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# Preparation and Some Properties of Cobalt(III) Complexes with D-Penicillaminate and Its Derivatives

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Three kinds of [Co(terdentate-*N,O,S*)$_2$] type complexes were newly prepared; here terdentate-*N,O,S* denotes D-penicillaminate (D-pen), *S*-methyl-D-penicillaminate (D-smp) and *S*-methyl-L-cysteinate (L-smc). Each of the D-smp and L-smc complexes was chromatographically separated into three possible isomers; the D-pen complex was separated into two isomers. These isomers were characterized from their electronic absorption, CD and $^1$H NMR spectra. Two isomers isolated for [Co(D-pen)$_2$]$^-$ were assigned to *trans(N)* and *trans(O)*, respectively, on the basis of the spectral behavior of the sulfur-to-metal charge transfer band and the reaction with dimethyl sulfate. Three isomers for [Co(D-smp)$_2$]$^+$ were derived from each of two isomers for [Co(D-pen)$_2$]$^-$ by the reaction with dimethyl sulfate. The electronic absorption and CD spectral behaviors are discussed in relation to the comparison of the thioether and thiolato type complexes.

Some cobalt(III) complexes with the thioether type terdentate-*N,O,S* ligands such as L-methionine and *S*-methyl-L-cysteine have been reported,[1-3] and the electronic absorption and CD spectral properties of the thioether type sulfur atom which takes *R* or *S* configuration by coordination have been investigated.[4,5] The contributions of the coordinated thiolato type sulfur atom to the electronic absorption and CD spectra would be interesting in comparison with those of the thioether type sulfur atom; but the electronic absorption and CD spectral behaviors have been little known.[6]

In the present paper, the cobalt(III) complexes with the thioether or thiolato type terdentate-*N,O,S* ligands, [Co(L-smc)$_2$]$^+$, [Co(D-smp)$_2$]$^+$ and [Co(D-pen)$_2$]$^-$, were prepared for the first time and their isomers were chromatographically separated. The three isomers for each of the L-smc and D-smp complexes are characterized from their electronic absorption spectra in comparison with the bis(L-methioninato)cobalt(III) complex, [Co(L-met)$_2$]$^+$.[1] The absolute configurations of the coordinated sulfur atoms for the L-smc and D-smp complexes are suggested on the basis of the $^1$H NMR spectra. The two isomers for the [Co(D-pen)$_2$]$^-$ complex are assigned on the basis of the spectral behavior of their sulfur-to-metal charge transfer bands and the formation ratios of the D-smp isomers obtained by the reaction with dimethyl sulfate. The electronic absorption and CD spectra are mainly discussed in relation to the comparison of the thioether and thiolato type complexes. A preliminary report has been presented for the [Co(L-smc)$_2$]$^+$ complex.[7]

## Experimental

*1) Bis(*S*-methyl-L-cysteinato)cobalt(III) Perchlorate: [Co(L-smc)$_2$]ClO$_4$.* Three isomers of [Co(L-smc)$_2$]$^+$ were isolated by a procedure similar to that used for those of [Co(L-met)$_2$]$^+$.[1] A solution containing 2.7 g of cobalt(II) chloride hexahydrate in 10 cm$^3$ of water was added to a hot solution (*ca.* 70 °C) containing *S*-methyl-L-cysteine (3.0 g) in 50 cm$^3$ of water, and to the mixture 0.5 g of activated charcoal was added. Eight grams of lead dioxide were gradually added to the mixture, which was mechanically stirred at *ca.* 70 °C for 20 min. After cooling to room temperature, the reaction mixture was filtered to remove the activated charcoal and any excess of lead dioxide. A saturated aqueous solution of sodium sulfate (1.5 g) was added to the filtrate and the lead sulfate precipitated was filtered off. The filtrate was poured onto a column of Dowex 50W-X8 (200—400 mesh, H$^+$ form). After the column had been swept with water, two eluates, violet (A-1) and red (A-2), were obtained by eluting with a 0.3 mol dm$^{-3}$ aqueous solution of sodium perchlorate. Another eluate, blue-violet (A-3), was obtained quickly from the remaining adsorbed band by eluting with 0.5 mol dm$^{-3}$ aqueous solution of sodium perchlorate, though the A-3 could be eluted with 0.3 mol dm$^{-3}$ aqueous solution of sodium perchlorate. It was found, from the absorption and CD spectral measurements, that A-1, A-2, and A-3 were *trans*(*S*), *trans*(*O*), and *trans*(*N*) isomers, respectively. These eluates were separately concentrated to a small volume with a rotary evaporator at 30 °C and then the deposited sodium perchlorate was filtered off. To each of the filtrates was added a large amount of ethanol. The crude isomers from A-1 and A-3 were recrystallized from as little water as possible by cooling in an ice bath after adding an appropriate amount of ethanol. The isomer from A-2 was less soluble than the other two and was recrystallized from as little warm water (*ca.* 30 °C) as possible by cooling in an ice bath. The pure isomers were washed with ethanol and ether, and then dried in a vacuum desiccator over sulfuric acid. Found for *trans*(*S*) isomer (A-1): C, 21.70; H, 4.03; N, 6.32%. Found for *trans*(*O*) isomer (A-2): C, 21.50; H, 4.13; N, 6.08%. Found for *trans*(*N*) isomer (A-3): C, 21.33; H, 3.99; N, 6.17%. Calcd for [Co(L-smc)$_2$]ClO$_4$·H$_2$O=CoC$_8$H$_{16}$N$_2$O$_8$S$_2$Cl·H$_2$O: C, 21.70; H, 4.09; N, 6.32%.

