September, 1983] *Bull. Chem. Soc. Jpn.*, ***56***, *2631—2637 (1983)*

Preparation and Stereochemistry of Cobalt(III) Complexes with *S*-Alkyl-L-cysteinate, *N,N'*-Trimethylenebis(*S*-methyl-L-cysteinate), and *S,S'*-Ethylene(or -Trimethylene)bis(L-cysteinate)

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(Received March 8, 1983)

Five cobalt(III) complexes of [Co(terdentate-*N,S,O*)$_2$] and [Co(sexidentate-N_2,S_2,O_2)] types were prepared; here terdentate-*N,S,O* denotes *S*-ethyl-L-cysteinate (L-sec) and *S*-benzyl-L-cysteinate (L-sbc), and sexidentate-N_2,S_2,O_2 denotes *N,N'*-trimethylenebis(*S*-methyl-L-cysteinate) (L,L-tbsmc), *S,S'*-ethylenebis(L-cysteinate) (L,L-ebc), and *S,S'*-trimethylenebis(L-cysteinate) (L,L-tbc). Three isomers, *trans(S)*, *trans(N)*, and *trans(O)*, were chromatographically isolated for each of the bis L-sec and L-sbc complexes, while only the *trans(O)* isomer was isolated for each of the L,L-tbsmc, L,L-ebc, and L,L-tbc complexes. These isomers were characterized from their absorption, CD, and ^{1}H and ^{13}C NMR spectra. The *trans(O)* isomers of the bis type and L,L-tbsmc complexes, which were assigned to a mixture of *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*) configurations concerning the coordinated sulfur atoms, showed a similar CD spectral behavior to each other in the whole region. The *trans(O)*-*R*(*S*),*R*(*S*) L,L-ebc isomer and *trans(O)*-*S*(*S*),*S*(*S*) L,L-tbc one showed characteristic absorption and CD spectral behavior in the sulfur-to-metal charge transfer band region.

Cobalt(III) complexes with multidentate thioether type ligands such as *S*-methyl-L-cysteine, L-methionine, and their derivatives exhibited an extreme specificity concerning the formation of geometrical isomers.[1—12] The causes for the specificity were mostly related to the stereochemical property of the coordinated sulfur atoms of the thioether ligands.[8,9,11] The stereochemical behavior of the chiral sulfur donor atoms was reflected in the CD spectra of the complexes.[5,8,11] However, it is difficult to specify directly the contribution due to the chiral sulfur donor atoms to the CD spectra of the complexes, because of the overlap with the CD contribution due to other optically active sources in the complexes and an apprehension of sulfur inversion.[7,9] The present work was attempted to investigate the contribution of the chiral sulfur donor atoms of the thioether ligands such as *S*-alkyl-L-cysteine and its derivatives to the CD spectra of the cobalt(III) complexes, especially in the sulfur-to-metal charge transfer band region.

Cobalt(III) complexes with thioether type terdentate-*N,S,O* ligands, [Co(L-sec)$_2$]$^+$ and [Co(L-sbc)$_2$]$^+$, were prepared and chromatographically separated into three geometrical isomers: *trans(S)*, *trans(N)*, and *trans(O)*. For cobalt(III) complexes with a thioether type sexidentate-N_2,S_2,O_2 ligand, [Co(L,L-tbsmc)]$^+$, where two nitrogen donor atoms were bridged by trimethylene (*N,N*-bridge), and [Co(L,L-ebc)]$^+$ and [Co(L,L-tbc)]$^+$, where two sulfur donor atoms were bridged by ethylene and trimethylene (*S,S*-bridge), only *trans(O)* isomers were selectively obtained. All isomers were characterized from their absorption and CD spectra in comparison with those of the three isomers of bis(*S*-methyl-L-cysteinato)cobalt(III) complex, [Co(L-smc)$_2$]$^+$,[10] and the configurations of the coordinated sulfur atoms of the isomers were suggested on the basis of the ^{1}H and ^{13}C NMR spectra. The CD spectral change due to the substitution of the *S*-alkyl group in the L-terdentate-*N,S,O* ligands was investigated for each of the three isomers of the bis type complexes. The CD spectral differences among the *trans(O)* isomers of the bis type, the *N,N*-bridge and the *S,S*-bridge complexes are discussed in relation to the configurations of the chiral sulfur donor atoms of the thioether ligands.

Experimental

Preparation of Ligands. *1)*: *S*-Ethyl-L-cysteine was prepared from L-cysteine and ethyl iodide according to the method of Frankel *et al.*[13] Found: C, 40.18; H, 7.39; N, 9.44%. Calcd for L-Hsec=$C_5H_{11}NO_2S$: C, 40.24; H, 7.43; N, 9.38%.

2): *N,N'*-Trimethylenebis(*S*-methyl-L-cysteine) was prepared by the same procedure as that for *N,N'*-ethylenebis(*S*-methyl-L-cysteine),[9] using 1,3-dibromopropane instead of 1,2-dibromoethane. Found: C, 39.29; H, 7.07; N, 8.37%. Calcd for L,L-H$_2$tbsmc·1.5H$_2$O=$C_{11}H_{22}N_2O_4S_2\cdot 1.5H_2O$: C, 39.15; H, 7.46; N, 8.30%.

3): *S,S'*-Ethylenebis(L-cysteine) was prepared from L-cysteine and 1,2-dibromoethane according to the method of Magee *et al.*[2] Found: C, 35.72; H, 5.96; N, 10.47%. Calcd for L,L-H$_2$ebc=$C_8H_{16}N_2O_4S_2$: C, 35.80; H, 6.01; N, 10.43%.

