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Inversion at Selenium in $[M^{III}(RSeCH_2CH_2NH_2)\{N(CH_2CH_2NH_2)_3\}]^{3+}$ (M^{III}=Co, Rh; R=CH_3, CH_3CH_2, $C_6H_5CH_2$) and $[Co(CH_3SeCH_2COO)\{N(CH_2CH_2NH_2)_3\}]^{2+}$

Kiyohiko Nakajima, Katsuhiko Tozaki, Masaaki Kojima, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464

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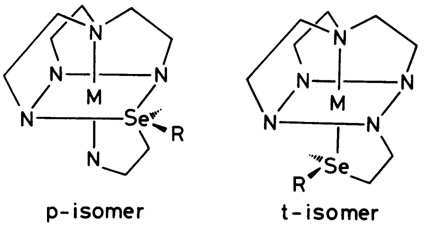
The selenoether (selenide) complexes, *t*-$[Co(RSeCH_2CH_2NH_2)(tren)]^{3+}$ (*t=trans(tertiary amine nitrogen, Se)*; R=CH_3, CH_3CH_2, $C_6H_5CH_2$; tren=tris(2-aminoethyl)amine), *p*-$[Rh(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ (*p=cis-(tertiary amine nitrogen, Se)*), and *t*-$[Co(CH_3SeCH_2COO)(tren)]^{2+}$ were prepared and resolved for the first time by the chemical or SP-Sephadex column chromatographic method. Racemization of these complexes in aqueous solutions was studied at an ionic strength of 0.25 ($NaClO_4$) in the pH and temperature ranges of 4.00—6.91 and 0.25—33.50 °C, respectively. The racemization rates were independent of pH and an intramolecular inversion mechanism was suggested. The $\Delta G^{\neq}_{25\,°C}$ values for inversion of *t*-$[Co(RSeCH_2CH_2NH_2)(tren)]^{3+}$ decreases in the order of CH_3 (95.2 kJ mol^{-1})>CH_3CH_2 (89.4)>$C_6H_5CH_2$ (87.7), while the $\Delta H^{\neq}$ values are almost the same (95—97 kJ mol^{-1}). The variable-temperature ^{13}C NMR study of *p*-$[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ yielded the inversion rate constant, 10 s^{-1} at the coalescence temperature (*ca.* 60 °C), which is much larger than that of the corresponding *t*-isomer (8.5×10^{-3} s^{-1} at 60 °C). The difference in inversion rate between the isomers seems to be related to the steric crowding around the Se-R group of the complex. The rhodium(III) complex racemizes slower than the corresponding cobalt(III) complex. The values of thermodynamic parameters for *t*-$[Co(CH_3SeCH_2COO)(tren)]^{2+}$ are nearly the same as those for *t*-$[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$.

Many sulfonium ions have been resolved and the racemization can be followed in solution by conventional techniques such as polarimetry.[1] The activation energy for inversion has been reported to be 105—120 kJ mol^{-1}, and larger values are to be expected for inversion at selenium in analogous selenonium ions.[1] It is known that both thioethers (sulfides) and selenoethers (selenides) form metal complexes formally analogous to sulfonium and selenonium ions, respectively. However, activation energy for inversion at the sulfur and selenium donor atoms in metal complexes is much smaller than that for their organic counterparts.[2] For example, the rates of inversion at sulfur and selenium in the Pd^{II}, Pt^{II}, and Pt^{IV} complexes have been reported to be in the range of 10^4—10^{-1} s^{-1} by the ^1H or ^{13}C dynamic NMR method.[2] Thus, neither optically active thioether nor selenoether complexes, in which the sulfur or selenium atom is the sole source of optical activity, have been reported.

Studies on chiral cobalt(III)-thioether complexes,[3,4] on the other hand, suggest that the rate of inversion at sulfur in these complexes is slower than those for the Pd^{II}, Pt^{II}, and Pt^{IV} complexes. Since inversion at a coordinated selenoether site will be slower than that at a corresponding thioether site,[1] a selenoether ligand coordinated to cobalt(III) would be fairly stable toward inversion and might permit optical activity.