*2) Bis(*S*-methyl-D-penicillaminato)cobalt(III) Bromide: [Co(D-smp)$_2$]Br.* This complex was prepared by the reaction of bis(D-penicillaminato)cobalt(III) complex (*vide infra*) with dimethyl sulfate. About 10 cm$^3$ of dimethyl sulfate was added drop by drop to a solution containing 1 g of the brown isomer of [Co(D-pen)$_2$]$^-$ 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 was separated into two layers, a brown (upper) layer and a cloudy colorless (lower) layer. The former changed gradually to reddish violet. After being allowed

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to stand at room temperature for about 6 h, the reddish violet solution was separated and poured onto a column (3.5 cm × 30 cm) of Dowex 50W-X8 (200—400 mesh, $NH_4^+$ form). After the column had been swept with water, the adsorbed reddish violet band was eluted with a 0.05 mol $dm^{-3}$ aqueous solution of ammonium bromide. Three bands, dark red (B-1), reddish violet (B-2), and red (B-3), were progressively eluted in this order. Their absorption spectral measurements showed that B-1, B-2, and B-3 were *trans*(*O*), *trans*(*N*), and *trans*(*S*) isomers, respectively. The eluates were separately concentrated with a rotary evaporator below 20 °C. The ammonium bromide deposited was filtered off and a small amount of acetone was added to the filtrate. The three isomers obtained were recrystallized from as little water as possible by adding acetone. The isomers were washed with ethanol, acetone and ether, and then dried in a vacuum desiccator over calcium chloride. Found for *trans*(*O*) isomer (B-1): C, 31.11; H, 5.25; N, 6.07%. Found for *trans*(*N*) isomer (B-2): C, 30.25; H, 5.29; N, 6.05%. Calcd for $[Co(D\text{-}smp)_2]Br = CoC_{12}H_{24}N_2O_4S_2Br$: C, 31.11; H, 5.25; N, 6.05%. Found for *trans*(*S*) isomer (B-3): C, 28.23; H, 5.66; N, 5.59%. Calcd for $[Co(D\text{-}smp)_2]Br \cdot 2H_2O$: C, 28.26; H, 5.61; N, 5.65%.

Similarly, the green isomer of $[Co(D\text{-}pen)_2]^-$ gave three isomers of $[Co(D\text{-}smp)_2]^+$ by the reaction with dimethyl sulfate. However, the formation ratio of the three D-smp isomers derived from the green isomer of $[Co(D\text{-}pen)_2]^-$ differs from that of the three isomers from the brown isomer of $[Co(D\text{-}pen)_2]^-$; *trans*(*O*) : *trans*(*N*) : *trans*(*S*) = 20:65:15 for the D-smp isomers derived from the brown isomer and 69:18:13 from the green isomer. It seems that the difference in formation ratio reflects the geometrical configuration of $[Co(D\text{-}pen)_2]^-$ which is the starting complex.

