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Preparation and Some Properties of Cobalt(III) Complex with D- and/or L-Selenomethioninates

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A novel cobalt(III) complex with D- and/or L-selenomethioninates (D- and/or L-semet) functioning as terdentate-*N,O,Se* ligand was prepared and separated into the five geometrical isomers, trans(N), trans(O), trans(Se), cis,cis,cis, and trans,trans,trans. Of these isomers *trans(N)*- and *trans(O)*-[Co(D- or L-semet)$_2$]$^+$ and *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$, which were obtained as the crystalline state, were optically resolved by the column chromatographic method. All the isomers were characterized by the electronic absorption, ^{1}H NMR, and CD spectra. The trans(N), trans(O), and cis,cis,cis isomers in the crystalline state take the selective configurations with respect to the absolute configuration, R(Se) or S(Se), of the two coordinated selenium atoms. While, these isomers in an aqueous solution are a mixture of some configurations in the equilibrium state. For the inversion on the asymmetric selenium donor atom of the trans(N) and cis,cis,cis isomers, the rate constants and the $\Delta G^{\neq}$ values are investigated on the basis of the absorption and ^{1}H NMR spectral changes. The trans(N) and cis,cis,cis isomers showed the characteristic CD spectral behavior in the d-d absorption band region depending on the inversion on the asymmetric selenium donor atoms.

Biochemical roles of selenium-containing amino carboxylates have been remarked in association with transition metals.[1] One of them selenomethioninate (semet) has three donor sites and is potentially terdentate-*N,O,Se* ligand, which has a framework similar to methioninate (met). Accordingly, the stereochemistry of the cobalt(III) complex with semet can be compared effectively with those of the methioninato cobalt(III) complex[2] and its analogues.[3–5] Hence, in order to examine the spectrochemical and stereochemical properties of the coordinated selenium atom, we have undertaken the preparation of the cobalt(III) complex with D- and/or L-selenomethioninates.

In this work, the cobalt(III) complex with D- and/or L-selenomethioninates were prepared and chromatographically separated into the five geometrical isomers: *trans(N)*-, *trans(O)*-, and *trans(Se)*-[Co(D- or L-semet)$_2$]$^+$,[6] and *cis,cis,cis*- and *trans,trans,trans*-[Co(D-semet)(L-semet)]$^+$ (Fig. 1). All isomers were characterized by their electronic absorption spectra in comparison with those of the isomers of the cobalt(III) complex with D- and/or L-methioninates.[2] For the trans(N) and cis,cis,cis isomers which exhibited the electronic absorption, CD, and ^{1}H NMR spectral changes with time in an aqueous solution, an inversion on the asymmetric selenium donor atom is investigated by the spectrophotometric method. The CD spectral behaviors are also discussed in relation to the absolute configuration of the asymmetric selenium donor atom.

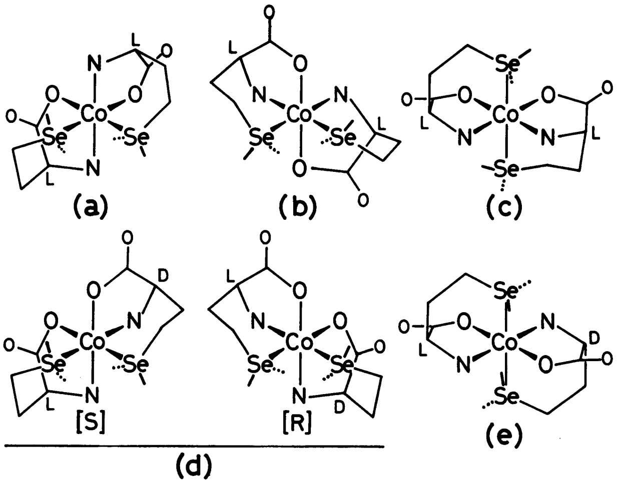

Fig. 1. Possible geometrical isomers of [Co(L-semet)$_2$]$^+$ and [Co(D-semet)(L-semet)]$^+$: (a) trans(N), (b) trans(O), (c) trans(Se), (d) cis,cis,cis, and (e) trans,trans,trans.