This paper reports resolution, characterization, and kinetic studies on inversion of *p*-$[M^{III}(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ [5] (M^{III}=Co, Rh; tren=tris(2-aminoethyl)amine), *t*-$[Co(RSeCH_2CH_2NH_2)(tren)]^{3+}$ [5] (R=CH_3, CH_3CH_2, $C_6H_5CH_2$), and *t*-$[Co(CH_3SeCH_2COO)(tren)]^{2+}$ (Fig. 1). In these complexes, the configuration of the selenium atom is the sole source of chirality. A preliminary report on $[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ has been published.[6]



p-isomer t-isomer

Fig. 1. Two geometrical isomers of $[M(RSeCH_2CH_2NH_2)(tren)]^{3+}$.

Experimental

Materials. *p*-$[Co(SeCH_2CH_2NH_2)(tren)](ClO_4)_2$,[6,7] *t*-$[Co(SeCH_2CH_2NH_2)(tren)]ZnCl_4\cdot2H_2O$,[6,7] and *p*-$[Rh(SeCH_2CH_2NH_2)(tren)](ClO_4)_2$[7] were prepared as described earlier.

p-*$[Co(CH_3SeCH_2CH_2NH_2)(tren)]Cl_3\cdot2.5H_2O$.* This complex was prepared by methylating *p*-$[Co(SeCH_2CH_2NH_2)(tren)](ClO_4)_2$ according to the procedure analogous to that for *p*- and *t*-$[Co(CH_3SCH_2CH_2NH_2)(tren)]^{3+}$.[3] To a dimethyl sulfoxide (DMSO) solution (50 cm^3) of *p*-$[Co(SeCH_2CH_2NH_2)(tren)](ClO_4)_2$ (2.64 g, 5 mmol) was added CH_3I (7.10 g, 50 mmol). Within a few minutes the color of the solution changed from dark brown to orange-red. The solution was allowed to stand for 5 h at room temperature, diluted with 1×10^{-3} mol dm^{-3} HCl (500 cm^3), and the excess CH_3I was extracted with $CHCl_3$ (150 cm$^3\times2$). The orange-red aqueous layer was applied on a column (ϕ1.5 cm$\times$2 cm) of SP-Sephadex C-25. The adsorbed product was washed with water, and then eluted with 1 mol dm^{-3} $NaClO_4$. The effluent was evaporated under reduced pressure to yield red crystals of the perchlorate of the complex (2.5 g). The complex was converted into the chloride by use of a column (ϕ1.5 cm$\times$6 cm) of Dowex 1X8 (Cl^- form). The effluent containing the chloride was evaporated to a small volume. On addition of ethanol the concentrate yielded red fine crystals, which were collected by filtration and recrystallized from water by adding ethanol. Yield: 0.8 g. Found: C, 21.84; H, 6.69; N, 14.36%. Calcd for $C_9H_{32}N_5Cl_3CoO_{2.5}Se$: C, 21.85; H, 6.52; N, 14.16%.

t-*$[Co(CH_3SeCH_2CH_2NH_2)(tren)]Br_3\cdot H_2O$,* t-*$[Co(CH_3CH_2$-*

SeCH$_2$CH$_2$NH$_2$)(tren)]Br$_3$·4H$_2$O, and t-*[Co(C$_6$H$_5$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]Cl$_3$·2H$_2$O.* These complexes were prepared from *t*-[Co(SeCH$_2$CH$_2$NH$_2$)(tren)]ZnCl$_4$·2H$_2$O and an appropriate alkylating reagent (CH$_3$I, CH$_3$CH$_2$I, and C$_6$H$_5$CH$_2$Br) by a method similar to that for *p*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]Cl$_3$·2.5H$_2$O. The CH$_3$-, CH$_3$CH$_2$-, and C$_6$H$_5$CH$_2$-substituted complexes adsorbed on SP-Sephadex C-25 were eluted with 1 mol dm^{-3} NaBr, LiBr, and LiCl, respectively. Each eluate was concentrated to a small volume, and then mixed with ethanol, yielding crystals of the complex. Yields: 80—98%. Found: C, 17.95; H, 5.04; N, 11.99%. Calcd for C$_9$H$_{29}$N$_5$Br$_3$CoOSe: C, 17.98; H, 4.86; N, 11.65%. Found: C, 17.71; H, 4.93; N, 10.32%. Calcd for C$_{10}$H$_{37}$N$_5$Br$_3$CoO$_4$Se: C, 17.95; H, 5.57; N, 10.46%. Found: C, 32.11; H, 5.92; N, 12.85%. Calcd for C$_{15}$H$_{35}$N$_5$Cl$_3$CoO$_2$Se: C, 32.07; H, 6.28; N, 12.47%.