*3) Potassium Bis(*D*-penicillaminato)cobaltate(III)*: *K[Co(*D*-pen)$_2$]*. *Method A*: To a solution containing 1.6 g of cobalt(II) chloride hexahydrate in 10 $cm^3$ of water was added 2.0 g of D-penicillamine. After the mixture was stirred for a few minutes, the pH was adjusted to *ca.* 7 by the addition of 3.0 mol $dm^{-3}$ aqueous solution of potassium hydroxide. The color of the solution changed from red to brown. After the reaction mixture had been allowed to stand at room temperature for about 6 h, a small amount of acetone was added to it. Then it was kept in a refrigerator overnight. Brown needle crystals (C-1) deposited. These crystals were collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator over calcium chloride. Found for brown isomer (C-1): C, 27.18; H, 5.19; N, 6.48%. Calcd for $K[Co(D\text{-}pen)_2] \cdot 2H_2O = KCoC_{10}H_{18}N_2O_4S_2 \cdot 2H_2O$: C, 27.99; H, 5.19; N, 6.53%.

The filtrate was poured onto a column (3.5 cm × 30 cm) of Dowex 1-X8 (100—200 mesh, $Cl^-$ form) in order to see the formation of the other isomers of $[Co(D\text{-}pen)_2]^-$. After the column had been swept with water, the adsorbed brown band was eluted with a 0.07 mol $dm^{-3}$ aqueous solution of potassium chloride. The eluate of a broad band was collected in 10 $cm^3$ portions in a fraction collector. The absorption and CD spectral measurements indicated that the eluate contained two kinds of complexes. The earlier fractions contained a complex which did not have the sulfur-to-metal charge transfer band (*ca.* $33.0 \times 10^3$ $cm^{-1}$)[1,2] and the later fractions showed the same spectra as that of the brown crystalline complex isolated before.

*Method B*: A hot solution (*ca.* 60 °C) containing 1 g of $[Co(NH_3)_6]Cl_3$[8] in 30 $cm^3$ of water was adjusted to pH 7 with 3.0 mol $dm^{-3}$ aqueous solution of sodium hydroxide. To this solution were added 2 g of D-penicillamine and 0.5 g of activated charcoal. The mixture was mechanically stirred at 60 °C for 15 min. The reaction mixture was filtered in order to remove activated charcoal after cooling to room temperature. The filtrate was poured onto a column (4 cm × 60 cm) of QAE-Sephadex A-25 ($Cl^-$ form). After the column had been swept with water, the adsorbed brown band was eluted with 0.1 mol $dm^{-3}$ aqueous solution of potassium chloride. Five colored bands: brown (C-1), yellow, red brown, dark green, and green (C-2), were eluted in this order. Of these five eluates, the brown (C-1) and green (C-2) eluates produced the thioether type complexes by the reaction with dimethyl sulfate, but the remaining ones did not. These results and the absorption spectral measurements suggest that the brown and green eluates contained the desired complex and the remaining three did not. The brown (C-1) eluate showed the same absorption and CD spectra as the isomer isolated in Method A. The green (C-2) eluate was concentrated to a small volume with a rotary evaporator below 20 °C and the deposited potassium chloride was filtered off. A small amount of acetone was added to the filtrate. The green complex obtained was recrystallized from a small amount of water by adding acetone. The complex was washed with ethanol and ether, and then dried in a vacuum desiccator over calcium chloride. Found for the green isomer (C-2): C, 20.19; H, 4.07; N, 4.85%. Calcd for $K[Co(D\text{-}pen)_2] \cdot 3H_2O \cdot 2KCl$: C, 20.19; H, 4.06; N, 4.71%.

*4) Potassium (*L*-Penicillaminato)(*D*-penicillaminato)cobaltate(III)*: *K[Co(*L*-pen)(*D*-pen)]*. This complex was prepared by the method of Hodgson *et al.*[9] Found: C, 29.12; H, 4.92; N, 6.84%. Calcd for $K[Co(L\text{-}pen)(D\text{-}pen)] \cdot H_2O = KCoC_{10}H_{18}N_2O_4S_2 \cdot H_2O$: C, 29.26; H, 4.91; N, 6.82%.

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

The $^1H$ NMR spectra were recorded in deuterium oxide on a JEOL JNM-MH-100 or 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 Assignments*. Three geometrical isomers are possible for the present $[Co(terdentate\text{-}N,O,S)_2]$ type complex. The isomers are designated as *trans*(*S*), *trans*(*O*), and *trans*(*N*) with respect to the coordinated atoms, N, O, and S (Fig. 1). The three isomers were chromatographically isolated for each of $[Co(L\text{-}smc)_2]^+$ and $[Co(D\text{-}smp)_2]^+$, and only two isomers for $[Co(D\text{-}pen)_2]^-$. Their absorption and CD spectra are shown in Figs. 2—6 and are summarized in Tables 1 and 2. Of the three isomers for $[Co(L\text{-}smc)_2]^+$, the first eluted