Experimental

Preparation of Complex. A solution containing 1.8 g of $CoCl_2 \cdot 6H_2O$ in 10 cm^3 of water was added to a suspension containing 3.0 g of the racemic Hsemet[7] in 50 cm^3 of water. After the mixture was stirred at 60 °C for 5 min, to this were added 0.5 g of activated charcoal and 8.0 g of PbO_2. The mixture was further stirred at 60 °C for 20 min and then filtered to remove insoluble materials. The dark brown filtrate was poured onto an SP-Sephadex C-25 column (Na$^+$ form, 4×100 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.015 mol dm^{-3} aqueous solution of Na_2SO_4. A circulating-chromatographic technique was employed for the separation of the isomers. After circulating the eluates in the same column several times, the eluates were separated into the five colored ones, dark violet (A-1), yellow (A-2), violet (A-3), red-violet (A-4), and yellow (A-5) in this order. It was found from the absorption spectral measurements that the eluates A-1, A-4, and A-5 contained *trans(O)*-, *trans(N)*-, and *trans(Se)*-[Co(D- or L-semet)$_2$]$^+$, respectivily, and the eluate A-3 contained *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$. The formation ratio of the isomers, trans(O): cis,cis,cis: trans(N): trans(Se), was about 1 : 7 : 9 : 1. Each eluate except the eluate A-2 was concentrated with a rotary evaporator below 25 °C and Na_2SO_4 deposited was filtered off. The filtrate was then passed through a QAE-Sephadex A-25 column (ClO_4^- form, 2.5×20 cm) by eluting with water. The eluate was concentrated with a rotary evaporator again and the crystals were collected by filtration. The A-5 isomer could not be obtained as a solid because of the small amount of the eluate A-5, and then the concentration of the A-5 isomer was evaluated on the basis of the plasma emission spectral analysis. The A-2 isomer, whose formation was very poor, could not be separated as a pure form because of the isomerization during the procedure of the chromatographic separation. Found for A-1: C, 21.18; H, 3.96; N. 4.92%. Calcd for $[\mathrm{Co(semet)_2}]\mathrm{ClO_4}\cdot\mathrm{H_2O}=\mathrm{CoC_{10}H_{20}N_2O_8ClSe_2}\cdot\mathrm{H_2O}$: C, 21.20; H, 3.91; N. 4.94%. Found for A-3: C, 22.02; H, 3.66; N, 5.08%. Found for A-4: C, 21.99; H. 3.71; N, 5.09%. Calcd for $[\mathrm{Co(semet)_2}]\mathrm{ClO_4}$: C, 21.89; H, 3.67; N, 5.11%.

Resolution of Isomers. $(-)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(D-semet)$_2$]ClO$_4$ and $(+)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(L-semet)$_2$]ClO$_4$. About 0.1 g of *trans*(*N*)-[Co(D- or L-semet)$_2$]ClO$_4$ (A-4) was dissolved in a small amount of water and poured onto an SP-Sephadex C-25 column (Na$^+$ form, 3.5×100 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.015 mol dm^{-3} aqueous solution of K$_2$[Sb$_2$(*d*-tart)$_2$]·H$_2$O. After circulating the eluates in the same column twice, the eluates were separated into the two bands and then fractionated. It was found from the CD spectral measurements that the earlier moving band contained $(-)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(D-semet)$_2$]$^+$ and the later one contained $(+)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(L-semet)$_2$]$^+$. Each of the fractions was concentrated to a small volume with a rotary evaporator below 25 °C and deposited K$_2$[Sb$_2$(*d*-tart)$_2$] was filtered off. The filtrate was converted into the perchlorate salt using a QAE-Sephadex A-25 column (ClO$_4^-$ form) by eluting with water. The eluate was concentrated to a small volume again and kept in a refrigerator for several days. The resulting crystals were collected by filtration.

$(-)^{\mathrm{CD}}_{550}$-[*R*]- and $(+)^{\mathrm{CD}}_{550}$-[*S*]-*cis,cis,cis*-[Co(D-semet)(L-semet)]ClO$_4$. *cis,cis,cis*-[Co(D-semet)(L-semet)]ClO$_4$ (A-3) was resolved by a procedure similar to that used for the trans(N) isomer, using the racemic cis,cis,cis isomer (0.1 g) instead of the trans(N) one. The earlier moving adsorbed band contained $(-)^{\mathrm{CD}}_{550}$-[*R*]-*cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ and the later one contained the $(+)^{\mathrm{CD}}_{550}$-[*S*] one.

$(-)^{\mathrm{CD}}_{600}$-*trans*(*O*)-[Co(D-semet)$_2$]ClO$_4$ and $(+)^{\mathrm{CD}}_{600}$-*trans*(*O*)-[Co(L-semet)$_2$]ClO$_4$. *trans*(*O*)-[Co(D- or L-semet)$_2$]ClO$_4$·H$_2$O (A-1) was also resolved by a procedure similar to that used for the trans(N) isomer, except for using about 0.02 g of the trans(O) isomer and an SP-Sephadex C-25 column (Na$^+$ form, 3.0×40 cm). The earlier moving adsorbed band contained $(+)^{\mathrm{CD}}_{600}$-*trans*(*O*)-[Co(L-semet)$_2$]$^+$ and the later one contained $(-)^{\mathrm{CD}}_{600}$-*trans*(*O*)-[Co(D-semet)$_2$]$^+$.

The $\Delta\varepsilon$ values of the trans(N), cis,cis,cis, and trans(O) isomers were evaluated from their absorption spectral data.

Kinetic Measurements. The inversion on the asymmetric selenium donor atom of *trans*(*N*)-[Co(D- or L-semet)$_2$]$^+$ and *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ in the aqueous solution was monitored spectrophotometrically with a JASCO UVIDEC-1 spectrophotometer equipped with a thermostated cell compartment. The concentrations of the isomers were ca. 1.5×10^{-3} mol dm^{-3}. The temperature of the solutions, *T*, was in the range of 16.9—25.9 °C and kept constant within ±0.1 °C by use of a temperature-controlled circulating bath, Yamato-Komatsu CTR-220. The absorbance changes with time were followed at 511 nm for the trans(N) isomer and at 556 nm for the cis,cis,cis one, respectively. The first-order rate constant, *k*, for the trans(N) or cis,cis,cis isomer was determined from the plot of $\ln\{(A_0-A_\infty)/(A_t-A_\infty)\}$ against time, where A_0, A_∞, and A_t stand for absorbances at the initial state, at equilibrium, and at time t, respectively.

