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Preparation and Spectral Properties of Cobalt(III) Complexes with *S,S'*-Ethylenebis(L-homocysteinate) and *S,S'*-Trimethylenebis(L-homocysteinate)

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Three cobalt(III) complexes of [Co(sexidentate-N_2,S_2,O_2)] and [Co(terdentate-N,S,O)$_2$] types were prepared; where sexidentate-N_2,S_2,O_2 denotes *S,S'*-ethylenebis(L-homocysteinate) (L,L-ebhc) and *S,S'*-trimethylenebis(L-homocysteinate) (L,L-tbhc), and terdentate-*N,S,O* denotes L-ethioninate (L-eth). Each of the L,L-ebhc and L,L-tbhc complexes was chromatographically separated into two isomers, *trans(O)* and *trans(N)*, and the L-eth complex was separated into three isomers, *trans(O)*, *trans(N)*, and *trans(S)*. These isomers were characterized by their electronic absorption, CD, and ^{13}C NMR spectra. The stereoselectivity in the formation of each geometrical isomer for the L,L-ebhc and L,L-tbhc complexes is discussed in relation to the flexibilities of the *S,S*-bridged backbone chelate ring and the L-homocysteinate moiety.

Cobalt(III) complexes with sexidentate-N_2,S_2,O_2 ligands such as *S,S'*-ethylenebis(L-cysteinate) (L,L-ebc), *S,S'*-trimethylenebis(L-cysteinate) (L,L-tbc), *N,N'*-ethylenebis(*S*-methyl-L-cysteinate) (L,L-ebsmc), *N,N'*-trimethylenebis(*S*-methyl-L-cysteinate) (L,L-tbsmc), and *N,N'*-ethylenebis(L-methioninate) (L,L-ebm) exhibit an extreme *trans(O)* selectivity concerning the formation of the geometrical isomers,[1—3] where the expectant isomers are *trans(O)* and *trans(N)* for the *S,S*-bridge complexes, and *trans(O)* and *trans(S)* for the *N,N*-bridge ones.[4] Of these complexes the *N,N*-bridge L,L-tbsmc one revealed the formation of the *trans(S)* isomer which isomerized rapidly to the *trans(O)* one.[1] This stereoselective behavior seems to relate not only to the flexibility of the bridged ethylene or trimethylene backbone chelate ring of the sexidentate-N_2,S_2,O_2 ligand but also to that of the L-cysteinate or L-homocysteinate moiety of the ligand. The present work was undertaken in continuation of the previous work[1] in order to investigate the stereoselectivity in the formation of the geometrical isomers.

In the present paper, the cobalt(III) complexes with sexidentate-N_2,S_2,O_2 ligands, *S,S'*-ethylenebis(L-homocysteinate) (L,L-ebhc) and *S,S'*-trimethylenebis(L-homocysteinate) (L,L-tbhc), [Co(L,L-ebhc)]$^+$ and [Co(L,L-tbhc)]$^+$, were prepared and chromatographically separated into two geometrical isomers, *trans(O)* and *trans(N)*, respectively. All isomers were characterized by their electronic absorption, CD, and ^{13}C NMR spectra, and their stereochemical and spectrochemical features are discussed. Bis(L-ethioninato)cobalt(III) complex, [Co(L-eth)$_2$]$^+$, which corresponds to the non-bridge type of the above *S,S*-bridge complexes, was also prepared and separated into the *trans(O)*, *trans(N)*, and *trans(S)* isomers. Their spectral behaviors are compared with those of the three isomers of [Co(L-met)$_2$]$^+$ [5] in order to investigate the influence due to the change of the substituent on the sulfur donor atom in the L-terdentate-*N,S,O* ligand.

Experimental

Preparation of Ligands. **1)** *S,S'*-Ethylenebis(L-homocysteine) was prepared by a procedure modified from that used for the preparation of *S*-(carboxymethyl)-L-homocysteinate,[6,7] using 1,2-dibromoethane instead of chloroacetic acid. L-Methionine (30 g) and 1,2-dibromoethane (8.6 cm^3) were dissolved in 400 cm^3 of concentrated hydrochloric acid and the solution was refluxed for 24 h. The solution was concentrated with a rotary evaporator until it became syrupy and then neutralized with 28% aqueous ammonia. The resultant crystalline product was filtered, washed well with water, and dried in a vacuum desiccator. Yield; 9.5 g (32%). Found: C, 40.28; H, 6.80; N, 9.42%. Calcd for L,L-H_2ebhc=$C_{10}H_{20}N_2O_4S_2$: C, 40.28; H, 6.76; N, 9.39%.