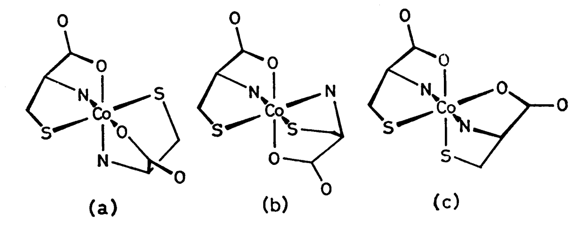

Fig. 1. Three possible isomers of $[Co(terdentate\text{-}N,O,S)_2]$ type complexes: (a) *trans*(*S*), (b) *trans*(*O*), and (c) *trans*(*N*).

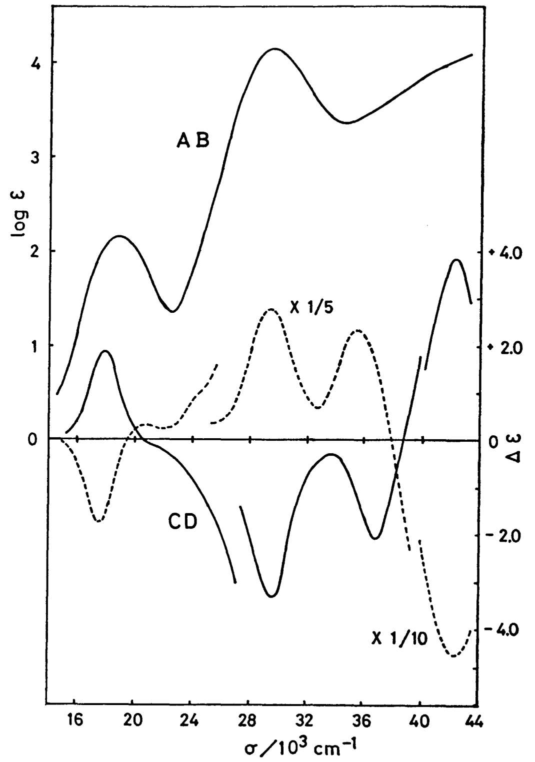

Fig. 2. Absorption and CD spectra of *trans*(*S*)-[Co(L-smc)$_2$]$^+$ (——) and *trans*(*S*)-[Co(D-smp)$_2$]$^+$ (----).

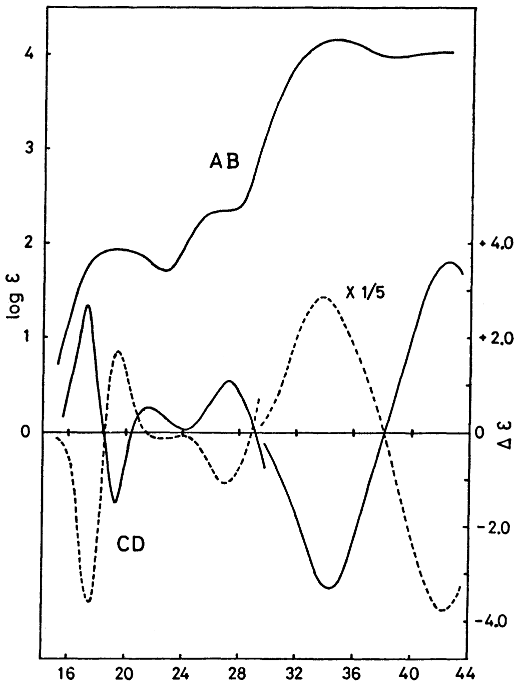

Fig. 3. Absorption and CD spectra of *trans*(*O*)-[Co(L-smc)$_2$]$^+$ (——) and *trans*(*O*)-[Co(D-smp)$_2$]$^+$ (----).

A-1, whose sulfur-to-metal charge transfer band is located at lower energy ($29.47\times10^3$ cm$^{-1}$) than those of the remaining two isomers ($34.47\times10^3$ cm$^{-1}$ for A-2 and $32.13\times10^3$ cm$^{-1}$ for A-3),[1,2] was determined to be the *trans*(*S*) isomer by the X-ray crystal structure analysis.[10] The absorption spectra of the isomers for [Co(L-smc)$_2$]$^+$ correspond quite well with those of the [Co(L-met)$_2$]$^+$ complex,[1] respectively, over the whole region (Figs. 2—4 and Table 1). Accordingly, A-1 can be assigned to *trans*(*S*), A-2 to *trans*(*O*), and A-3 to *trans*(*N*). The same consideration for the absorption spectra of the [Co(L-smc)$_2$]$^+$ isomers is also valid for those of the three isomers, B-1, B-2 and B-3, of [Co(D-smp)$_2$]$^+$ derived from the isomers, C-1 and C-2, of [Co(D-pen)$_2$]$^-$. In the first absorption band region, B-1 shows a broad band with a vague shoulder on the higher energy side, B-2 a band with an explicit shoulder on the lower energy side, and B-3 apparently a sharp band (Fig. 5 and Table 1). These splittings of the first absorp-