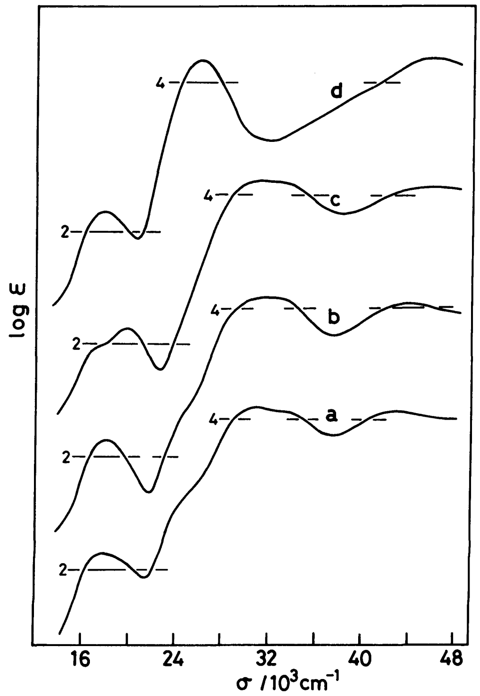

Fig. 2. Absorption spectra of [Co(D- or L-semet)$_2$]$^+$ and [Co(D-semet)(L-semet)]$^+$: (a) trans(O), (b) cis,cis,cis, (c) trans(N), and (d) trans(Se).

The activation parameters were yielded from the Eyring treatment of log (k/T) vs. T^{-1}.

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. The concentration of *trans*(*Se*)-[Co(D- or L-semet)$_2$]$^+$ (A-5 isomer) was determined with a Jarrel-Ash Model 96-975 Plasma Atom Co. The ^{1}H NMR spectra were recorded in deuterium oxide with a JEOL JNM-FX-100 NMR spectrometer at the prove temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference.

Results and Discussion

Characterization. Five geometrical isomers are possible for the cobalt(III) complex with D- and/or L-selenomethioninates: trans(N), trans(O), and trans(Se) for [Co(D- or L-semet)$_2$]$^+$, and cis,cis,cis and trans,trans,trans for [Co(D-semet)(L-semet)]$^+$, as in the case of the cobalt(III) complex with D- and/or L-methioninates[2] and its analogues (Fig. 1).[3–5] As shown in Fig. 2 and Table 1, each absorption spectrum of the present five isomers is quite similar to that of the corresponding isomers of [Co(D- or L-met)$_2$]$^+$ and [Co(D-met)(L-met)]$^+$, though the first absorption bands of the selenomethioninato isomers and, especially, the charge-transfer bands due to the selenium to metal (ca. 30—33×10^3 cm^{-1} for A-1, A-3, and A-4, and ca. 26×10^3 cm^{-1} for A-5) shift significantly to lower energy than those of the methioninato isomers.[2] These results are consistent with the absorption behavior observed for the

Table 1. Absorption Spectral Data of Equilibrium State for [Co(D- or L-semet)$_2$]$^+$ and [Co(D-semet)(L-semet)]$^+$

Complex	d–d band	Charge transfer band
trans(*N*)-[Co(D- or L-semet)$_2$]$^+$	17.44 (1.99 sh) 19.49 (2.21)	31.06 (4.18) 32.68 (4.16 sh) 45.66 (4.12)
trans(*O*)-[Co(D- or L-semet)$_2$]$^+$	17.61 (2.21) 19.27 (2.14 sh) 24.88 (3.01 sh)	30.67 (4.16) 32.95 (4.11 sh) 42.74 (4.10)
trans(*Se*)-[Co(D- or L-semet)$_2$]$^+$	17.67 (2.27)	25.97 (4.28) 45.66 (4.30)
cis,cis,cis-[Co(D-semet)(L-semet)]$^+$	17.94 (2.26) 25.07 (2.74 sh)	31.55 (4.20) 43.67 (4.13)

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

[Co(bidentate-*N,Se* or -*N,S*)(en or tn)$_2$] type complexes.[8,9] Accordingly, the A-1, A-3, A-4, and A-5 isomers are assignable to trans(O), cis,cis,cis, trans(N), and trans(Se), respectively. Hence, it is noted that the selenium to metal charge-transfer bands for the three cis(Se) type selenomethioninato isomers split distinctly in comparison with the sulfur to metal charge-transfer band for the three cis(S) type methioninato isomers (Fig. 2).[2] The absorption spectrum of the A-2 isomer could not be measured because of the its partial isomerization to the cis(Se) type isomer during the chromatographic separation. However, it is probable that the eluate A-2 mainly contains the trans,trans,-trans isomer, because the eluate A-2 exhibits the selenium to metal charge-transfer band in a similar position (ca. $26\times10^3\,cm^{-1}$) to *trans*(*Se*)-[Co(D- or L-semet)$_2$]$^+$, whose band locates at lower energy than those of the cis(Se) type isomers.