4): *S,S'*-Trimethylenebis(L-cysteine) was prepared by the same procedure as in 3), using 1,3-dibromopropane instead of 1,2-dibromoethane. Found: C, 38.04; H, 6.35; N, 9.73%. Calcd for L,L-H$_2$tbc=$C_9H_{18}N_2O_4S_2$: C, 38.28; H, 6.42; N, 9.92%.

Preparation of Complexes. *5) Bis*(S-*methyl*-L-*cysteinato*)*cobalt(III) Perchlorate*: [*Co*(L-*smc*)$_2$]*ClO*$_4$. This complex was prepared and separated into three geometrical isomers: *trans(S)*, *trans(N)*, and *trans(O)*, by the method described in a previous paper.[10]

6) Bis(S-*ethyl*-L-*cysteinato*)*cobalt(III) Bromide*: [*Co*(L-*sec*)$_2$]*Br*. This complex was prepared by the same procedure as that for [Co(L-smc)$_2$]ClO$_4$ described in 5), using L-Hsec instead of L-Hsmc. The reaction mixture was poured onto a column (3 cm×50 cm) containing Dowex 50W-X8 resin (200—400 mesh, NH$_4^+$ form). After sweeping the column with water, the adsorbed band was eluted with 0.3 mol dm^{-3} aqueous solution of NH$_4$Br. Three bands: violet (A-1), red (A-2), and blue-violet (A-3), were eluted in this order. Their absorption and CD spectra of the fractions showed that A-1 contained the *trans(S)* isomer, A-2 the *trans(O)* one, and A-3 the *trans(N)* one. The formation ratio of the isomers, *trans(S)* : *trans(O)* : *trans(N)*, was about 3 : 2 : 1. The three eluates were separately concentrated to a small volume in a rotary evaporator. The deposit, NH$_4$Br, was filtered off and to each of the filtrates was added a large amount of ethanol. The crude isomers, A-1, A-2, and A-3, were recrystallized from as little water as possible by cooling in an ice bath after adding an appropriate amount of ethanol. Found for *trans(S)* isomer (A-1): C, 27.57; H, 4.57; N, 6.59%. Found for *trans(O)* isomer (A-2): C, 27.33; H, 4.40; N, 6.60%. Calcd for $[Co(L\text{-sec})_2]Br=CoC_{10}H_{20}N_2O_4S_2Br$: C, 27.59; H, 4.63; N, 6.43%. Found for *trans(N)* isomer (A-3): C, 26.44; H, 4.84; N, 6.17%. Calcd for $[Co(L\text{-sec})_2]Br\cdot H_2O$: C, 26.50; H, 4.89; N, 6.18%.

*7) Bis(*S-*benzyl-*L-*cysteinato)cobalt(III) Chloride*: *[Co(*L*-sbc)*$_2$*]-Cl.* To a solution of L-Hsbc (5.0 g) in 400 cm^3 of hot water–ethanol (1 : 1.4) mixture were added a solution of $Co(CH_3COO)_2\cdot 4H_2O$ (4.0 g) in 60 cm^3 of water and lead dioxide (10 g). The mixture was stirred at 65 °C for 10 min, whereupon the solution became violet. The reaction mixture was cooled to room temperature and filtered to remove insoluble materials. The filtrate was concentrated to *ca.* 200 cm^3 in a rotary evaporator and then poured onto a column (4 cm × 100 cm) containing SP-Sephadex C-25 resin (Na^+ form). After sweeping the column with water, the adsorbed band was eluted with 0.03 mol dm^{-3} aqueous solution of NaCl. Three bands: red-violet (B-1), violet (B-2), and dark violet (B-3), were eluted in this order. The absorption and CD spectra of the fractions showed that B-1 contained the *trans(O)* isomer, B-2 the *trans(S)* one, and B-3 the *trans(N)* one. The formation ratio of the isomers, *trans(S)* : *trans(O)* : *trans(N)*, was about 6 : 3 : 1. The three eluates were separately concentrated to a small volume in a rotary evaporator. To each solution was added a large amount of ethanol. The deposit, NaCl, was filtered off and the filtrates were again separately concentrated almost to dryness in a rotary evaporator. The resultant crystals of the three isomers, B-1, B-2, and B-3, were collected by filtration and washed with acetone and ether, and then dried in a vacuum desiccator. Found for *trans(O)* isomer (B-1): C, 45.42; H, 4.63; N, 5.38%. Calcd for $[Co(L\text{-sbc})_2]Cl\cdot 0.5H_2O=CoC_{20}H_{24}N_2O_4S_2Cl\cdot 0.5H_2O$: C, 45.85; H, 4.81; N, 5.35%. Found for *trans(S)* isomer (B-2): C, 40.07; H, 4.46; N, 5.02%. Calcd for $[Co(L\text{-sbc})_2]Cl\cdot H_2O\cdot NaCl$: C, 40.62; H, 4.43; N, 4.74%. Found for *trans(N)* isomer (B-3): C, 44.03; H, 4.90; N, 5.24%. Calcd for $[Co(L\text{-sbc})_2]Cl\cdot 1.5H_2O$: C, 44.32; H, 5.02; N, 5.17%.

8) N,N′-*Ethylenebis(*S-*methyl-*L-*cysteinato)cobalt(III) Perchlorate*: *[Co(*L,L*-ebsmc)]ClO*$_4$. This complex was prepared by the method described in a previous paper,[9] and only *trans(O)* isomer was isolated.