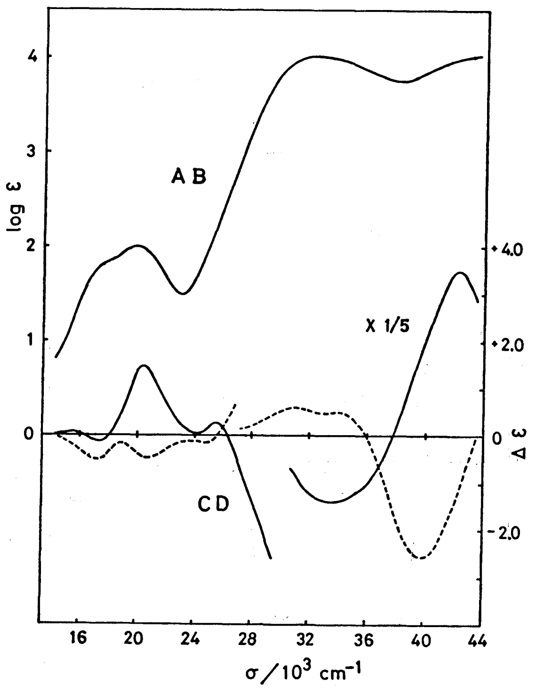

Fig. 4. Absorption and CD spectra of *trans*(*N*)-[Co(L-smc)$_2$]$^+$ (——) and *trans*(*N*)-[Co(D-smp)$_2$]$^+$ (----).

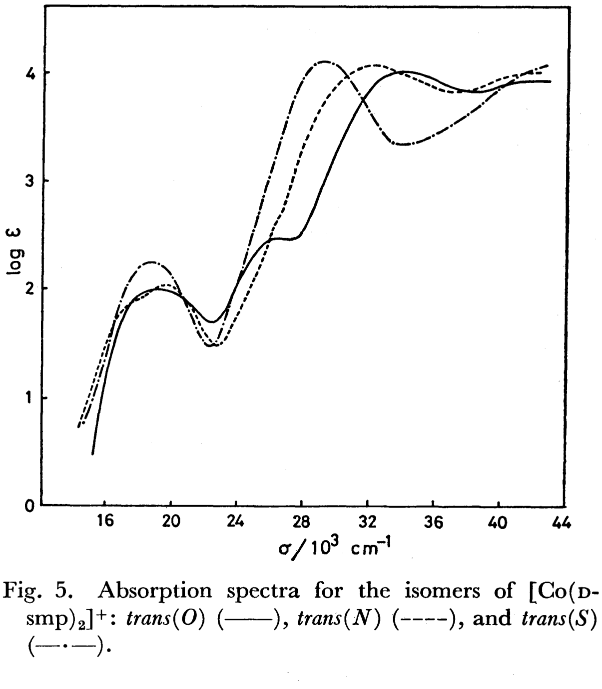

Fig. 5. Absorption spectra for the isomers of [Co(D-smp)$_2$]$^+$: *trans*(*O*) (——), *trans*(*N*) (----), and *trans*(*S*) (—·—).