Inversion on the Asymmetric Selenium Donor Atom. When the crystals of *trans*(*N*)-[Co(D- or L-semet)$_2$]ClO$_4$ were dissolved in water, the absorption spectral change was observed with time at room temperature and the absorption spectrum exhibited two distinct isosbestic points at 552 and 652 nm (Fig. 3). This spectrum attained equilibrium after 4.5 h, and the absorption spectrum at equilibrium coincided with that of the eluate A-4 obtained by the chromatographic separation. Further, the solution at equilibrium exhibited only the same adsorbed band as that of the eluate A-4 in the rechromatographic separation. Similar trend was also observed for *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$, namely, the absorption spectrum exhibited the isosbestic points at 463 and 645 nm and attained equilibrium after 6 h. These absorption spectral changes for the trans(N) and cis,cis,cis isomers were simultaneously accompanied by the CD and ^{1}H NMR spectral changes (vide infra). Accordingly, it seems to indicate that the spectral changes for the trans(N) and cis,cis,cis isomers are caused by the inversion on the asymmetric selenium donor atom of the ligand. These are confirmed by the following ^{1}H NMR spectral behaviors.

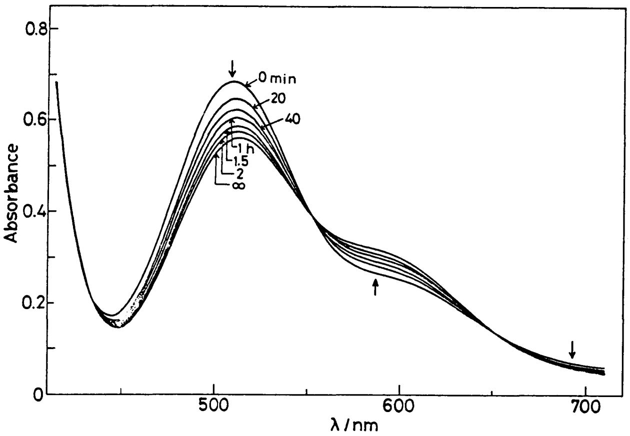

Fig. 3. Change in absorption spectrum with time for *trans*(*N*)-[Co(D- or L-semet)$_2$]$^+$ in water at 25.9 °C. The measured times are indicated on the spectral curves. Trends of the spectral change with time are shown by arrows.

Just after *trans*(*N*)-[Co(D- or L-semet)$_2$]ClO$_4$ was dissolved in water, the ^{1}H NMR spectrum exhibited only one resonance line at 2.04 ppm in the *Se*-methyl proton region as shown in Fig. 4-a. Taking the configuration, R(Se) or S(Se), of the asymmetric selenium donor atom into consideration, the ^{1}H NMR spectrum of the R(Se),R(Se) or S(Se),S(Se) isomer having C_2 axis can be expected to exhibit only one resonance line in the corresponding region, while the R(se),S(Se) isomer to exhibit two resonance lines. The present result suggests that the trans(N) isomer in the crystalline state is either R(Se),R(Se) or S(Se),S(Se). The model constructions reveal that the two asymmetric selenium donor atoms take the R(Se)$_D$,R(Se)$_D$ or S(Se)$_L$,S(Se)$_L$ configuration for *trans*(*N*)-[Co(D- or L-semet)$_2$]$^+$, because the S(Se)$_D$,S(Se)$_D$ or R(Se)$_L$,-R(Se)$_L$ configuration has the intramolecular steric interaction between the two *Se*-methyl groups, where

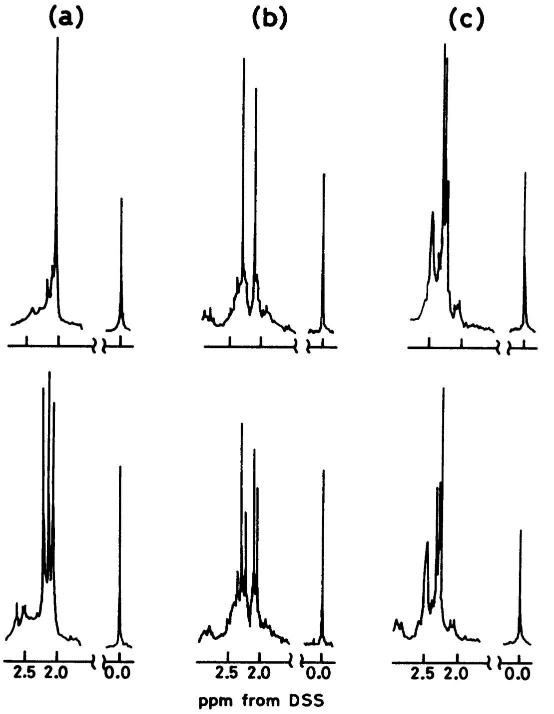

Fig. 4. ^{1}H NMR spectra of [Co(D- or L-semet)$_2$]$^+$ and [Co(D-semet)(L-semet)]$^+$: (a) trans(N), (b) cis,cis,cis, and (c) trans(O); initial state (upper) and equilibrium state (lower).