9) N,N′-*Trimethylenebis(*S-*methyl-*L-*cysteinato)cobalt(III) Perchlorate*: *[Co(*L,L*-tbsmc)]ClO*$_4$. This complex was prepared by the same procedure as that for $[Co(L,L\text{-ebsmc})]ClO_4$ described in 8), using L,L-H_2tbsmc instead of L,L-H_2ebsmc. The reaction mixture was filtered to remove the excess of lead dioxide. The filtrate was poured onto a column (3 cm × 35 cm) containing Dowex 50W-X8 resin (200—400 mesh, Na^+ form). After sweeping the column with water, the adsorbed band was eluted with 0.2 mol dm^{-3} aqueous solution of $NaClO_4$. Two bands, pink-violet and violet, were eluted in this order. It was found, from their absorption and CD spectra of the fractions, that the earlier eluate contained the *trans(S)* isomer and the later eluate the *trans(O)* one. The formation ratio of the isomers, *trans(S)* : *trans(O)*, was about 3 : 7. The two eluates were separately concentrated to a small volume in a rotary evaporator below 30 °C and the deposit, NaCl, was filtered off. To each of the filtrates was added an appropriate amount of ethanol and then kept in a refrigerator. Dark-red crystals appeared for each of the filtrates. The absorption and CD spectra showed that both crystals were *trans(O)* isomer. Namely, the *trans(S)* isomer in the earlier eluate isomerized to the *trans(O)* one during the procedure after elution. Found: C, 27.54; H, 4.35; N, 5.87%. Calcd for $[Co(L,L\text{-tbsmc})]ClO_4\cdot H_2O=CoC_{11}H_{20}N_2O_8S_2Cl\cdot H_2O$: C, 27.25; H, 4.57; N, 5.78%.

10) N,N′-*Ethylenebis(*L-*methioninato)cobalt(III) Perchloride*: *[Co(*L,L*-ebm)]ClO*$_4$. This complex was prepared and isolated by the same procedure as that for $[Co(L,L\text{-ebsmc})]ClO_4$ described in 8), using L,L-H_2ebm.[2] The only isomer obtained showed the identical absorption and CD spectra with those of *trans(O)*-$[Co(L,L\text{-ebm})]^+$ prepared by Magee *et al.*[2] Found: C, 29.64; H, 4.63; N, 5.70%. Calcd for $[Co(L,L\text{-ebm})]ClO_4=CoC_{12}H_{22}N_2O_8S_2Cl$: C, 29.98; H, 4.61; N, 5.83%.

11) S,S′-*Ethylenebis(*L-*cysteinato)cobalt(III) Chloride and Nitrate*: *[Co(*L,L*-ebc)]X*; $X^-=Cl^-$, NO_3^-. A suspension of L,L-H_2ebc (4.1 g) in 250 cm^3 of water was adjusted to pH 8 by the addition of an aqueous solution of NaOH (1 mol dm^{-3}). To this were added a solution of $CoCl_2\cdot 6H_2O$ (4.1 g) in 50 cm^3 of water and lead dioxide (10 g). The mixture was stirred at 60 °C for 20 min, whereupon the solution became purple. The reaction mixture was cooled to room temperature and filtered to remove insoluble materials. The filtrate was poured onto a column (4 cm × 60 cm) containing SP-Sephadex C-25 resin (Na^+ form). After sweeping the column with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} aqueous solution of NaCl. Only one purple band was eluted and fractionated. The absorption and CD spectra of the fractions showed that the eluate contained only *trans(O)* isomer. The eluate was concentrated to a small volume in a rotary evaporator and the deposit, NaCl, was filtered off. To the filtrate was added an appropriate amount of ethanol and then ether. The resultant violet complex was recrystallized from water by adding ethanol. Found: C, 24.90; H, 4.31; N, 7.51%. Calcd for $[Co(L,L\text{-ebc})]Cl\cdot H_2O=CoC_8H_{14}N_2O_4S_2Cl\cdot H_2O$: C, 25.37; H, 4.27; N, 7.40%. This chloride salt was converted to the nitrate salt by use of an anion-exchange column containing QAE-Sephadex A-25 resin (NO_3^- form). The nitrate salt showed the identical absorption and CD spectra to those of the chloride salt. Found: C, 23.26; H, 3.97; N, 10.28%. Calcd for $[Co(L,L\text{-ebc})]NO_3\cdot H_2O=CoC_8H_{14}N_3O_7S_2\cdot H_2O$: C, 23.71; H, 3.98; N, 10.37%.

12) S,S′-*Trimethylenebis(*L-*cysteinato)cobalt(III) Chloride and Nitrate*: *[Co(*L,L*-tbc)]X*; $X^-=Cl^-$, NO_3^-. This complex was prepared by the same procedure as that for $[Co(L,L\text{-ebc})]X$ described in 11), using L,L-H_2tbc instead of L,L-H_2ebc. The absorption and CD spectra of the chloride and nitrate salts were identical. Found for chloride salt: C, 26.31; H, 4.80; N, 6.42%. Calcd for $[Co(L,L\text{-tbc})]Cl\cdot 2H_2O=CoC_9H_{16}N_2O_4S_2Cl\cdot 2H_2O$: C, 26.31; H, 4.92; N, 6.82%. Found for nitrate salt: C, 25.18; H, 4.43; N, 9.92%. Calcd for $[Co(L,L\text{-tbc})]NO_3\cdot 1.5H_2O=CoC_9H_{16}N_3O_7S_2\cdot 1.5H_2O$: C, 25.24; H, 4.47; N, 9.81%.

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 aqueous solution at room temperature.

The ^{1}H and ^{13}C 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.