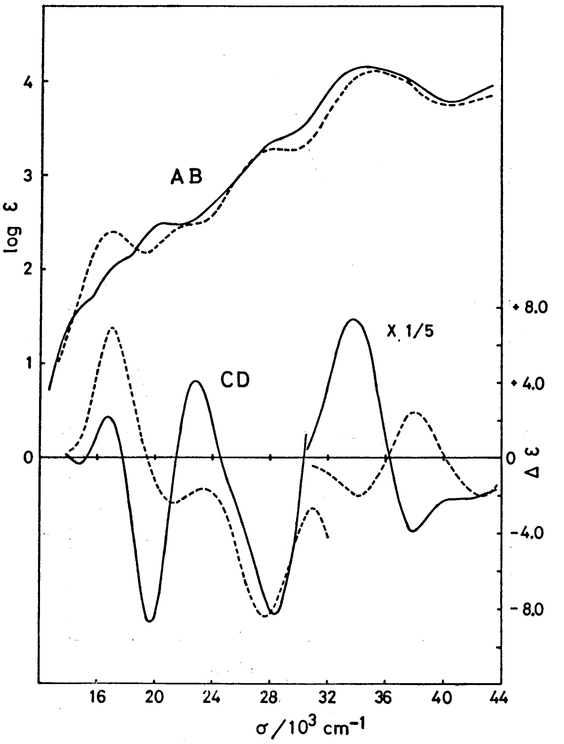

Fig. 6. Absorption and CD spectra of *trans*($N$)-[Co(D-pen)$_2$]$^-$ (——) and *trans*($O$)-[Co(D-pen)$_2$]$^-$ (----).

tion bands agree well with those which can be expected from the semiempirical calculation[11] on the basis of the ligand field order $N>S>O$.[2,3] Furthermore, the sulfur-to-metal charge transfer band of B-3 ($29.33\times10^3$ cm$^{-1}$) locates at lower energy side than those of the remaining two isomers ($34.27\times10^3$ cm$^{-1}$ for B-1 and $32.40\times10^3$ cm$^{-1}$ for B-2).[1,2] These facts indicate that B-1 is *trans*($O$), B-2 *trans*($N$), and B-3 *trans*($S$).

Of three possible isomers for [Co(D-pen)$_2$]$^-$, only two isomers were obtained, though several preparative methods were attempted. The absorption spectral behavior of [Co(D-pen)$_2$]$^-$, which belongs to [Co($N$)$_2$($O$)$_2$($S$)$_2$] type having two thiolato groups instead of thioether ones, differs from those of [Co(L-smc)$_2$]$^+$ and [Co(D-smp)$_2$]$^+$ (Fig. 6 and Table 1). The notable difference is observed in the region of (27.0—28.5) × $10^3$ cm$^{-1}$ (*vide infra*).

In the first absorption band region, the splitting for C-1 differs strikingly from that for C-2. Namely, the first absorption band of C-1 is composed of three components (14.1, 17.1 and $20.53\times10^3$ cm$^{-1}$) and that of C-2 two components (17.10 and $22.0\times10^3$ cm$^{-1}$). However, from the absorption spectral difference in the first absorption band region, it is difficult to distinguish their geometrical structures at present. Recently, it was recognized also for the geometrical isomers having two thiolato donor atoms that the sulfur-to-metal charge transfer band of *trans*($S$) isomer appears at lower energy than that of *cis*($S$) one as the case of thioether type complex.[6] The charge transfer bands of the present two isomers are close in maximum position to each other (Fig. 6 and Table 1), specifically, the band of C-1 locates at $33.80\times10^3$ cm$^{-1}$ and that of C-2 at $34.93\times10^3$ cm$^{-1}$. In addition to this fact, *cis*·*cis*·*cis*-[Co(L-pen)(D-pen)]$^-$, which was determined by the X-ray crystal structure analysis,[9] shows the corresponding charge transfer band at $33.77\times10^3$ cm$^{-1}$. Taking these facts into consideration, it is probable that the two isomers isolated are *cis*($S$) rather than *trans*($S$).

All isomers of the present complexes isomerized in water as was the case of cobalt(III) complexes with terdentate amino carboxylate ligands[12—14] and each isomer generated the mixture of the three isomers after a few days. The isomerization is conspicuous for the isomers of [Co(D-smp)$_2$]$^+$ in comparison with those of [Co(L-smc)$_2$]$^+$ and [Co(L-met)$_2$]$^+$. The three isomers of [Co(D-smp)$_2$]$^+$ were derived from C-1 and from C-2 of [Co(D-pen)$_2$]$^-$. Accordingly, it is probable that the reaction of the coordinated thiolato donor atoms