the subscripts, D and L, correspond to the absolute configurations, R(C) and S(C), for the asymmetric carbon atom of the selenomethioninate. In the aqueous solution, two resonance lines at 2.10 and 2.19 ppm gradually appeared and their intensities increased with time, and finally three resonance lines with the equal intensities were observed at equilibrium (Fig. 4-a). The two resonance lines which newly appeared seems to be due to the R(Se),S(Se) configuration. Accordingly, the ^{1}H NMR spectral behavior suggests that *trans(N)*-[Co(D- or L-semet)$_2$]$^+$ in the aqueous solution at equilibrium is a mixture of the R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{D}$ and S(Se)$_\mathrm{L}$,S(Se)$_\mathrm{L}$ configurations and the R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{D}$ and R(Se)$_\mathrm{L}$,S(Se)$_\mathrm{L}$ ones (1 : 2). Namely, the absorption and ^{1}H NMR spectral behaviors of *trans(N)*-[Co(D- or L-semet)$_2$]$^+$ indicate that the inversion on the asymmetric selenium donor atom takes place as follows:

$$\mathrm{R(Se)_D,R(Se)_D} \longrightarrow \mathrm{R(Se)_D,S(Se)_D} \qquad (1a)$$

$$\mathrm{S(Se)_L,S(Se)_L} \longrightarrow \mathrm{R(Se)_L,S(Se)_L} \qquad (1b)$$

Similar trend was also observed for the cis,cis,cis iomer. *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ has [R] and [S] configurations based on the chiral arrangement of the coordinated atoms, N, O, and Se.[10] Moreover, four geometrical isomers for each of the [R] and [S] configurations, R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$, R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$, S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$, and S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$, are possible. Just after the perchlorate salt of the cis,cis,cis isomer was dissolved in water, the ^{1}H NMR spectrum exhibited two resonance lines at 2.11 and 2.30 ppm (Fig. 4-b). This spectrum indicates that the cis,cis,cis isomer in the crystalline state takes only one configuration of the four geometrical isomers. While, in the aqueous solution of this isomers two resonance line at 2.06 and 2.24 ppm gradually appeared and their intensities increased with time, though they were accompanied by the minor two resonance lines at 2.14 and 2.37 ppm (Fig. 4-b). At equilibrium, the intensity ratio of the resonance lines at 2.06, 2.11, 2.24, and 2.30 ppm was about 2 : 3 : 2 : 3 (Fig. 4-b). The model constructions for the cis,cis,cis isomer reveal that the [R]-S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ or [S]-R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ isomer has the intramolecular steric interaction between the *Se*-methyl group and the amine protons in the other D- or L-semet ligand. Further, the [R]-S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ or [S]-R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ isomer has the interaction between the two *Se*-methyl groups. While, the [R]-R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ or [S]-S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ isomer and the [R]-R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ or [S]-S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ one have only a little intramolecular steric interaction. The steric interaction in the cis,cis,cis isomer seems to increase in the order [R]-R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ or [S]-S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$<[R]-R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ or [S]-S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$<[R]-S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ or [S]-R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$<[R]-S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ or [S]-R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$. Therefore, the ^{1}H NMR spectral behavior suggests that *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ in the aqueous solution at equilibrium takes mainly a mixture of the [R]-R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ and [S]-S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ configurations and the [R]-R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ and [S]-S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ ones containing the minor [R]-S(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ and [S]-R(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ ones. From these consideration, the cis,cis,cis, isomer in the crystalline state seems to take the [R]-R(Se)$_\mathrm{D}$,R(Se)$_\mathrm{L}$ and [S]-S(Se)$_\mathrm{D}$,S(Se)$_\mathrm{L}$ configurations. The absorption and ^{1}H NMR spectral behaviors for *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ indicate the following inversion on the asymmetric selenium donor atom:

$$\mathrm{[R]\text{-}R(Se)_D,R(Se)_L} \longrightarrow \mathrm{[R]\text{-}R(Se)_D,S(Se)_L} \qquad (2a)$$

$$\mathrm{[S]\text{-}S(Se)_D,S(Se)_L} \longrightarrow \mathrm{[S]\text{-}S(Se)_D,R(Se)_L} \qquad (2b)$$

For *trans(O)*-[Co(D- or L-semet)$_2$]$^+$, three isomers, R(Se),R(Se), R(Se),S(Se), and S(Se),S(Se), are possible as well as the trans(N) isomer. In contrast with the trans(N) and cis,cis,cis isomers, the ^{1}H NMR spectral change of the trans(O) isomer could be measured, although the absorption spectral change occurred too fast to be followed. Just after the perchlorate salt of the trans(O) isomer was dissolved in water, the ^{1}H NMR spectrum showed two intense resonance lines at 2.26 and 2.29 ppm and one minor resonance line at 2.23 ppm (Fig. 4-c). This fact suggests that the trans(O) isomer in the crystalline state takes mainly the R(Se),S(Se) configuration having C_1 symmetry. After 20 min, the inversion reaction attained the equilibrium and the intensities of the two resonance lines at 2.26 and 2.29 ppm are weaker than that at 2.23 ppm (Fig. 4-c). The model constructions reveal that the steric

Table 2. Rate Constants for Inversion on Selenium Atom

Complex	$t/°C$	k_{obsd}/s^{-1}
	16.9	$(7.62\pm0.15)\times10^{-5}$
trans(*N*)-[Co(D- or L-semet)$_2$]$^+$	21.7	$(1.74\pm0.08)\times10^{-4}$
	25.9	$(3.34\pm0.12)\times10^{-4}$
	16.9	$(7.50\pm0.11)\times10^{-5}$
cis,cis,cis-[Co(D-semet)(L-semet)]$^+$	21.7	$(1.39\pm0.05)\times10^{-4}$
	25.9	$(2.29\pm0.09)\times10^{-4}$

