninato),[14] and [Co(L- or D-asp)(dien)]$^+$ (asp; aspartate),[15] indicating the proximity of the thioether and COO^- groups in the spectrochemical series.[3-6] The CD spectra of the L-smp isomers in the corresponding region give useful information for the assignments of their geometrical configurations. As shown in Fig. 1, (b) and (c) are quasi-antipodal in overall form, while (a) is symmetrical in comparison with (b) and (c), as in the case of the three isomers of [Co(D-asp)(dien)]$^+$.[15] Indeed, the CD spectrum of the B-1 isomer assigned to *trans*(N_1N) configuration shows a quite similar CD pattern to that of [Co(L-smp)$(NH_3)_3]^{2+}$, which has no chirality arising from the skew pair of the chelate rings (Figs. 2 and 5, and Table 1). On the other hand, the B-2 and B-3 isomers exhibit an almost enantiomeric CD spectral pattern in the first absorption band region, reflecting a quasi-antipodal relationship between the two isomers. The relationship of the B-2 and B-3 isomers is comparable with that of the u^1-*cis* and u^2-*cis* isomers of [Co(L-asp)(dien)]$^+$,[16] namely, the CD spectra of the B-2 and B-3 isomers correspond to those of the u^2-*cis* and u^1-*cis* isomers of [Co(L-asp)(dien)]$^+$,[15] respectively, in the first absorption band region. From this viewpoint, the B-2 and B-3 isomers are tentatively assigned to *trans*(N_1O) and *trans*(N_1S), respectively. The same conclusion is also obtained by comparing the CD spectra of the B-2 and B-3 isomers with those of the *Δ*- and *Λ-unsym-cis*(*O*) isomers of [Co(ida)-(dien)]$^+$ and [Co(L-alama)(dien)]$^+$.[14] Namely, in the first absorption band region, the B-2 isomer shows the CD pattern corresponding to the *Δ-unsym-cis*(*O*) isomer and prefers *trans*(N_1O), while the B-3 isomer shows the pattern appropriate to the *Λ-unsym-cis*(*O*) isomer and prefers *trans*(N_1S). The CD spectral behavior of the L-smp isomers in the first absorption band region and the results that the reaction of the L-pen isomers with dimethyl sulfate proceeded with retention of their geometrical configurations allow us to assign the A-2 and B-2 isomers as *trans*(N_1O), and the A-3 and B-3 isomers as *trans*(N_1S).

The thioether type sulfur atom takes the *R*(*S*) or *S*(*S*) configuration when coordinated with a cobalt(III) ion. As shown in Fig. 6, each isomer of [Co(L-smp)-(dien)]$^{2+}$, and [Co(L-smp)$(NH_3)_3]^{2+}$ exhibit a single peak in the *S*-methyl protons region (2.23 ppm for *trans*(N_1N), 2.22 ppm for *trans*(N_1O) and 2.18 ppm for *trans*(N_1S) of the dien complex, and 2.07 ppm for the triammine complex). In general, for the cobalt(III) complexes with the thioether type ligands having *S*-methyl group, the *S*-methyl protons signals of the *R*(*S*) and *S*(*S*) configurations can be distinguished.[5,6,17,18] The present results suggest that the sulfur atoms of the four complexes take either *R*(*S*) or *S*(*S*). If the sulfur center in the *trans*(N_1N) and *trans*(N_1O) isomers takes *R* configuration, a repulsion exists between an *S*-methyl group and an ethylenediamine moiety of the dien. There is no such repulsion in the *S*-form coordination. Accordingly, it is probable that the sulfur atoms of the *trans*(N_1N) and *trans*(N_1O) isomers take *S* configuration. Similarly, model inspection of the interligand interaction between the *S*-methyl group and amino group for the *trans*(N_1S) isomer or ammine group for the triammine complex suggests that the coordinated sulfur atoms have *S* configuration.

Absorption and CD Spectra. In the energy region higher than the charge transfer band at about 34×10^3 cm^{-1}, the absorption and CD spectra of the isomers of [Co(L-pen)(dien)]$^+$ are quite similar to those of the L-smp isomers (Figs. 2—4 and Table 1). The triammine complexes, [Co(L-pen)$(NH_3)_3]^+$ and [Co-(L-smp)$(NH_3)_3]^{2+}$, also exhibit similar absorption and CD spectral behavior to the dien complexes (Fig. 5 and Table 1). The CD pattern of the triammine complexes are due to the coordination of L-pen and

L-smp, respectively. In this region, the CD pattern of the present complexes seems to depend mainly on the absolute configuration of L-thiolato and L-thioether type ligands. In the higher energy region, the similarity of CD pattern in the present L-pen and L-smp isomers should be noted and compared with the difference in CD pattern between the corresponding isomers of $[Co(D\text{-pen})_2]^-$ and $[Co(D\text{-smp})_2]^+$.[6] In the lower energy region [$(14—30)\times10^3$ cm^{-1}], in contrast to the higher energy region, the absorption and CD spectra of the L-pen isomers deviate from those of the L-smp ones. First, the first absorption bands of the L-pen isomers shift to lower energy than those of the L-smp ones and are broader because of a thiol coordination.[6,7,19] The CD spectra of the [Co(L-pen)(dien)]$^+$ isomers consist of three components in the first absorption band region, as seen in Figs. 2—4. This CD pattern corresponds well with that of $[Co(L\text{-pen})(NH_3)_3]^+$ and it seems that the coordinated dien contributes little to the CD pattern in the first absorption band region. Secondly, the absorption and CD spectral differences between the L-pen and L-smp isomers are remarkable in the region of $(24—30)\times10^3$ cm^{-1}. The L-smp isomers exhibit the second absorption band as a shoulder, while the L-pen isomers exhibit two more intense absorption bands in the corresponding region (Figs. 2—4 and Table 1). The CD spectra of the *trans(N$_1$O)* and *trans(N$_1$S)* isomers of [Co(L-pen)(dien)]$^+$ consist of two positive bands, which correspond well with the two absorption components in this region. *Trans(N$_1$N)* isomer of [Co(L-pen)(dien)]$^+$ and $[Co(L\text{-pen})(NH_3)_3]^+$ which are more symmetrical in configuration than the *trans(N$_1$O)* and *trans(N$_1$S)* isomers show a positive CD band with a vague shoulder in the higher energy side (Figs. 2 and 5). Similar absorption and CD spectral behavior can also be observed for the other penicillaminato mixed complexes of [Co(L-pen)(terdentate)] type, where terdentate denotes L-histidinate, L-2,4-diaminobutylate and L-ornithinate.[20] The sign of the two CD bands depends on the absolute configuration of the optically active penicillaminate coordinated, namely, a positive sign for the L-pen and negative one for the D-pen,[20] as in the case of *trans(N)*- and *trans(O)*-$[Co(D\text{-pen})_2]^-$.[6] The L-pen mixed complexes commonly show two positive CD bands, while the $[Co(D\text{-pen})_2]^-$ isomers seem to show a negative CD band in the corresponding region.[6] This difference in CD pattern may be due to the lowering of symmetry of the thiolato type complexes.

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