p-*[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]X$_3$ (X=Br, ClO$_4$).* This complex was prepared from *p*-[Rh(SeCH$_2$CH$_2$NH$_2$)(tren)](ClO$_4$)$_2$ and CH$_3$I by the same method as that described for *p*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$, and isolated as the bromide and the perchlorate. Yields: 80—85%. Found: C, 17.43; H, 4.37; N, 11.14%. Calcd for C$_9$H$_{27}$N$_5$Br$_3$RhSe: C, 17.24; H, 4.34; N, 11.17%. Found: C, 15.67; H, 4.30; N; 10.50%. Calcd for C$_9$H$_{27}$N$_5$Cl$_3$O$_{12}$RhSe: C, 15.77; H, 3.97; N, 10.22%.

t-*[Co(SeCH$_2$COO)(tren)]Cl and* t-*[Co(CH$_3$SeCH$_2$COO)(tren)](ClO$_4$)$_2$.* The *t*-[Co(SeCH$_2$COO)(tren)]Cl complex was prepared by a method analogous to that for [Co(SeCH$_2$COO)(en)$_2$]$^{+}$[8] (en=ethylenediamine). Time required for the oxidation of Co$^{\mathrm{II}}$-N$_4$ (N$_4$=tren or (en)$_2$) species with the diselenide, (HOOCCH$_2$Se-)$_2$[9] was longer for the tren complex than that for the en complex. To a deoxygenated aqueous solution (5 cm^3) of CoCl$_2$·6H$_2$O (2.20 g, 6.0 mmol) was added a deoxygenated aqueous solution (9 cm^3) containing tren·3HCl (1.53 g, 6.0 mmol) and NaOH (0.72 g, 18.0 mmol). The color of the solution changed from light red to violet. Then a deoxygenated aqueous solution (10 cm^3) containing (HOOCCH$_2$Se-)$_2$ (0.828 g, 3.0 mmol) and NaOH (0.24 g, 6.0 mmol) was added to the solution and the mixture was allowed to stir for 5 days under a nitrogen atmosphere. The color of the solution changed from violet to dark brown and brown fine crystals were deposited. The crystals were collected by filtration, washed with ethanol, and air dried. Yield: 0.18 g. No evidence indicative of the presence of the other isomer was obtained either in the ^{1}H NMR spectrum of the isolated complex or by column chromatography (column: SP-Sephadex C-25; eluent: 0.05 mol dm^{-3} Na$_2$SO$_4$) of the reaction mixture. The complex was used for the subsequent reaction without any purification.

The complex was methylated by the same method as that for *p*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$, and the product was isolated as the perchlorate. Yield: 65%. Found: C, 19.44; H, 4.17; N, 10.08%. Calcd for C$_9$H$_{23}$N$_4$Cl$_2$CoO$_{10}$Se: C, 19.37; H, 4.16; N, 10.10%. The bromide of the complex was obtained from the perchlorate by means of Dowex 1X8 (Br$^-$ form).

Resolution of the Complexes. All the complexes except for *p*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ were partially resolved. Complete resolution of the complexes was not attempted because they are likely to racemize.

$(-)^{CD}_{480}$-t-*[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]Br$_3$·1.5H$_2$O.* To an aqueous solution (2 cm^3) of *t*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]Br$_3$·H$_2$O (0.21 g, 3.43 mmol) was added Ag$_2$[Sb$_2$(*d*-tart)$_2$] (0.258 g, 3.43 mmol, *d*-tart=(*R*,*R*)-tartrate ion). The silver bromide precipitated was removed by filtration, and the filtrate was slowly evaporated to dryness over P$_2$O$_5$ in a vacuum desiccator to yield a glassy material, which was broken up, suspended in ethanol, filtered, and washed with ethanol. The product was dissolved in a small amount of cold water. To the solution was added sodium tetraphenylborate to give a precipitate immediately. It was filtered, washed with water, and dissolved in a small amount of acetone. To this solution was added excess LiBr followed by addition of ethanol to yield an orange-red precipitate. It was collected by filtration, washed with ethanol, and air dried. Yield: 0.10 g. Found: C, 17.37; H, 4.85; N, 11.62%. Calcd for C$_9$H$_{30}$N$_5$Br$_3$CoO$_{1.5}$Se: C, 17.19; H, 5.04; N, 11.99%.