Table 3. Thermodynamic Parameters for Inversion on Selenium Atom

Complex	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{25°C}$
	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
trans(*N*)-[Co(D- or L-semet)$_2$]$^+$	116.1 ± 1.4	76.7 ± 5.0	93.2 ± 0.1
cis,cis,cis-[Co(D-semet)(L-semet)]$^+$	87.2 ± 2.0	-23.1 ± 7.0	94.1 ± 0.1

interaction in the trans(O) isomer increases in the order S(Se)$_D$,S(Se)$_D$ or R(Se)$_L$,R(Se)$_L$<R(Se)$_D$,S(Se)$_D$ or R(Se)$_L$,S(Se)$_L$<R(Se)$_D$,R(Se)$_D$ or S(Se)$_L$,(Se)$_L$. Therefore, in the aqueous solution at equilibrium, the trans(O) isomer seems to take a mixture of the S(Se)$_D$,S(Se)$_D$ and R(Se)$_L$,R(Se)$_L$ configurations (C_2 symmetry) and the R(Se)$_D$,S(Se)$_D$ and R(Se)$_L$,S(Se)$_L$ ones (C_1 symmetry) (ca. 1 : 1). Accordingly, the ^{1}H NMR spectral behavior seems to indicate the following inversion:

$$\mathrm{R(Se)_D,S(Se)_D} \longrightarrow \mathrm{S(Se)_D,S(Se)_D} \quad (3a)$$

$$\mathrm{R(Se)_L,S(Se)_L} \longrightarrow \mathrm{R(Se)_L,R(Se)_L} \quad (3b)$$

Rate constants of the inversion on the asymmetric selenium donor atom for the equations (1) and (2) were determined by monitoring the change in absorbance with time. The absorbance at 511 nm of *trans*(*N*)-[Co(D- or L-semet)$_2$]$^+$ in the aqueous solution at a constant temperature decreased monotonically with time (Fig. 3). The plot of $\ln\{(A_0-A_\infty)/(A_t-A_\infty)\}$ against time gave a straight line, from which the first-order rate constants of the inversion were obtained (Fig. 5-a and Table 2). Similarly, the absorption spectral data for the cis,cis,cis isomer were treated in the same way (Fig. 5-b and Table 2). The rate constant of the trans(N) isomer agreed well with that of the cis,cis,cis one. These rate constants for the inversion are in agreement with those of *t*-[Co(RSeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ (R=CH$_3$, CH$_3$CH$_2$, and C$_6$H$_5$CH$_2$, and tren=N(CH$_2$CH$_2$NH$_2$)$_3$) and *t*-[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$.[11] These suggest that the inversion for the present isomers arises from a mechanism similar to that for the tren cobalt(III) complexes with RSeCH$_2$CH$_2$NH$_2$ (R=CH$_3$, CH$_3$CH$_2$, and C$_6$H$_5$CH$_2$).[11]

Eyring treatments of $\log(k/T)$ vs. T^{-1} yielded activation parameters for the trans(N) and cis,cis,cis isomers (Table 3). Their $\Delta G^{\ddagger}$ values at 25 °C resemble each other and agree well with those of the tren cobalt(III) complexes with RSeCH$_2$CH$_2$NH$_2$ (R=CH$_3$, CH$_3$CH$_2$, and C$_6$H$_5$CH$_2$).[11] Taking account of the stereochemical differences between the trans(O) isomer and the trans(N) or cis,cis,cis one, whose inversion

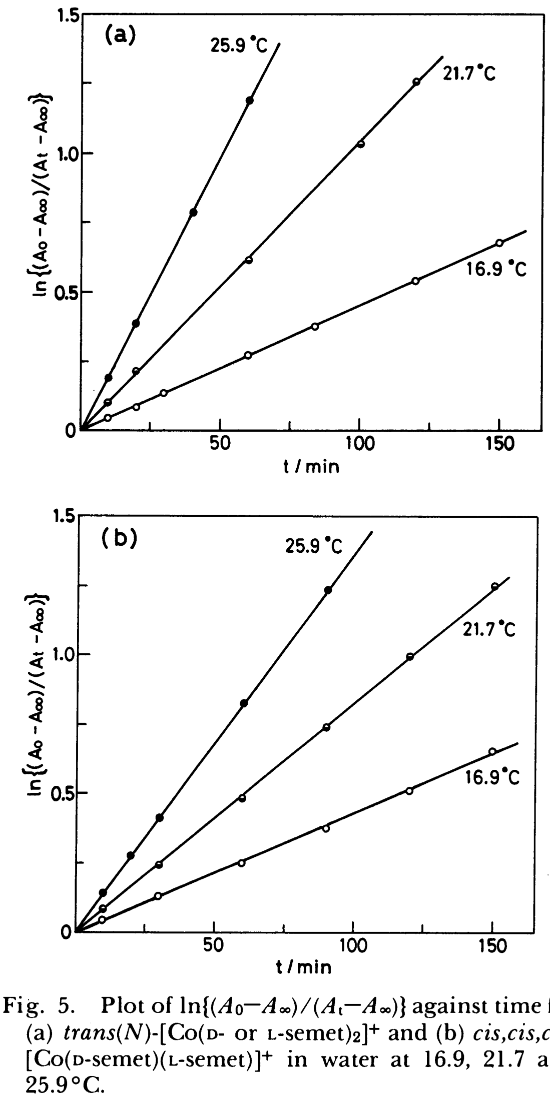

Fig. 5. Plot of $\ln\{(A_0-A_\infty)/(A_t-A_\infty)\}$ against time for (a) *trans*(*N*)-[Co(D- or L-semet)$_2$]$^+$ and (b) *cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ in water at 16.9, 21.7 and 25.9 °C.