2) *S,S'*-Trimethylenebis(L-homocysteine) was prepared by the same procedure as in **1)**, using 1,3-dibromopropane instead of 1,2-dibromoethane. Found: C, 30.68; H, 8.08; N, 6.40%. Calcd for L,L-H_2tbhc·6.5H_2O=$C_{11}H_{35}N_2O_{10.5}S_2$: C, 30.90; H, 8.26; N, 6.55%.

Preparation of Complexes. **3) [*S,S'*-Ethylenebis(L-homocysteinato)]cobalt(III) Bromide and Perchlorate: [Co(L,L-ebhc)]X; X=Br$^-$ and ClO$_4^-$.** A suspension containing 4.0 g of L,L-H_2ebhc in 50 cm^3 of water was adjusted to pH 9 with a 1 mol dm^{-3} aqueous solution of NaOH. To this were added a solution containing 4.0 g of $CoCl_2 \cdot 6H_2O$ in 10 cm^3 of water, 2.0 g of PbO_2, and 0.2 g of activated charcoal. The mixture was stirred at ca. 60 °C for 30 min and then filtered. The filtrate was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 5 cm×43 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} aqueous solution of KBr. Two colored bands, brown (A-1) and violet (A-2), were eluted in this order. It was found from the absorption and CD spectral measurements that the eluates A-1 and A-2 contained *trans(N)*- and *trans(O)*-[Co(L,L-ebhc)]$^+$, respectively. The formation ratio of the isomers, *trans(N)*:*trans(O)*, was about 1:1. Each of the eluates A-1 and A-2 was concentrated to a small volume with a rotary evaporator below 25 °C and the deposited KBr was filtered off. Each filtrate was passed through a column of Sephadex G-10 (3 cm×53 cm), and eluted with water in order to eliminate KBr. Each eluate was concentrated to a small volume. To the eluate A-1 was added a small amount of ethanol and the solution was kept in a refrigerator for several days. The resultant violet crystals were collected by filtration. To the eluate A-2 an excess amount of aqueous solution of $NaClO_4$ was added and then a small amount of acetone. The solution was kept in a refrigerator for 4 d. The brown crystals which appeared were collected by filtration and obtained as perchlorate salt. Found for A-1: C, 22.74; H, 4.32; N, 5.36%. Calcd for $[Co(L,L\text{-ebhc})]Br \cdot 0.4KBr \cdot 2.5H_2O = CoC_{10}H_{18}N_2O_4S_2Br \cdot 0.4KBr \cdot 2.5H_2O$: C, 22.84; H, 4.41; N, 5.33%. Found for A-2: C, 25.49; H, 4.29; N, 5.94%. Calcd for $[Co(L,L\text{-ebhc})]ClO_4 \cdot H_2O$: C, 25.51; H, 4.28; N, 5.95%.

4) **[*S,S′*-Trimethylenebis(L-homocysteinato)]cobalt(III) Perchlorate: [Co(L,L-tbhc)]ClO₄.** This complex was prepared and chromatographed by the same procedure as in **3**), using L,L-H_2tbhc instead of L,L-H_2ebhc. Two colored bands, brown (B-1) and violet (B-2), were eluted in this order. It was found from the absorption and CD spectral measurements that the eluates B-1 and B-2 contained *trans(N)*- and *trans(O)*-$[Co(L,L\text{-tbhc})]^+$, respectively. The formation ratio of the isomers, *trans(N)* and *trans(O)*, was about 1:14. The B-1 isomer could not be isolated as a solid, because the fast-moving band (B-1) contained a very small amount. Therefore, the concentration of the B-1 isomer was measured by a plasma emission spectral analysis. The eluate B-2 was converted into the perchlorate salt by use of an anion-exchange column (ClO_4^- form). Found for B-2: C, 26.46; H, 4.53; N, 5.59%. Calcd for $[Co(L,L\text{-tbhc})]ClO_4 \cdot 1.5H_2O = CoC_{11}H_{20}N_2O_8S_2Cl \cdot 1.5H_2O$: C, 26.75; H, 4.70; N, 5.67%.