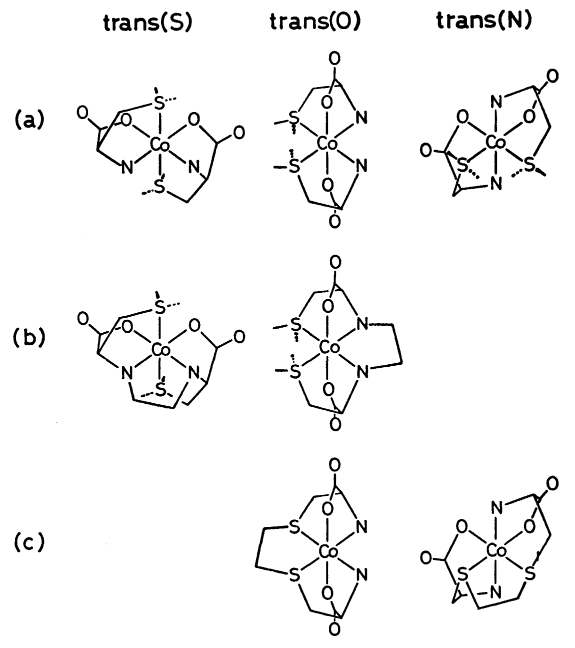

Fig. 1. The possible geometrical isomers of [Co(L-sec)$_2$]$^+$ and [Co(L-sbc)$_2$]$^+$ (a), [Co(L,L-ebsmc)]$^+$ (b), and [Co(L,L-ebc)]$^+$ (c).

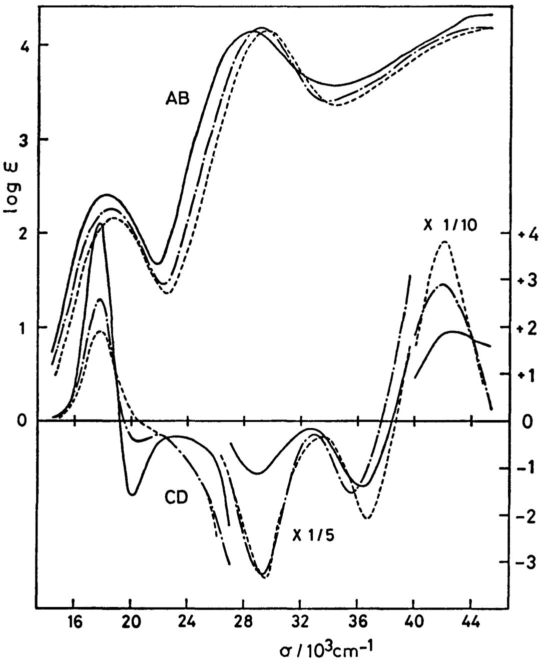

Fig. 2. Absorption and CD spectra of *trans(S)* isomers: [Co(L-sbc)$_2$]$^+$ (——), [Co(L-sec)$_2$]$^+$ (—·—·—), and [Co(L-smc)$_2$]$^+$ (-----).

Results and Discussion

*Structural Assignments. Bis(*L*-terdentate-*N,S,O*) Type Complexes*: For the [Co(L-sec)$_2$]$^+$ and [Co(L-sbc)$_2$]$^+$ complexes which belong to a [Co(N)$_2$(S)$_2$(O)$_2$] type, three geometrical isomers, *trans(S)*, *trans(N)*, and *trans(O)*, are possible (Fig. 1(a)). Their absorption and CD spectra are shown in Figs. 2—4, together with those of the [Co(L-smc)$_2$]$^+$ isomers; the data are summarized in Tables 1 and 2. Splitting patterns of the first absorption bands and maximum positions of the sulfur-to-metal charge transfer bands of the present isomers correspond well with those of the three isomers of [Co(L-smc)$_2$]$^+$.[10] Their CD spectral behavior could be classified into CD patterns of the three L-smc isomers (Figs. 2—4). Accordingly, A-1 and B-2 isomers can be assigned confidently as *trans(S)*, A-2 and B-1 isomers as *trans(O)*, and A-3 and B-3 isomers as *trans(N)*. The formation of the three geometrical isomers de-

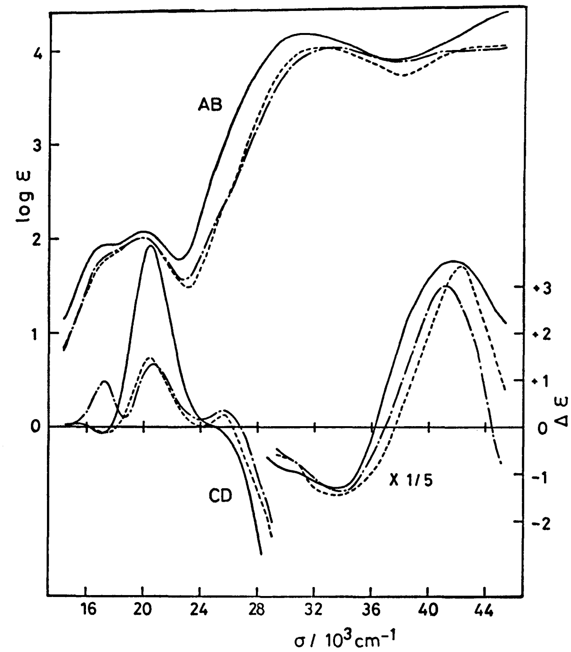

Fig. 3. Absorption and CD spectra of *trans(N)* isomers: [Co(L-sbc)$_2$]$^+$ (——), [Co(L-sec)$_2$]$^+$ (—·—·—), and [Co(L-smc)$_2$]$^+$ (-----).