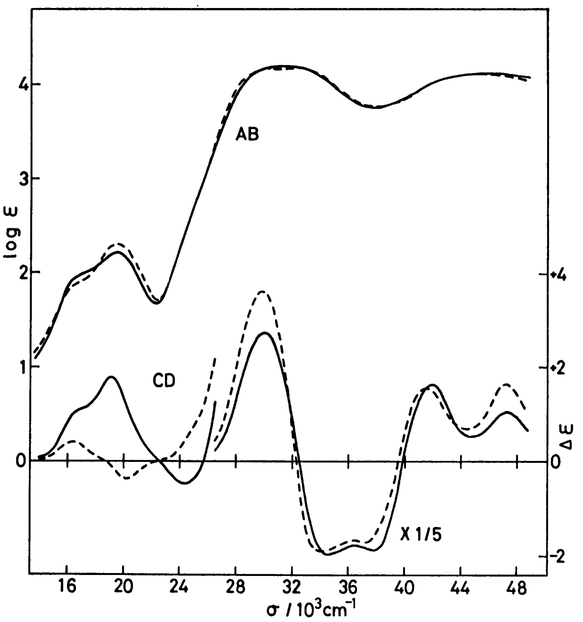

Fig. 6. Absorption and CD spectra of the $(+)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(L-semet)$_2$]$^+$: initial state (----) and equilibrium state (——).

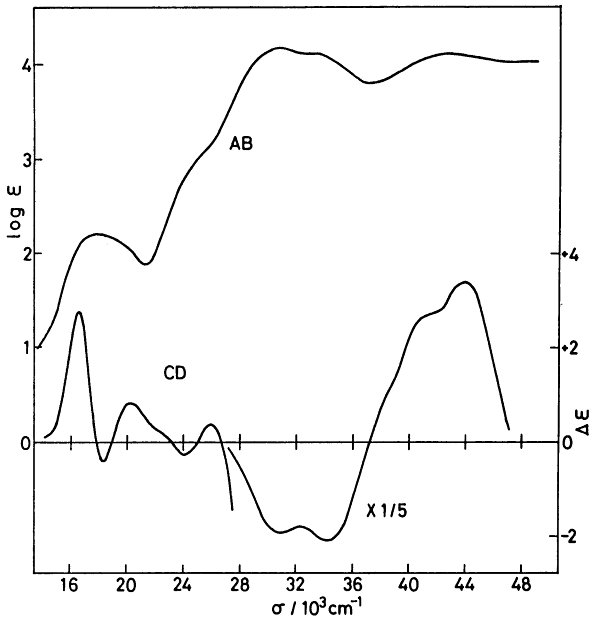

Fig. 8. Absorption and CD spectra of the $(+)^{\mathrm{CD}}_{600}$-*trans*(*O*)-[Co(L-semet)$_2$]$^+$.

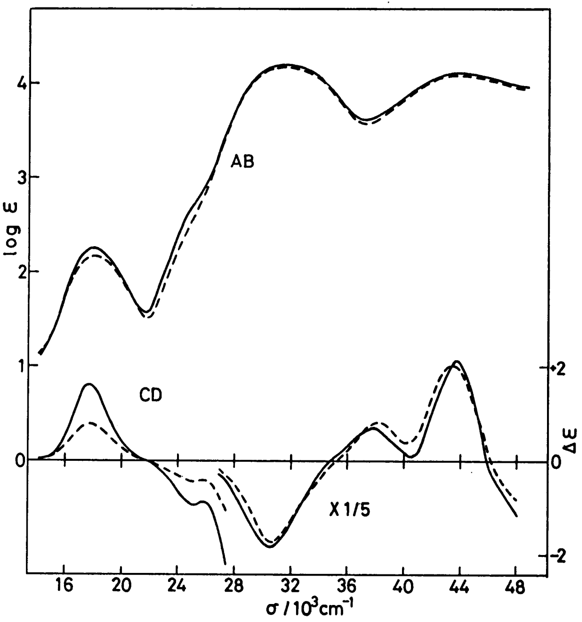

Fig. 7. Absorption and CD spectra of the $(+)^{\mathrm{CD}}_{550}$-[*S*]-*cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$: initial state (----) and equilibrium state (——).

mechanism may resemble each other, a somewhat overvalued differences in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ between the trans(N) and cis,cis,cis isomers seems to reflect the difference in the stereochemistry around the selenium donor atoms during the kinetic processes, as mentioned about the ^{1}H NMR spectral behavior. Namely, the difference in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ seems to associate with the steric effect and rotational freedom for the methyl group on the selenium donor atom on going from the initial to the transitional state.