Table 1. Absorption data of [Co(terdentate-$N,O,S$)$_2$] type complexes

| Complex | First band | Second band | Charge transfer band |
|---|---|---|---|
| *trans*($S$)-[Co(L-smc)$_2$]$^+$ | 18.73(2.18) | | 29.47(4.16) |
| *trans*($O$)-[Co(L-smc)$_2$]$^+$ | 19.40(1.93) | 26.48(2.34) | 34.47(4.16) |
| *trans*($N$)-[Co(L-smc)$_2$]$^+$ | 17.5 (1.81 sh)<br>19.87(2.01) | | 32.13(4.03) |
| *trans*($O$)-[Co(D-smp)$_2$]$^+$ | 19.20(1.99) | 26.47(2.46) | 34.27(4.00) |
| *trans*($N$)-[Co(D-smp)$_2$]$^+$ | 17.5 (1.86 sh)<br>19.73(2.04) | | 32.40(4.06) |
| *trans*($S$)-[Co(D-smp)$_2$]$^+$ | 18.80(2.25) | | 29.33(4.10) |
| *trans*($N$)-[Co(D-pen)$_2$]$^-$ | 14.1 (1.44 sh)<br>17.1 (2.02 sh)<br>20.53(2.48) | 28.0 (3.36 sh) | 33.80(4.16) |
| *trans*($O$)-[Co(D-pen)$_2$]$^-$ | 17.10(2.38)<br>22.0 (2.40 sh) | 28.30(3.28) | 34.93(4.11) |
| *cis*·*cis*·*cis*-[Co(L-pen)(D-pen)]$^-$ [a] | 17.27(2.21)<br>21.1 (2.41 sh) | 24.4 (2.85 sh) | 33.77(4.25) |

a) Ref. 9. Wave numbers and log ε values (in parentheses) are given in $10^3$ cm$^{-1}$ and mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively. sh denotes a shoulder.

TABLE 2. CD DATA OF [Co(terdentate-*N*,*O*,*S*)$_2$] TYPE COMPLEXES

| Complex | First band region | Second band region | Charge transfer band region |
|---|---|---|---|
| *trans*(*S*)-[Co(L-smc)$_2$]$^+$ | 17.87(+1.92) | | 29.63(−16.5) |
| | | | 36.80(−11.1) |
| | | | 42.27(+40.1) |
| *trans*(*O*)-[Co(L-smc)$_2$]$^+$ | 17.23(+2.70) | 27.20(+1.08) | 34.47(−18.3) |
| | 19.25(−1.44) | | 42.80(+18.3) |
| | 21.60(+0.57) | | |
| *trans*(*N*)-[Co(L-smc)$_2$]$^+$ | 15.47(+0.06) | 25.60(+0.23) | 33.54(−7.80) |
| | 17.33(−0.11) | | 42.27(+17.3) |
| | 20.43(+1.44) | | |
| *trans*(*O*)-[Co(D-smp)$_2$]$^+$ | 17.40(−3.61) | 26.86(−1.07) | 33.87(+14.6) |
| | 19.40(+1.71) | | 42.33(−19.1) |
| | 22.27(−0.12) | | |
| *trans*(*N*)-[Co(D-smp)$_2$]$^+$ | 17.17(−0.53) | 24.87(−0.14) | 31.07(+3.11) |
| | 20.73(−0.48) | | 33.93(+2.55) |
| | | | 39.87(−12.9) |
| *trans*(*S*)-[Co(D-smp)$_2$]$^+$ | 17.60(−1.76) | | 29.47(+14.1) |
| | 20.73(+0.32) | | 35.60(+11.6) |
| | | | 42.40(−46.3) |
| *trans*(*N*)-[Co(D-pen)$_2$]$^-$ | 14.83(−0.34) | 22.83(+4.17) | 33.73(+36.9) |
| | 16.73(+2.24) | 28.40(−8.27) | 37.93(−19.5) |
| | 19.73(−8.68) | | 41.00(−10.7) |
| *trans*(*O*)-[Co(D-pen)$_2$]$^-$ | 17.03(+6.96) | 27.67(−8.43) | 34.13(−10.2) |
| | 21.27(−2.43) | | 38.03(+12.5) |
| | | | 42.60(−10.0) |

Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in $10^3$ cm$^{-1}$ and mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively.

of [Co(D-pen)$_2$]$^-$ with dimethyl sulfate was accompanied by the isomerization. In the preparations, the *trans*(*N*) isomer formed dominantly for the [Co(D-smp)$_2$]$^+$ complex derived from C-1 and the *trans*(*O*) isomer for the complex from C-2, as described in the experimental section. These results suggest that *trans*(*N*) is preferable for C-1 and *trans*(*O*) for C-2. In addition, considering the fact that the thiolato type ligand prevents the formation of *trans*(*S*) isomer because of the trans effect,$^{6)}$ it is tentatively assigned that C-1 is *trans*(*N*) and C-2 *trans*(*O*).