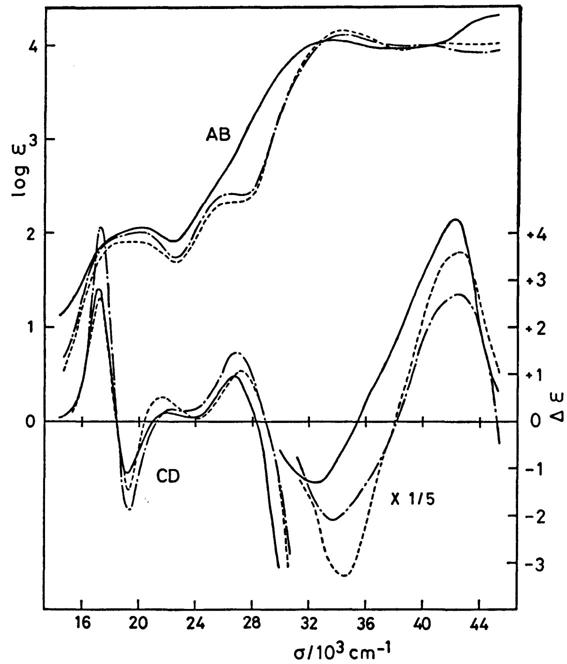

Fig. 4. Absorption and CD spectra of *trans(O)* isomers: [Co(L-sbc)$_2$]$^+$ (——), [Co(L-sec)$_2$]$^+$ (—·—·—), and [Co(L-smc)$_2$]$^+$ (-----).

TABLE 1. ABSORPTION DATA OF [Co(terdentate-*N*,*S*,*O*)$_2$] AND [Co(sexidentate-*N*$_2$,*S*$_2$,*O*$_2$] TYPE COMPLEXES

Complex	First band	Second band	Charge transfer band
trans(*S*)-[Co(L-smc)$_2$]$^+$ a)	18.73 (2.18)		29.47 (4.16)
trans(*N*)-[Co(L-smc)$_2$]$^+$ a)	17.5 (1.81 sh) 19.87 (2.01)		32.13 (4.03)
trans(*O*)-[Co(L-smc)$_2$]$^+$ a)	19.40 (1.93)	26.48 (2.34)	34.47 (4.16)
trans(*S*)-[Co(L-sec)$_2$]$^+$	18.42 (2.22)		29.15 (4.17)
trans(*N*)-[Co(L-sec)$_2$]$^+$	17.7 (1.85 sh) 19.88 (2.01)		33.00 (4.03)
trans(*O*)-[Co(L-sec)$_2$]$^+$	18.0 (1.92 sh) 20.00 (2.01)	26.39 (2.42)	34.60 (4.11)
trans(*S*)-[Co(L-sbc)$_2$]$^+$	18.25 (2.41)		28.41 (4.16)
trans(*N*)-[Co(L-sbc)$_2$]$^+$	17.2 (1.93 sh) 19.96 (2.07)		31.06 (4.18)
trans(*O*)-[Co(L-sbc)$_2$]$^+$	18.2 (1.96 sh) 20.20 (2.05)		33.67 (4.05)
trans(*O*)-[Co(L,L-ebsmc)]$^+$ b)	18.4 (2.10 sh) 20.83 (2.37)	26.7 (2.49 sh)	34.01 (4.07)
trans(*O*)-[Co(L,L-tbsmc)]$^+$	18.69 (1.97) 20.0 (1.94 sh)	26.0 (2.48 sh)	33.61 (4.09)
trans(*O*)-[Co(L,L-ebc)]$^+$	17.61 (2.48)	27.9 (2.27 sh)	35.21 (4.06)
trans(*O*)-[Co(L,L-tbc)]$^+$	17.76 (2.29)		32.3 (3.86 sh) 35.59 (4.08)

a) Ref. 10. b) 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.

creases with the order of *trans(S)*, *trans(O)*, and *trans(N)* for both of [Co(L-sec)$_2$]$^+$ and [Co(L-sbc)$_2$]$^+$. This order runs parallel to the crowdedness of the *S*-alkyl groups of the ligands in each isomer.

Another type of three isomers arising from the chiralities of the coordinated sulfur atoms of the ligands, *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*), are possible for each of the three geometrical isomers. The ^{1}H NMR spectrum of the *trans(S)* L-sec isomer exhibits only one set of triplet peaks in the methyl proton region (1.48 ppm from DSS), while the spectra of the *trans(O)* and *trans(N)* L-sec isomers show two sets of triplet peaks, respectively (1.39 and 1.52 ppm for the *trans(O)*, and 1.39 and 1.43 ppm for the *trans(N)*). The *trans(S)* L-sbc isomer shows a single peak due to the aromatic protons (7.36 ppm), while the *trans(O)* and *trans(N)* isomers show a peak with a shoulder at the higher magnetic field (7.44 ppm for the *trans(O)* and 7.43 ppm for the *trans(N)*). Furthermore, the ^{13}C NMR spectrum of the *trans(S)* isomer shows four peaks due to the aromatic carbons (128.4, 129.9, 130.5 and 139.6 ppm), while the *trans(O)* and *trans(N)* isomers show multiple peaks in the corresponding region. These NMR spectral behaviors of the L-sec and L-sbc isomers are quite similar to those of the three isomers of [Co(L-smc)$_2$]$^+$.[10] Inspection of models suggests that the *trans(S)* isomers take the *S*(*S*),*S*(*S*) configuration, the *trans(N)* isomers a mixture of *R*(*S*),*S*(*S*) and *S*(*S*),*S*(*S*) ones, and the *trans(O)* isomers a mixture of *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*) ones, as in the case of the three isomers of the L-smc complex.[10]