t-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ was also partially resolved by column chromatography. An aqueous solutoin of the complex (*ca.* 70 mg) was charged on the top of an SP-Sephadex C-25 column (ϕ2 cm×30 cm). By elution with 0.15 mol dm^{-3} Na$_2$[Sb$_2$(*d*-tart)$_2$], the column showed a single band, however, the front and the tail fractions of the band showed enantiomeric CD patterns.

$(-)^{CD}_{480}$-t-*[Co(CH$_3$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$, $(-)^{CD}_{475}$*-t-*[Co(C$_6$H$_5$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$, and $(-)^{CD}_{330}$*-p-*[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$.* The racemic complexes were resolved by the same method as that for $(-)^{\mathrm{CD}}_{480}$-*t*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ except that AgBCS·H$_2$O (BCS=(*1R,3S,4S,7R*)-3-bromo-9-camphorsulfonate ion) was used ([complex]:[BCS$^-$]=1:1) instead of Ag$_2$[Sb$_2$(*d*-tart)$_2$] for the former two complexes. The BCS$^-$ and [Sb$_2$(*d*-tart)$_2$]$^{2-}$ ions were not converted into achiral anions such as Cl$^-$, because these complexes racemize rather fast in solution.

$(-)^{CD}_{475}$- and $(+)^{CD}_{475}$-t-*[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$.* The racemic complex was resolved with AgBCS·H$_2$O([complex]:[BCS$^-$]=1:2) by a method similar to that for $(-)^{\mathrm{CD}}_{480}$-*t*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$. The silver bromide precipitated was filtered off, and the filtrate was evaporated over P$_2$O$_5$ in a vacuum desiccator to yield fine crystals consisting of two different colors, pink and deep orange-red. The two kinds of crystals which show enantiomeric CD patterns were separated by hand picking. The pink $(-)^{\mathrm{CD}}_{475}$-isomer was converted into the perchlorate by the same method as that for $(-)^{\mathrm{CD}}_{480}$-*t*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]Br$_3$·1.5H$_2$O except that LiClO$_4$·3H$_2$O was used instead of LiBr.

Racemization Studies. Rates of racemization were determined by monitoring the change in CD strength at 480 nm (*t*-[Co(RSeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$; R=CH$_3$, CH$_3$CH$_2$), 475 nm (*t*-[Co(C$_6$H$_5$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ and *t*-[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$), and 330 nm (*p*-[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$) as a function of reaction time. The complex concentrations were *ca.* 10^{-3} mol dm^{-3}, and the measurements were made at an ionic strength of 0.25 (NaClO$_4$) and in the pH and temperature ranges of 4.00—6.91 and 0.25—33.50 °C, respectively. The inversion rate of *p*-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ was determined by monitoring the change in the ^{13}C NMR spectrum in the temperature range of 30—60 °C.

Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. ^{13}C NMR spectra were obtained in D$_2$O with a JEOL FX-60 FT NMR spectrometer using dioxane as an internal reference.

Results and Discussion

Preparation, Partial Resolution, and Characterization

TABLE 1. ABSORPTION SPECTRAL DATA OF THE COMPLEXES

Complex	$\tilde{\nu}_{\mathrm{max}}/\mathrm{cm}^{-1}$	$\log(\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1})$
p-$[\mathrm{Co(CH_3SeCH_2CH_2NH_2)(tren)}]^{3+}$	20120	2.29
	32700	4.01
	42550	4.14
t-$[\mathrm{Co(CH_3SeCH_2CH_2NH_2)(tren)}]^{3+}$	20280	2.17
	32800	4.15
	45500	4.16[a)]
t-$[\mathrm{Co(CH_3CH_2SeCH_2CH_2NH_2)(tren)}]^{3+}$	20240	2.16
	32700	4.14
	44500	4.14[a)]
t-$[\mathrm{Co(C_6H_5CH_2SeCH_2CH_2NH_2)(tren)}]^{3+}$	20140	2.24
	31950	4.22
	44250	4.33
t-$[\mathrm{Co(CH_3SeCH_2COO)(tren)}]^{2+}$	20160	2.14
	33000	4.09
	44800	4.09
p-$[\mathrm{Rh(CH_3SeCH_2CH_2NH_2)(tren)}]^{3+}$	31650	2.87
	41500	4.09

a) Shoulder.