5) **Bis(L-ethioninato)cobalt(III) Bromide: [Co(L-eth)₂]Br.** This complex was prepared by the same procedure as that used for $[Co(L\text{-met})_2]Br$,[5] using L-Heth instead of L-Hmet. The reaction mixture was poured onto a column of Dowex 50W-X8 (200—400 mesh, NH_4^+ form, 3.5 cm×40 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} aqueous solution of NH_4Br. Three colored bands, dark-red (C-1), brown-red (C-2), and red-violet (C-3), were eluted in this order. The eluates C-1, C-2, and C-3 contained *trans(S)*-, *trans(N)*-, and *trans-(O)*-$[Co(L\text{-eth})_2]^+$, respectively. Each of the three eluates was separately concentrated with a rotary evaporator below 30 °C. The deposited NH_4Br was filtered off and a large amount of ethanol was added to the filtrate. The crude isomers, C-1, C-2, and C-3, were recrystallized from as little water as possible by adding ethanol, respectively. Found for C-1:

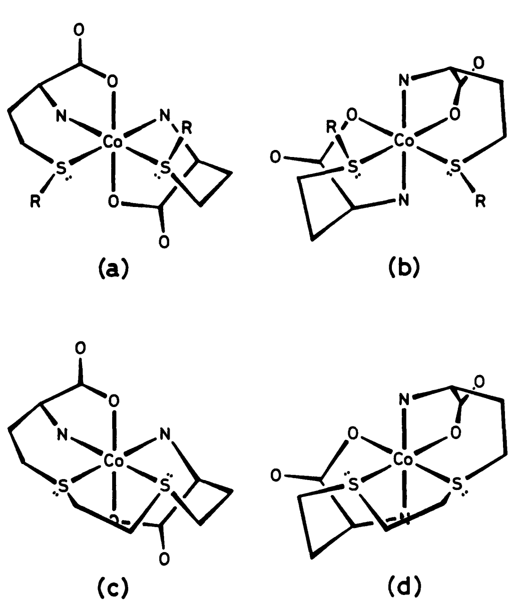

Fig. 1. Probable configurations of *trans*(*O*) and *trans*(*N*) for $[Co(L\text{-eth})_2]^+$ ($R = C_2H_5$): (a) *trans*(*O*)-*R*(*S*),*R*(*S*) and (b) *trans*(*N*)-*S*(*S*),*S*(*S*), and for $[Co(L,L\text{-ebhc})]^+$: (c) *trans*(*O*)-*R*(*S*),*R*(*S*) and (d) *trans*(*N*)-*S*(*S*),*S*(*S*).

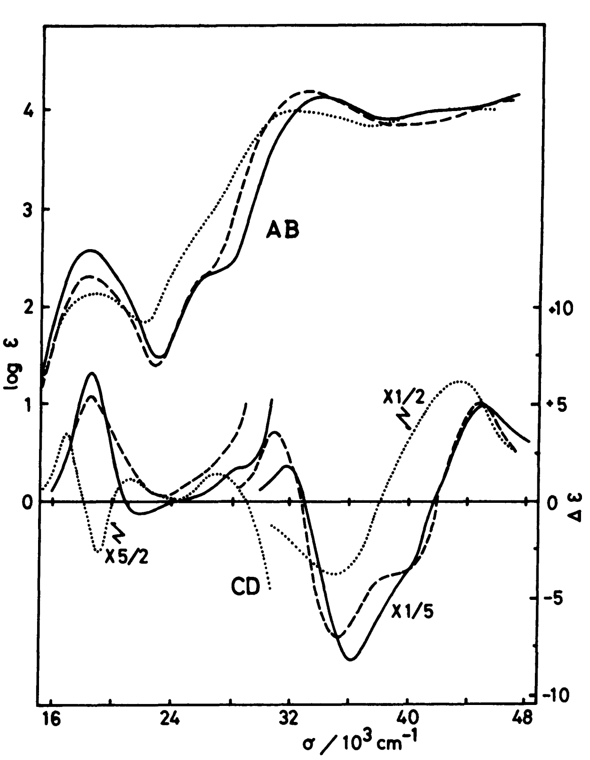

Fig. 2. Absorption and CD spectra of the *trans*(*O*) isomer for $[Co(L,L\text{-ebhc})]^+$ (——), $[Co(L,L\text{-tbhc})]^+$ (-----), and $[Co(L\text{-eth})_2]^+$ (······).