*$^1$H NMR and CD Spectra.* The $^1$H NMR spectra of *trans*(*S*)-[Co(L-smc)$_2$]$^+$ and -[Co(D-smp)$_2$]$^+$ show a single peak in the *S*-methyl proton region (2.22 ppm for the L-smc isomer and 2.16 ppm for the D-smp one), like that of *trans*(*S*)-[Co(L-met)$_2$]$^+$.$^{1)}$ In the column chromatographic separation of the *trans*(*S*) isomers, all the fractions of each isomer showed the same CD spectra. The X-ray crystal structure analysis$^{10)}$ showed that the two coordinated sulfur atoms of *trans*(*S*)-[Co(L-smc)$_2$]ClO$_4\cdot$H$_2$O take the *S*(*S*),*S*(*S*) configuration which has C$_2$ symmetry. These results suggest that the two sulfur atoms in *trans*(*S*)-[Co(D-smp)$_2$]$^+$ take selectively the *R*(*S*),*R*(*S*) configuration. In contrast with the *trans*(*S*) isomers, the $^1$H NMR spectra of the *trans*(*N*) and *trans*(*O*) isomers suggest that each of them is a mixture of some configurations of the coordinated sulfur atoms. The *trans*(*N*) isomer shows three signals due to *S*-methyl protons (2.16, 2.09, and 2.00 ppm) for [Co(L-smc)$_2$]$^+$ and two signals (2.12 and 2.04 ppm) for [Co(D-smp)$_2$]$^+$. Inspection of models concerning the crowd of *S*-methyl groups of the ligand coordinated suggests that *trans*(*N*)-[Co(L-smc)$_2$]$^+$ consists of *S*(*S*),*S*(*S*), and *R*(*S*),*S*(*S*) configurations, and *trans*(*N*)-[Co(D-smp)$_2$]$^+$ of *R*(*S*),*S*(*S*) and *R*(*S*),*R*(*S*) ones. The *trans*(*O*) isomer shows two signals (2.29 and 2.18 ppm) for [Co(L-smc)$_2$]$^+$ and three signals (2.22, 2.18, and 2.12 ppm) for [Co(D-smp)$_2$]$^+$. Similarly, model inspections suggest that *trans*(*O*)-[Co(L-smc)$_2$]$^+$ and -[Co(D-smp)$_2$]$^+$ are a mixture of *S*(*S*),*S*(*S*), *R*(*S*),*S*(*S*), and *R*(*S*),*R*(*S*) configurations, respectively. These $^1$H NMR spectral behaviors of the *trans*(*N*) and *trans*(*O*) isomers are also similar to that of the corresponding isomers of [Co(L-met)$_2$]$^+$.$^{1)}$ In the present [Co(terdentate-*N*,*O*,*S*)$_2$] type complex having two thioether groups, it should be noted that only the *trans*(*S*) isomer shows a distinguishable selectivity concerning the orientation of *S*-methyl groups; the reason for this selectivity is unknown at present.

The CD spectra of the [Co(D-smp)$_2$]$^+$ isomers are almost enantiomeric to those of the [Co(L-smc)$_2$]$^+$ ones, respectively, reflecting the similarity of their rigid frameworks (Figs. 2—4 and Table 2). The CD spectral behavior of the [Co(D-pen)$_2$]$^-$ isomers is in contrast to those of the [Co(D-smp)$_2$]$^+$ and [Co(L-smc)$_2$]$^+$ ones (Fig. 6 and Table 2). In the first absorption band region, the *trans*(*O*)-[Co(D-pen)$_2$]$^-$ isomer shows two CD bands corresponding to two absorption components, and the *trans*(*N*) isomer clearly shows three CD bands corresponding to three absorption components. In the sulfur-to-metal charge transfer band region ((33—35) × $10^3$ cm$^{-1}$), the *trans*(*N*) and *trans*(*O*) isomers show enantiomeric CD patterns. The absorption and CD spectra in the region of $(27-28)\times10^3\ \mathrm{cm}^{-1}$ are noted as a characteristic difference of the thiolato and thioether type complexes. In this region, each of the D-pen isomers shows an extra band (at $28.30\times10^3\ \mathrm{cm}^{-1}$ for *trans*(*O*) and $28.0\times10^3\ \mathrm{cm}^{-1}$ for *trans*(*N*)) which does not appear for the spectra of the thioether type complexes, and the CD bands in this region commonly have a negative sign. Similar absorption and CD spectral behaviors were also observed for the three isomers of $[\mathrm{Co}(\text{L-pen})(\mathrm{dien})]^+$.[15] These absorption bands seem to be characteristic for the thiol coordination of the pen ligand, and the sign of the CD band in the corresponding region seems to depend on the absolute configuration (*R*(*C*) or *S*(*C*)) of the optically active penicillaminate coordinated.

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