of the Complexes. The selenoether complexes of cobalt(III) and rhodium(III) were prepared by alkylating the corresponding selenolato complexes with the appropriate alkyl halides. The reactions proceeded almost quantitatively. Column chromatography of the reaction mixtures showed a single band, and the selenoether complexes thus obtained should have the same geometrical configurations as those of the respective parent selenolato complexes. The geometrical configurations of $[\mathrm{Co(SeCH_2CH_2NH_2)(tren)}]^{2+}$ have been assigned on the basis of the elution order in column chromatography.[6,7)] The structure of the rhodium(III) complex, p-$[\mathrm{Rh(SeCH_2CH_2NH_2)(tren)}](\mathrm{ClO_4})_2$ has been determined by the X-ray method.[7)]

The first d-d absorption band of t-$[\mathrm{Co(RSeCH_2CH_2NH_2)(tren)}]^{3+}$ shifts to lower energy as R is changed from $\mathrm{CH_3}$ through $\mathrm{CH_3CH_2}$ to $\mathrm{C_6H_5CH_2}$ (Table 1).

Both p- and t-isomers of $[\mathrm{Co(RSeCH_2CH_2NH_2)(tren)}]^{3+}$ exhibit a strong Se to $\mathrm{Co^{III}}$ charge-transfer (CT) band at 32000—33000 cm^{-1}, while the rhodium(III) complex gives the corresponding band at 41500 cm^{-1}. The positions of the CT bands are nearly the same as those for the parent selenolato complexes.[7)]

The $[\mathrm{Co(CH_3SeCH_2COO)(tren)}]^{2+}$ complex forms one geometrical isomer as confirmed by chromatography and ^{1}H NMR spectroscopy. The corresponding thioether complex, $[\mathrm{Co(CH_3SCH_2COO)(tren)}]^{2+}$ and analogous $[\mathrm{Co\{CH_3SCH(CH_3)COO\}(tren)}]^{2+}$ also form one geometrical isomer,[10)] and the structure of the latter complex has been determined to have the t-configuration by X-ray analysis.[11)] These thioether complexes show the first absorption band ($[\mathrm{Co(CH_3SCH_2COO)(tren)}]^{2+}$: 20620 cm^{-1}, $[\mathrm{Co\{CH_3SCH(CH_3)COO\}(tren)}]^{2+}$: 20640 cm^{-1}) between those of the p-(20530 cm^{-1}) and t-isomer (20790 cm^{-1}) of $[\mathrm{Co(CH_3SCH_2CH_2NH_2)(tren)}]^{3+}$.[10)] The first absorption band (20160 cm^{-1}) of $[\mathrm{Co(CH_3SeCH_2COO)(tren)}]^{2+}$ is also observed between the p-(20120 cm^{-1}) and t-isomer (20280 cm^{-1}) of $[\mathrm{Co(CH_3SeCH_2CH_2NH_2)(tren)}]^{3+}$. Selective formation of the thio and selenoether complexes and similarities in absorption spectra between these complexes will strongly support that the present $[\mathrm{Co(CH_3SeCH_2COO)(tren)}]^{2+}$ complex is the t-isomer.