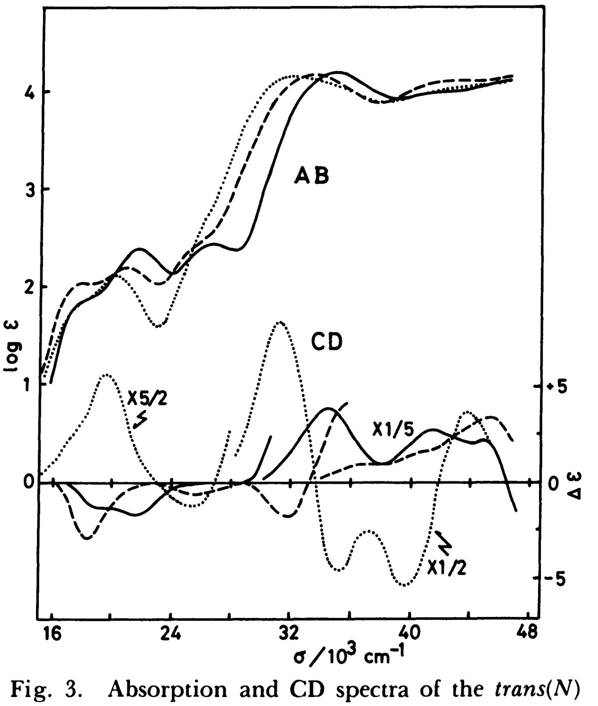

Fig. 3. Absorption and CD spectra of the *trans*(*N*) isomer for $[Co(L,L\text{-ebhc})]^+$ (——), $[Co(L,L\text{-tbhc})]^+$ (-----), and $[Co(L\text{-eth})_2]^+$ (······).

C, 31.62; H, 5.42; N, 5.90%. Calcd for [Co(L-eth)$_2$]Br·0.25C_2H_5OH=$CoC_{12}H_{24}N_2O_4S_2Br$·0.25$C_2H_5OH$: C, 31.40; H, 5.79; N, 5.89%. Found for C-2: C, 27.86; H, 5.80; N, 5.42%. Calcd for [Co(L-eth)$_2$]Br·3H_2O: C, 27.84; H, 5.86; N, 5.43%. Found for C-3: C, 28.64; H, 5.51; N, 5.63%. Calcd for [Co(L-eth)$_2$]Br·2H_2O: C, 28.87; H, 5.61; N, 5.61%.

Measurements. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and UVIDEC-610 spectrophotometers and the CD spectra with a JASCO J-20 spectropolarimeter. All measurements were carried out in aqueous solution at room temperature. The concentration of *trans(N)*-[Co(L,L-tbhc)]$^+$ was measured with a Jarrel-Ash Model 96—975 Plasma Atom Co. The ^{13}C NMR spectra were recorded in deuterium oxide on a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. Sodium 2,2-dimethyl-2-silapentate-5-sulfonate (DSS) was used as an internal reference.

Results and Discussion

Structural Assignments. *S,S*-Bridge (L,L-sexidentate-N_2,S_2,O_2) Type Complexes. For each of the *S,S*-bridge complexes, [Co(L,L-ebhc)]$^+$ and [Co(L,L-tbhc)]$^+$, two geometrical isomers, *trans(O)* and *trans(N)*, are expected (Fig. 1). The absorption and CD spectra of the A-1, A-2, B-1, and B-2 isomers are shown in Figs. 2 and 3, and their data are summarized in Tables 1 and 2 together with those of *trans(O)*-, *trans(N)*-, and *trans(S)*-[Co(L-eth)$_2$]$^+$. Four isomers of the *S,S*-bridge complexes exhibit commonly the sulfur-to-metal charge transfer bands in the region of 33—35×10^3 cm^{-1}, indicating that all isomers have a *cis(S)* configuration.[1,8—13] In the first d-d absorption band

Table 1. Absorption Spectral Data of [Co(sexidentate-N_2,S_2,O_2)]$^+$ and [Co(terdentate-N,S,O)$_2$]$^+$ Type Complexes