CD Spectra. The CD spectra at equilibrium of $(+)^{\mathrm{CD}}_{600}$-*trans*(*O*)- and $(+)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(D- or L-semet)$_2$]$^+$, and $(+)^{\mathrm{CD}}_{550}$-*cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ are shown in Figs. 6—8, together with those of the trans(N) and cis,cis,cis isomers just after dissolved in water, and their spectral data are summarized in Table 4. In the equilibrium state, the $(+)^{\mathrm{CD}}_{500}$-trans(N) isomer exhibits a quite similar CD spectral pattern in the whole region to *trans*(*N*)-[Co(L-met)$_2$]$^+$ (Fig. 6),[2] the $(+)^{\mathrm{CD}}_{550}$-cis,cis,cis isomer to [*S*]-*cis,cis,cis*-[Co(D-met)(L-met)]$^+$ [12] and -[Co(D-smp)(L-smp)]$^+$ (Fig. 7),[5] and the $(+)^{\mathrm{CD}}_{600}$-trans(O) isomer to *trans*(*O*)-[Co(L-met)]$^+$ (Fig. 8).[2] The CD bands of the semet isomers shift to the lower energy in the d-d transition and ligand to metal charge-transfer band regions than those of the corresponding met isomers as in the case of their absorption spectral behavior. These are in line with the fact that the CD spectra of the selenolato, selenenato, and selenoether cobalt(III) complexes shift to a lower energy than those of the corresponding thiolato, sulfenato, and thioether complexes.[8,9] These facts support that the present isomers are assigned to $(+)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(L-semet)$_2$]$^+$, $(+)^{\mathrm{CD}}_{550}$-[*S*]-*cis,cis,cis*-[Co(D-semet)-(L-semet)]$^+$, and $(+)^{\mathrm{CD}}_{600}$-*trans*(*O*)-[Co(L-semet)$_2$]$^+$, respectively.

For $(+)^{\mathrm{CD}}_{500}$-*trans*(*N*)-[Co(L-semet)$_2$]$^+$ and $(+)^{\mathrm{CD}}_{550}$-[*S*]-*cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$, the CD spectral changes, which are accompanied by their absorption and ^{1}H NMR spectral changes, were observed at room temperature (Figs. 6 and 7). These CD spectral changes seem to correspond with the equations (1b) and (2b). It is noteworthy that the CD pattern of the trans(N) isomer changes drastically with time and the

Table 4. CD Spectral Data of Equilibrium State for [Co(L-semet)$_2$]$^+$ and [Co(D-semet)(L-semet)]$^+$

Complex	d–d band region	Charge transfer band region
(+)$^{\text{CD}}_{500}$-*trans*(*N*)-[Co(L-semet)$_2$]$^+$	17.15(+1.12 sh)	30.12(+13.58)
	19.15(+1.80)	34.60(−9.92)
	24.51(−0.48)	38.02(−9.56)
		42.02(+8.24)
		47.17(+5.29)
(+)$^{\text{CD}}_{600}$-*trans*(*O*)-[Co(L-semet)$_2$]$^+$	16.50(+2.78)	30.86(−9.72)
	18.32(−0.44)	34.01(−10.47)
	20.20(+0.84)	41.15(+13.46 sh)
	24.04(−0.28)	43.86(+17.05)
	25.91(+0.38)	
(+)$^{\text{CD}}_{550}$-[*S*]-*cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$	17.70(+1.60)	30.49(−9.16)
	25.13(−0.95)	37.74(+3.45)
		43.67(+10.63)

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

CD spectrum exhibited the isodichroic point at 441.5 nm, without the change in the region of 27—46×10^3 cm^{-1} (Fig. 6). A similar CD spectral change was also observed for the cis,cis,cis isomer in the d-d transition band region (the isodichroic point at 458 nm) (Fig. 7). Judging from the investigations of the ^{1}H NMR and absorption spectral changes mentioned above, the CD spectra of initial state and equilibrium one for *trans*(*N*)-[Co(L-semet)$_2$]$^+$ suggest the change from the S(Se)$_\text{L}$,S(Se)$_\text{L}$ configuration to the mixture of the R(Se)$_\text{L}$,S(Se)$_\text{L}$ and S(Se)$_\text{L}$,S(Se)$_\text{L}$ configurations, and [*S*]-*cis,cis,cis*-[Co(D-semet)(L-semet)]$^+$ from the S(Se)$_\text{D}$,S(Se)$_\text{L}$ configuration to the mixture of S(Se)$_\text{D}$,R(Se)$_\text{L}$ and S(Se)$_\text{D}$,S(Se)$_\text{L}$ configurations. The results in this work indicate that the change of the configuration of the asymmetric selenium atoms contributes remarkably to the absorption and CD spectra in the d-d transition band region and differs significantly from the stereochemical behavior of the asymmetric sulfur atom in the methioninato complex.[2,13]

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6) [Co(D- or L-semet)$_2$]$^+$ denotes [Co(D-semet)$_2$]$^+$ and [Co(L-semet)$_2$]$^+$ are mixed in equal amount.

7) The racemic selenomethionine was obtained from the Sigma Chemical Company.

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