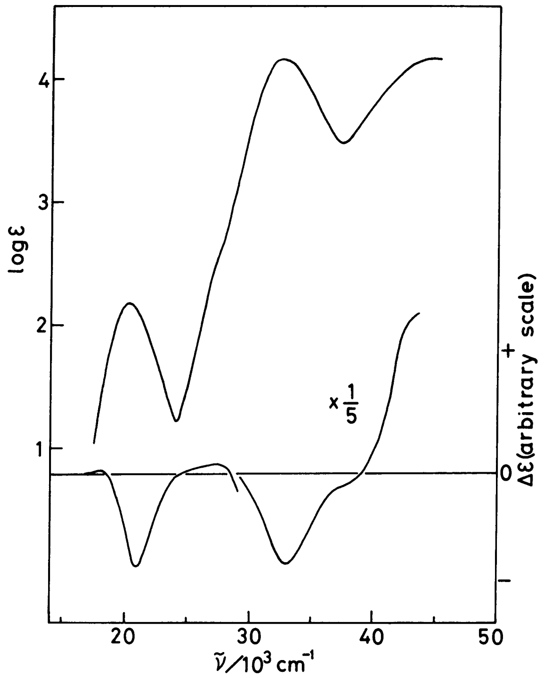


Fig. 2. Absorption and CD spectra of $(-)^{\mathrm{CD}}_{480}$-t-$[\mathrm{Co(CH_3SeCH_2CH_2NH_2)(tren)}]\mathrm{Br_3}\cdot1.5\mathrm{H_2O}$ in water.

The t-$[\mathrm{Co(RSeCH_2CH_2NH_2)(tren)}]^{3+}$ and p-$[\mathrm{Rh(CH_3SeCH_2CH_2NH_2)(tren)}]^{3+}$ complexes were partially resolved with $[\mathrm{Sb_2}(d\text{-tart})_2]^{2-}$ or BCS$^-$. The crystalline or glassy product obtained by slow evaporation of an aqueous solution containing the complex and the resolving agent shows strong CD in the d-d transition region when dissolved in water. The result indicates that the inversion occurs at selenium to form a less soluble diastereomer during slow evaporation. However, rates of inversion are moderately slow as discussed below. In the case of $[\mathrm{Co(CH_3SeCH_2COO)(tren)}](\mathrm{BCS})_2$, the pair of diastereomeric salts crystallized in different forms, which can be separated by hand picking.

All the resolved complexes show CD spectra similar or almost enantiomeric to that of $(-)^{\mathrm{CD}}_{480}$-t-$[\mathrm{Co(CH_3SeCH_2CH_2NH_2)(tren)}]^{3+}$ (Fig. 2). At present, the absolute configurations of selenium atoms in these tren complexes can not be assigned on the basis of the CD spectra. An analogous thioether complex, $(-)_{589}$-S(S),R(C)-t-$[\mathrm{Co\{CH_3SCH(CH_3)COO\}(tren)}]^{2+}$, whose absolute configuration has been determined by the X-ray method,[11)] exhibits a positive CD band in the S to $\mathrm{Co^{III}}$ CT band region (34000 cm^{-1}). On the other hand, Δ-$[\mathrm{Co(CH_3SCH_2CH_2NH_2)(en)_2}]^{3+}$[12)] and Δ-$[\mathrm{Co(CH_3SCH_2CH_2CH_2NH_2)(en)_2}]^{3+}$[13)] (en=ethylenediamine), in which both sulfur donor atoms are considered to have the same R configuration to reduce nonbonded interactions between the methyl group and the en chelate ring, also show a positive CD band in the corresponding CT region (35000 cm^{-1}). These results make

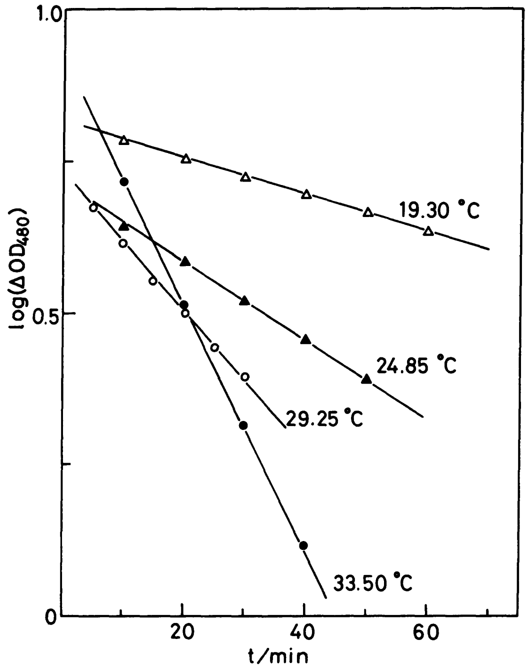


Fig. 3. Plot of log(ΔOD_{480}) against time for $(-)^{\mathrm{CD}}_{480}$-*t*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]$Br_3 \cdot 1.5H_2O$ in water (I=0.25, $NaClO_4$) at 19.30, 24.85, 29.25, and 33.50 °C.

the assignment of the absolute configurations for chiral selenium donor atoms difficult.