Complex	First band	Second band	Charge transfer band
trans(*O*)-[Co(L,L-ebhc)]$^+$	18.42 (2.58)	26.67 (2.34 sh)	34.25 (4.13)
trans(*N*)-[Co(L,L-ebhc)]$^+$	17.86 (1.85 sh)	26.74 (2.43)	34.72 (4.21)
	21.51 (2.39)		
trans(*O*)-[Co(L,L-tbhc)]$^+$	18.45 (2.30)	25.80 (2.27 sh)	33.33 (4.19)
trans(*N*)-[Co(L,L-tbhc)]$^+$	17.92 (2.02)		33.11 (4.17)
	20.75 (2.20)		47.62 (4.11)
trans(*S*)-[Co(L-eth)$_2$]$^+$	18.40 (2.01)		28.17 (4.05)
trans(*O*)-[Co(L-eth)$_2$]$^+$	19.00 (2.11)	26.67 (2.89 sh)	32.80 (3.98)
trans(*N*)-[Co(L-eth)$_2$]$^+$	17.54 (1.80 sh)		32.36 (4.14)
	20.00 (2.11)		

Wavenumbers and $\Delta\varepsilon$ 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 Spectral Data [Co(sexidentate-N_2,S_2,O_2)]$^+$ and [Co(terdentate-N,S,O)$_2$]$^+$ Type Complexes

Complex	First band region	Second band region	Charge transfer band region
trans(*O*)-[Co(L,L-ebhc)]$^+$	18.69 (+6.66)	28.17 (+1.61 sh)	31.95 (+9.23)
	21.74 (−0.64)		36.10 (−40.93)
			40.00 (−17.9 sh)
			44.84 (+24.48)
trans(*N*)-[Co(L,L-ebhc)]$^+$	19.23 (−1.31 sh)	28.17 (−0.10)	34.48 (+18.93)
	21.56 (−1.63)		41.67 (+13.36)
			44.84 (+11.14)
trans(*O*)-[Co(L,L-tbhc)]$^+$	18.69 (+5.45)		31.25 (+17.99)
			35.34 (−34.78)
			40.00 (−18.0 sh)
			44.84 (+25.19)
trans(*N*)-[Co(L,L-tbhc)]$^+$	18.32 (−2.95)	25.51 (−0.69)	31.85 (−1.82)
			36.23 (+4.42 sh)
			45.25 (+16.74)
trans(*S*)-[Co(L-eth)$_2$]$^+$	15.87 (+0.44)	25.97 (−0.21)	28.57 (+0.59)
	17.30 (−0.55)		35.09 (−1.89)
	19.20 (+0.34)		40.80 (+3.40)
trans(*O*)-[Co(L-eth)$_2$]$^+$	16.95 (+1.44)	27.03 (+0.62)	35.09 (−7.55)
	18.69 (−0.57)		43.48 (+12.40)
	20.83 (+0.53)		
trans(*N*)-[Co(L-eth)$_2$]$^+$	19.61 (+2.26)	25.32 (−0.51)	31.25 (+17.00)
			35.09 (−8.87)
			40.00 (−10.20)
			43.48 (+7.22)

Wavenumbers and $\Delta\varepsilon$ values (in parentheses) are given in 10^{3}cm^{-1} and mol^{-1}dm^{3}cm^{-1}, respectively. sh denotes a shoulder.

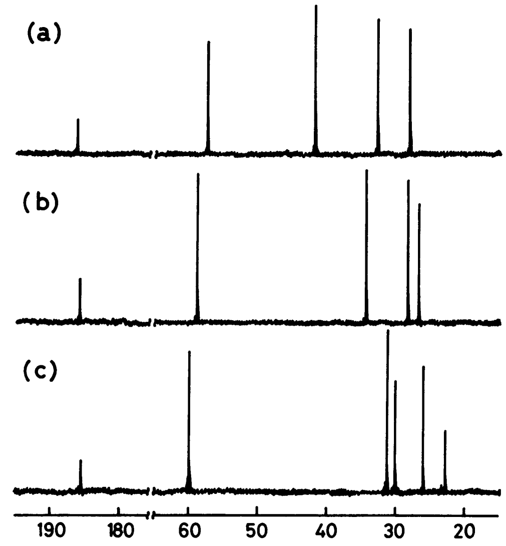

Fig. 4. ^{13}C NMR spectra of [Co(sexidentate-N_2,S_2,O_2)]$^+$: (a) *trans*(*N*) L,L-ebhc, (b) *trans*(*O*) L,L-ebhc, and (c) *trans*(*O*) L,L-tbhc.

region of [Co(L,L-ebhc)]$^+$, the A-1 isomer exhibits a band with an explicit shoulder on the lower energy side of the major peak and the A-2 one a broad band with a vague shoulder on the higher energy side (Figs. 2 and 3). These splittings of the first d-d absorption bands indicate that the A-1 and A-2 isomers are *trans(N)* and *trans(O)*, respectively.[1,13] The same relationship in absorption spectrum as the L,L-ebhc isomers is also observed for the B-1 and B-2 isomers of [Co(L,L-tbhc)]$^+$ (Figs. 2 and 3, and Table 1). Accordingly, the B-1 isomer can be assigned to *trans(N)* and the B-2 one to *trans(O)*.