N,N- *and* S,S-*Bridge(*L,L-*sexidentate*-N$_2$,S$_2$,O$_2$*) Type Complexes*: The possible geometrical isomers for [Co(L,L-ebsmc)]$^+$ [9] and [Co(L,L-tbsmc)]$^+$ are limited to two: *trans(S)* and *trans(O)*, because the two nitrogen donor atoms of the ligands were bridged by ethylene (L,L-ebsmc) and trimethylene (L,L-tbsmc) (Fig. 1(b)). Of the two isomers, only the *trans(O)* isomer was selectively formed and isolated for the L,L-ebsmc complex.[9] For the L,L-tbsmc complex, the *trans(S)* and *trans(O)* isomers were formed, but only the *trans(O)* isomer could be isolated, because the *trans(S)* L,L-tbsmc isomer isomerized to the *trans(O)* one during the procedure after elution. Two geometrical isomers, *trans(O)* and *trans(N)*, are possible for [Co(L,L-ebc)]$^+$ and [Co(L,L-tbc)]$^+$, where the two sulfur donor atoms of the ligands were bridged by ethylene (L,L-ebc) and trimethylene (L,L-tbc) (Fig. 1(c)). For each of the two *S*,*S*-bridge complexes, only the *trans(O)* isomer was selectively formed and isolated. The four isomers of the *N*,*N*- and *S*,*S*-bridge complexes which belong to a [Co(*N*)$_2$(*S*)$_2$(*O*)$_2$] type were assigned to *trans(O)* from the comparison of the absorption and CD spectra with the isomers of the bis type complexes mentioned above (Figs. 5 and 6 and Tables 1 and 2).

The *N*,*N*-bridge complexes, [Co(L,L-ebsmc)]$^+$ and [Co(L,L-tbsmc)]$^+$, have another chirality arising from the two nitrogen donor atoms. Of the two complexes, [Co(L,L-ebsmc)]$^+$ was confirmed to be *trans(O)*-*R*(*N*),*R*(*N*) isomer by the X-ray diffraction study.[9] Taking the rigid framework of the parental isomer, *trans*(*O*)-[Co(L-smc)$_2$]$^+$, into consideration, it is certain that the *trans(O)* L,L-tbsmc isomer prefers the *R*(*N*),*R*(*N*) configuration. The ^{1}H NMR spectrum of the *trans(O)* L,L-ebsmc isomer indicated that the two sulfur donor atoms took a mixture of *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*) configurations,[9] as in the case of *trans(O)*-[Co(L-smc)$_2$]$^+$. The ^{1}H NMR spectrum of the *trans(O)* L,L-tbsmc isomer shows multiple peaks in the *S*-methyl proton region, suggesting that the

Table 2. CD data of [Co(terdentate-*N*,*S*,*O*)$_2$] and [Co(sexidentate-*N*$_2$,*S*$_2$,O$_2$)] type complexes

Complex	First band region	Second band region	Charge transfer band region
trans(*S*)-[Co(L-smc)$_2$]$^+$ [a]	17.87 (+1.92)		29.63 (−16.5) 36.80 (−11.1) 42.27 (+40.1)
trans(*N*)-[Co(L-smc)$_2$]$^+$ [a]	15.47 (+0.06) 17.33 (−0.11) 20.43 (+1.44)	25.60 (+0.23)	33.54 (−7.8) 42.27 (+17.3)
trans(*O*)-[Co(L-smc)$_2$]$^+$ [a]	17.23 (+2.70) 19.25 (−1.44) 21.60 (+0.57)	27.20 (+1.08)	34.47 (−18.3) 42.80 (+18.3)
trans(*S*)-[Co(L-sec)$_2$]$^+$	17.70 (+2.59) 20.53 (−0.44)		29.41 (−16.4) 35.71 (−7.6) 41.32 (+28.9)
trans(*N*)-[Co(L-sec)$_2$]$^+$	17.21 (+0.98) 20.70 (+1.34)	25.64 (+0.35)	33.90 (−6.8) 41.15 (+14.8)
trans(*O*)-Co(L-sec)$_2$]$^+$	17.18 (+4.16) 19.38 (−1.91) 22.22 (+0.23)	26.95 (+1.47)	33.67 (−10.6) 42.55 (+13.4)
trans(*S*)-[Co(L-sbc)$_2$]$^+$	18.32 (+4.21) 20.08 (−1.24)		28.82 (−5.6) 36.23 (−7.0) 42.19 (+18.9)
trans(*N*)-[Co(L-sbc)$_2$]$^+$	15.27 (+0.08) 17.04 (−0.35) 20.37 (+3.88)		33.33 (−6.5) 41.67 (+17.9)
trans(*O*)-[Co(L-sbc)$_2$]$^+$	17.12 (+2.84) 19.18 (−1.10) 21.98 (+0.19)	26.67 (+1.00)	32.68 (−6.4) 42.37 (+21.5)
trans(*O*)-[Co(L,L-ebsmc)]$^+$ [b]	17.33 (+2.82) 19.27 (−2.68) 21.93 (+1.38)	24.57 (−0.17) 27.47 (+2.64)	33.67 (−10.8) 43.48 (+19.2)
trans(*O*)-[Co(L,L-tbsmc)]$^+$	16.78 (+2.09) 18.62 (−2.79) 21.28 (+0.29)	23.52 (−0.02) 26.04 (+0.63)	33.30 (−10.8) 42.60 (+29.9)
trans(*O*)-[Co(L,L-ebc)]$^+$	17.76 (+10.26) 20.45 (−6.59)	27.93 (+6.80)	32.00 (+6.9) 35.71 (−29.3) 40.32 (+21.3)
trans(*O*)-[Co(L,L-tbc)]$^+$	17.79 (+8.66) 20.28 (−5.29)		31.35 (+19.7) 35.37 (−30.6) 40.00 (+10.2)

a) Ref. 10. b) Ref. 9. Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in $10^3\,\text{cm}^{-1}$ and $\text{dm}^3\,\text{cm}^{-1}$, respectively. Sh denotes a shoulder.

chiral sulfur atoms take a mixture of *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*) configurations, like the *trans-(O)* L,L-tbsmc isomer does.