The ^{13}C NMR spectra of the *S*,*S*-bridge complexes were measured in order to estimate the configuration, *R*(*S*) or *S*(*S*), of the sulfur donor atom (Fig. 4). *trans(N)*- and *trans(O)*-[Co(L,L-ebhc)]$^+$ exhibit five resonance lines for ten carbon atoms (Fig. 4 (a) and (b)), and *trans(O)*-[Co(L,L-tbhc)]$^+$ exhibits six lines for eleven carbon ones (Fig. 4 (c)). These facts indicate that all isomers have C_2 symmetry, namely, the conformation of the *S*,*S*-bridged backbone chelate ring takes a gauche form for the ethylene bridge in the L,L-ebhc complex and a skew form for the trimethylene bridge in the L,L-tbhc one. It is considered, therefore, that each of the four isomers takes either the *R*(*S*),*R*(*S*) or *S*(*S*),*S*(*S*) configuration with respect to the two asymmetric sulfur donor atoms. The model constructions reveal that the two sulfur donor atoms of the *trans(N)* L,L-ebhc or *trans(N)* L,L-tbhc isomer take the *S*(*S*),*S*(*S*) configuration. On the other hand, the two *trans(O)* isomers are possible to take both of the *R*(*S*),*R*(*S*) and *S*(*S*),*S*(*S*) configurations, however, the *R*(*S*),*R*(*S*) one is more preferable than the other because there is less strain of the *S*,*S*-bridged backbone chelate ring.

Bis(L-ethioninato) Complexes. In order to investigate the spectral behavior due to the change of the substituent on the sulfur donor atom of the ligand, *trans(N)*-, *trans(S)*-, and *trans(O)*-[Co(L-eth)$_2$]$^+$ were prepared. Their absorption and CD data are summarized in Tables 1 and 2. Splittings of the first d-d absorption bands and the maximum positions (28—$33\times10^3\,\text{cm}^{-1}$) of the sulfur-to-metal charge transfer bands of the three isomers agree well with those of the corresponding three isomers of [Co(L-met)$_2$]$^+$, respectively.[5] The behavior of these absorption spectra confirms that the C-1, C-2, and C-3 isomers are *trans(S)*, *trans(N)*, and *trans(O)*, respectively.[14] Each of the three isomers exhibits a similar CD spectrum to that of the corresponding isomer of [Co(L-met)$_2$]$^+$,[5] suggesting that the CD contribution due to the change of the substituent on the two sulfur donor atoms is inconspicuous.

The ^{13}C NMR spectrum of *trans(S)*-[Co(L-eth)$_2$]$^+$ exhibits six resonance lines (13.00, 27.90, 30.45, 32.61, 58.40, and 186.03 ppm) for twelve carbon atoms, the *trans(N)* isomer fourteen lines (13.27, 14.30, 25.73, 26.06, 26.55, 27.79, 28.06, 28.98, 31.75, 32.56, 59.10, 60.78, 185.49, and 186.58 ppm), and the *trans(O)* isomer eight lines (14.36, 25.79, 26.98, 27.20, 28.66, 57.70, 187.44, and 187.93 ppm). Taking the configuration, *R*(*S*) or *S*(*S*), of the sulfur donor atom into consideration, the ^{13}C NMR spectrum of the *R*(*S*),*R*(*S*) or *S*(*S*),*S*(*S*) isomer having a twofold axis can be expected to exhibit six resonance lines, while the *R*(*S*),*S*(*S*) isomer to exhibit twelve. The present results suggest that the *trans(S)* isomer is either *S*(*S*),*S*(*S*) or *R*(*S*),*R*(*S*) and the other two isomers are a mixture of *R*(*S*),*S*(*S*), *R*(*S*),*R*(*S*), and/or *S*(*S*),*S*(*S*). These trends are in accord with those of the [Co(L-met)$_2$]$^+$ isomers.[5] Accordingly, taking the model constructions and the similarity in CD spectrum with the [Co(L-met)$_2$]$^+$ isomers into consideration, the *trans(S)* isomer prefers the *S*(*S*),*S*(*S*) configuration, the *trans(N)* isomer a mixture of the *R*(*S*),*S*(*S*) and *S*(*S*),*S*(*S*) ones, and the *trans(O)* isomer takes a mixture of the *R*(*S*),*R*(*S*), *R*(*S*),*S*(*S*), and *S*(*S*),*S*(*S*) ones, as in the case of [Co(L-met)$_2$]$^+$.[5] These results seem to support that the CD spectra of the three isomers of [Co(L-eth)$_2$]$^+$ resemble the corresponding isomers of [Co(L-met)$_2$]$^+$, respectively.