For each of the two *S*,*S*-bridge isomers, *trans(O)*-[Co(L,L-ebc)]$^+$ and *trans(O)*-[Co(L,L-tbc)]$^+$, the possible configurations of the sulfur donor atoms are limited to two: *R*(*S*),*R*(*S*) (C_2 symmetry) and *R*(*S*),*S*(*S*) (C_1 symmetry) for the L,L-ebc isomer, and *S*(*S*),*S*(*S*) (C_2 symmetry) and *R*(*S*),*S*(*S*) (C_1 symmetry) for the L,L-tbc isomer. As shown in Fig. 7(a), the ^{13}C NMR spectrum of the *trans(O)* L,L-ebc isomer shows four peaks for the eight carbons of the ligand. This means that the L,L-ebc isomer takes the *R*(*S*),*R*(*S*) configuration having C_2 symmetry, where the backbone five-membered chelate ring takes an asymmetric gauche form with δ conformation. Similarly, the *trans(O)* L,L-tbc isomer takes *S*(*S*),*S*(*S*) configuration having a skew-boat form with δ conformation for the backbone six-membered chelate ring, because the ^{13}C NMR spectrum shows five peaks for the nine carbons of the ligand (C_2 symmetry) (Fig. 7(b)).

Absorption and CD Spectra. As shown in Figs. 2—4, the absorption spectra in each group of the three geometrical isomers of the bis L-smc, L-sec, and L-sbc complexes are similar to each other except that the sulfur-to-metal charge transfer bands of the L-sbc isomers shift to somewhat lower energies in comparison with those of the L-smc and L-sec isomers. The overall CD pattern is similar in each group. However, some notable differences due to the substitution of the *S*-alkyl group can be observed in more minute detail. In the first absorption band region, the *trans(S)*-

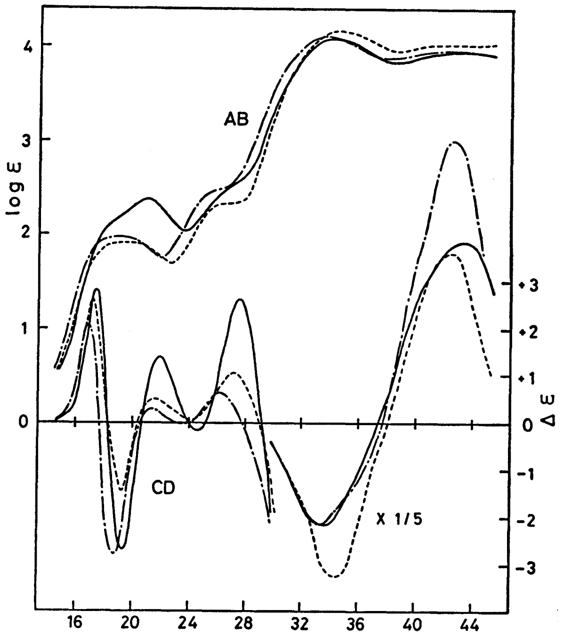

Fig. 5. Absorption and CD spectra of *trans(O)* isomers: [Co(L,L-ebsmc)]$^+$ (——), [Co(L,L-tbsmc)]$^+$ (—·—·—), and [Co(L-smc)$_2$]$^+$ (-----).

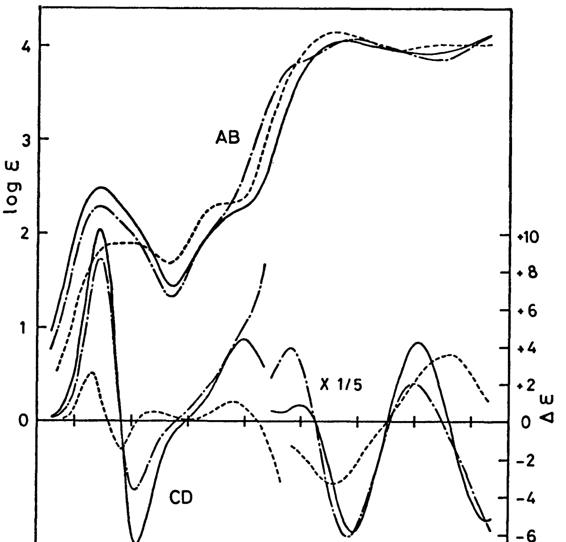

Fig. 6. Absorption and CD spectra of *trans(O)* isomers: [Co(L,L-ebc)]$^+$ (——), [Co(L,L-tbc)]$^+$ (—·—·—), and [Co(L-smc)$_2$]$^+$ (-----).

S(S),S(S) isomers commonly show a positive CD band (at *ca.* 18.0×10^3 cm^{-1}) whose intensity decreases with the order of the L-sbc, L-sec, and L-smc isomers, and a negative band at higher energy disappears in the L-smc isomer (Fig. 2). The *trans(N)* isomers assigned to the mixture of *R(S),S(S)* and *S(S),S(S)* configurations commonly show a positive CD band at 20.5×10^3 cm^{-1}. The L-smc and L-sbc isomers show two additional weak CD bands ((+) and (−) from lower energy), while the L-sec isomer shows one positive band

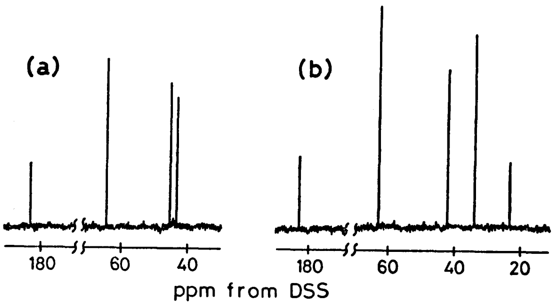

Fig. 7. ^{13}C NMR spectra of *trans(O)*-[Co(L,L-ebc)]$^+$ (a) and *trans(O)*-[Co(L,L-tbc)]$^+$ (b).