Formation of Isomers. The *trans(O)* and *trans(N)* isomers were formed for each [Co(L,L-ebhc)]$^+$ and [Co(L,L-tbhc)]$^+$ in this work, though the *trans(N)* L,L-tbhc isomer could not be isolated as a solid because of the very small amount. Contrary to the L,L-ebhc and L,L-tbhc complexes, only the *trans(O)* isomer was selectively formed for each of [Co(L,L-ebc)]$^+$ and [Co(L,L-tbc)]$^+$.[1] These results are probably related to the difference in flexibility between the N–S chelate rings of the L,L-ebhc or L,L-tbhc complex and the L,L-ebc or L,L-tbc one. For [Co(L,L-ebhc)]$^+$ and [Co(L,L-tbhc)]$^+$, namely, the ethylene and trimethylene bridges span the two sulfur donor atoms of the rather flexible six-membered N–S rings of the L-homocysteinate moieties, while the bridges in $[\mathrm{Co}(\text{L,L-ebc})]^+$ and $[\mathrm{Co}(\text{L,L-tbc})]^+$ span the sulfur donor atoms of the rigid five-membered N–S rings of the L-cysteinate moieties. In the case of the *N,N*-bridge L,L-sexidentate-N_2,S_2,O_2 type complexes,[1–3] on the other hand, of the expectant *trans(O)* and *trans(S)* isomers only the *trans(O)* one was selectively formed for the ethylene bridge complexes, $[\mathrm{Co}(\text{L,L-ebsmc})]^+$ and $[\mathrm{Co}(\text{L,L-ebm})]^+$, while the two geometrical isomers were formed for the trimethylene bridge complex, $[\mathrm{Co}(\text{L,L-tbsmc})]^+$, though the *trans(S)* isomer could not be isolated because of the isomerization to the *trans(O)* species during the procedure after elution.[1] These results are obviously caused by the difference in flexibility between the ethylene and trimethylene bridges, because both of the bridges span the nitrogen donor atoms of the rigid five-membered N–O rings of the ligands. From these results, it can be deduced that the selective formation of the isomers for the *S,S*-bridge complexes depends mainly on the flexibility of the N–S chelate rings of the ligand and the difference between the ethylene and trimethylene backbone bridges is a minor factor for the selective formation of the isomers.

Absorption and CD Spectra. The three geometrical isomers of $[\mathrm{Co}(\text{L-eth})_2]^+$ exhibit similar absorption and CD spectral behaviors to the corresponding isomers of $[\mathrm{Co}(\text{L-met})_2]^+$,[5] over the whole region, indicating that their spectra hardly change with the substitution of ethyl group for methyl one on the sulfur donor atoms (Tables 1 and 2). The CD spectra of the *trans(O)* and *trans(N)* isomers of $[\mathrm{Co}(\text{L,L-ebhc})]^+$ and $[\mathrm{Co}(\text{L,L-tbhc})]^+$ deviate significantly from those of the corresponding isomers of $[\mathrm{Co}(\text{L-eth})_2]^+$, respectively, although the absorption spectral patterns of the former isomers are similar to those of the latter, respectively, as shown in Figs. 2 and 3.