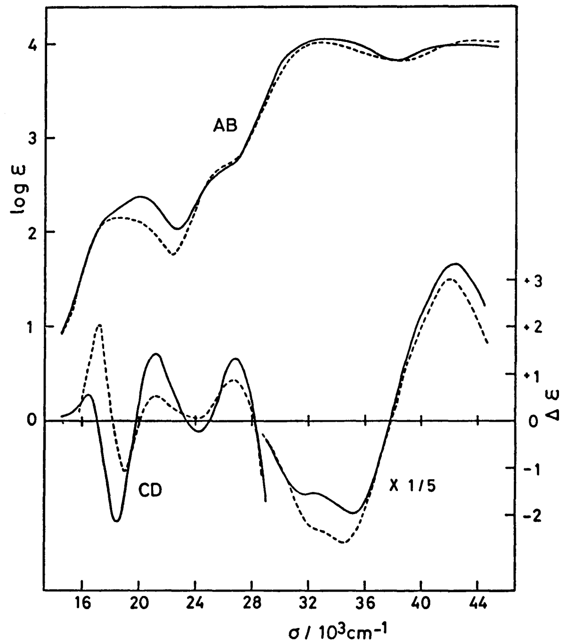

Fig. 8. Absorption and CD spectra of *trans(O)* isomers: [Co(L,L-ebm)]$^+$ (——) and [Co(L-met)$_2$]$^+$ (-----).

in the corresponding region (Fig. 3). In contrast to the *trans(S)* and *trans(N)* isomers, the *trans(O)* isomers assigned to the mixture of *R(S),R(S)*, *R(S),S(S)*, and *S(S),S(S)* configurations show quite similar CD spectral behavior in the whole region, with no significant differences. This good agreement in CD spectra seems to suggest that the CD contribution due to the coordinated sulfur atoms in the *trans(O)* isomers was almost cancelled out because of the mixture of *R(S),R(S)*, *R(S),S(S)*, and *S(S),S(S)* configurations.

The absorption and CD spectra of the *N,N*-bridge complexes are shown in Fig. 5, together with those of *trans(O)*-[Co(L-smc)$_2$]$^+$. The *trans(O)* L,L-ebsmc and L,L-tbsmc isomers show a CD pattern quite similar to that of *trans(O)*-[Co(L-smc)$_2$]$^+$ in the whole region, though the former two have an additional chilarity, *R(N),R(N)*, due to the bridged nitrogen donor atoms of the ligands. This result suggests that the CD contribution due to the chiral nitrogen atoms of the *N,N*-bridge *trans(O)* isomers is inconspicuous except for some increase in CD intensity. This trend is also valid for the CD spectra of *trans(O)*-[Co(L-met)$_2$]$^+$ [1] and *trans(O)*-[Co(L,L-ebm)]$^+$, where the two nitrogen donor atoms were bridged by ethylene (Fig. 8), though two conformations, chair and skew-boat, are probable for the six-membered N–S ring of the coordinated L-met. A similar CD spectral behavior was observed for a series of *cis*-[Co(ida)$_2$]$^-$, [Co(edta)]$^-$, and [Co(1,3-pdta)]$^-$.[14] In contrast to the *N*,*N*-bridge isomers, the CD spectral behaviors of the *S*,*S*-bridge *trans(O)* isomers differ significantly from that of *trans(O)*-[Co(L-smc)$_2$]$^+$ (Fig. 6 and Table 2). In the first absorption band region, the CD spectra of the *trans(O)* L,L-ebc and L,L-tbc isomers are remarkedly intensified in comparison with that of *trans(O)*-[Co(L-smc)$_2$]$^+$. Of the three CD bands in the first absorption band region of *trans-(O)*-[Co(L-smc)$_2$]$^+$, the two CD bands in the higher energy side change to one negative band, though the positive band at the lowest energy side remains unchanged. A remarkable deviation in absorption and CD spectra from *trans(O)*-[Co(L-smc)$_2$]$^+$ are observed in the region of (28—38)$\times 10^3$ cm^{-1}. Especially, it is noteworthy that the *trans(O)* L,L-tbc isomer shows another intense absorption component (at *ca.* 32.3$\times 10^3$ cm^{-1}) in addition to the charge transfer band (at 35.59$\times 10^3$ cm^{-1}) which commonly appears for the other *trans(O)* isomers. In this absorption band region, a new positive CD band appears for each of the two *S*,*S*-bridge isomers, namely, $\Delta\varepsilon = +19.7$ at 31.35$\times 10^3$ cm^{-1} for the L,L-tbc isomer and $\Delta\varepsilon = +6.9$ at 32.00$\times 10^3$ cm^{-1} for the L,L-ebc one. This positive CD band for the L,L-ebc isomer suggests that the isomer also has an absorption component in the corresponding region, as in the L,L-tbc isomer. This absorption component seems to arise from the splitting of the multiple thioether charge transfer band.[15] The appearance of the new positive CD band (at *ca.* 31.5$\times 10^3$ cm^{-1}) for the two *S*,*S*-bridge isomers suggests that *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*) configurations in the *trans(O)*-[Co(L-smc)$_2$]$^+$ were unified to only one configuration (*R*(*S*),*R*(*S*) for the *trans(O)* L,L-ebc isomer and *S*(*S*),*S*(*S*) for the L,L-tbc one) by bridging the sulfur atoms of the two cysteinates.

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