The absorption maxima of the sulfur-to-metal charge transfer bands (32—$35\times10^3\,\mathrm{cm}^{-1}$ for the *cis(S)* isomers) are shifted to lower energy in the order of L,L-ebhc>L,L-tbhc>non-bridge complex in either of the *trans(O)* and *trans(N)* isomers (Figs. 2 and 3). This order coincides with that for the *cis·cis·cis*-$[\mathrm{Co}(R,S\text{-ebp})]^+$, -$[\mathrm{Co}(R,S\text{-tbp})]^+$, -$[\mathrm{Co}(R,S\text{-tetp})]^+$, and -$[\mathrm{Co}(R\text{-smp})(S\text{-smp})]^+$.[15] This behavior reflects the order of the rigidities of the *S,S*-bridged backbone chelate rings. The first d-d absorption bands of the present *S,S*-bridge *trans(O)* isomers are almost unchanged from that of *trans(O)*-$[\mathrm{Co}(\text{L-eth})_2]^+$ as in the case of *trans(O)*-$[\mathrm{Co}(\text{L,L-ebc})]^+$, -$[\mathrm{Co}(\text{L,L-tbc})]^+$, and -$[\mathrm{Co}(\text{L-smc})_2]^+$, where L-smc denotes *S*-methyl-L-cysteinate.[1] However, the first absorption bands of the *S,S*-bridge *trans(N)* isomers significantly change from that of the *trans(N)* L-eth isomer, namely, the absorption components in the higher energy side are shifted to lower energy in accordance with the absorption spectral behavior of the sulfur-to-metal charge transfer bands mentioned above, though the components (ca. $17.9\times10^3\,\mathrm{cm}^{-1}$) in the lower energy side remain unchanged.

The deviation in CD spectrum between the *trans(O)* L,L-ebhc or L,L-tbhc isomer and *trans(O)*-$[\mathrm{Co}(\text{L-eth})_2]^+$ is quite similar to that between the *trans(O)* L,L-ebc or L,L-tbc isomer and *trans(O)*-$[\mathrm{Co}(\text{L-smc})_2]^+$ which possess a rigid L-cysteinate framework.[1] Accordingly, this deviation is attributed to the CD contribution due to the fixation of two sulfur donor atoms located in the cis position. In contrast to the *trans(O)* isomers, the CD spectra of the *S,S*-bridge *trans(N)* isomers change drastically from that of *trans(N)*-$[\mathrm{Co}(\text{L-eth})_2]^+$ (Fig. 3 and Table 2). In the first d-d absorption band region, *trans(N)*-$[\mathrm{Co}(\text{L-eth})_2]^+$ exhibits a positive CD band ($19.61\times10^3\,\mathrm{cm}^{-1}$) with a shoulder in the lower energy side, while the *S,S*-bridge *trans(N)* isomers exhibit negative CD bands (19.2 sh and $21.56\times10^3\,\mathrm{cm}^{-1}$ for the L,L-ebhc isomer and $18.32\times10^3\,\mathrm{cm}^{-1}$ for the L,L-tbhc one) which correspond to the two absorption components. In the ligand band region (36—$48\times10^3\,\mathrm{cm}^{-1}$) where the bridge L,L-isomer usually exhibits a similar CD pattern to that of the non-bridge L-isomer,[1,2] the *trans(N)* L,L-ebhc and L,L-tbhc isomers exhibit a reversed CD pattern to that of *trans(N)*-$[\mathrm{Co}(\text{L-eth})_2]^+$ (Fig. 3). Considered from another viewpoint, the CD spectra of the *S,S*-bridge *trans(N)* isomers seem roughly enantiomeric to those of the *S,S*-bridge *trans(O)* ones. These CD spectral changes of the *trans(N)* isomers seem to indicate an additional CD contribution besides that due to the fixation of the two sulfur donor atoms in the cis position. On this viewpoint, the present results may be considered as follows. When the two sulfur donor atoms of the non-bridge isomer are spanned by ethylene or trimethylene, the *S,S*-bridge *trans(O)* isomers retain the net configurational chirality of the non-bridge *trans(O)* one. While, the *S,S*-bridge *trans(N)* isomers obtain a configurational chirality of the L,L-sexidentate type which is quasi-enantiomeric geometrical isomers to the *S,S*-bridge *trans(O)* ones, though *trans(N)*-$[\mathrm{Co}(\text{L-eth})_2]^+$ is not quasi-enantiomeric to the *trans(O)* isomer. As a result, the *S,S*-bridge *trans(N)* isomers exhibit approximately enantiomeric CD spectra to the *S,S*-bridge *trans(O)* ones. The CD spectral behavior of the *trans(N)* isomers in this work suggest that care must be taken in relating the CD spectra to the absolute configurations of the complexes with sulfur-containing terdentate amino carboxylates and their sexidentate derivatives.

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