Inversion at the Coordinated Selenium Atom. Rates of inversion at selenium of the resolved complexes were determined by monitoring the change in CD strength as a function of time. Measurements were carried out over the temperature range of 0.25 to 33.50 °C in the pH region of 4.00 to 6.91. The CD strength at 480 nm of $(-)^{\mathrm{CD}}_{480}$-*t*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]Br_3 in water (I=0.25, $NaClO_4$) at a constant temperature decreases with time, and the plot of log(ΔOD_{480}) against time gave a straight line (Fig. 3), from which the first-order rate constants of racemization, k_r and inversion, $k_{\mathrm{inv}}=k_r/2$ were obtained. No detectable change in the absorption spectra was observed during the measurements.

Except for *t*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]$^{3+}$ and *t*-[Co(CH_3SeCH_2COO)(tren)]$^{2+}$ the optically active complexes were obtained as the diastereomeric salt with a resolving agent, and conversion into salts with achiral counter ions, was difficult because of racemization. Therefore, the effect of resolving agent on the rate of inversion should be taken into consideration. The inversion rate of $(-)^{\mathrm{CD}}_{480}$-*t*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)] Br[Sb_2(*d*-tart)$_2$] was compared with that of the bromide salt. The Br^-[Sb_2(*d*-tart)$_2$]$^{2-}$ salt in water shows the same CD pattern as the bromide in the d-d transition region, and the CD strength decreases with passage of time. However, the solution shows weak CD (residual CD) even after the reaction attained equilibrium, and the pattern of the CD spectrum is almost the same as that of the starting solution. On the other hand, a solution of racemic [Co($CH_3SeCH_2CH_2NH_2$)(tren)]Br_3 in 0.15 mol dm^{-3} Na_2[Sb_2(*d*-tart)$_2$] exhibits very weak CD (induced CD) immediately after dissolution of the complex, and the spectral pattern differs from that of the above residual CD. However, the spectrum gradually changes and finally gives the same pattern as that of the residual CD. These results indicate that the residual CD arises primarily from a shift of equilibrium between the (*R*)- and (*S*)-isomers caused by the presence of [Sb_2(*d*-tart)$_2$]$^{2-}$, contribution of the induced CD being very small. For the reaction of $(-)^{\mathrm{CD}}_{480}$-*t*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]Br[Sb_2(*d*-tart)$_2$], a plot of log ($\Delta OD_{\mathrm{obsd}} - \Delta OD_{\mathrm{res}}$) against time gave a straight line, where $\Delta OD_{\mathrm{obsd}}$ and ΔOD_{res} denote the observed and residual CD strengths, respectively, from which the rate of inversion was obtained (Fig. 4 and Table 2). The rate agrees with that of the corresponding bromide within the experimental error. The CD data for *p*-[Rh($CH_3SeCH_2CH_2NH_2$)(tren)]Br[Sb_2(*d*-tart)$_2$] were analyzed in the same way. For kinetic studies on racemization of *t*-[Co($RSeCH_2CH_2NH_2$)(tren)]$^{3+}$ (R=CH_3CH_2, $C_6H_5CH_2$) and *t*-[Co(CH_3SeCH_2COO)(tren)]$^{2+}$, the BCS^- salts were used. No CD remained after the reaction attained equilibrium, and the inversion rate was obtained from a straight line given by a plot of log(ΔOD) *vs.* time.

Attempts to resolve *p*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]$^{3+}$ by the chemical method with several resolving agents and by SP-Sephadex column chromatography were all unsuccessful. However, the complex exhibits nine signals in the ^{13}C NMR spectrum as shown in Fig. 5. The diastereotopic carbon resonances of the tren ligand (1,3 and 4,6 carbons in Fig. 5) arising from the presence

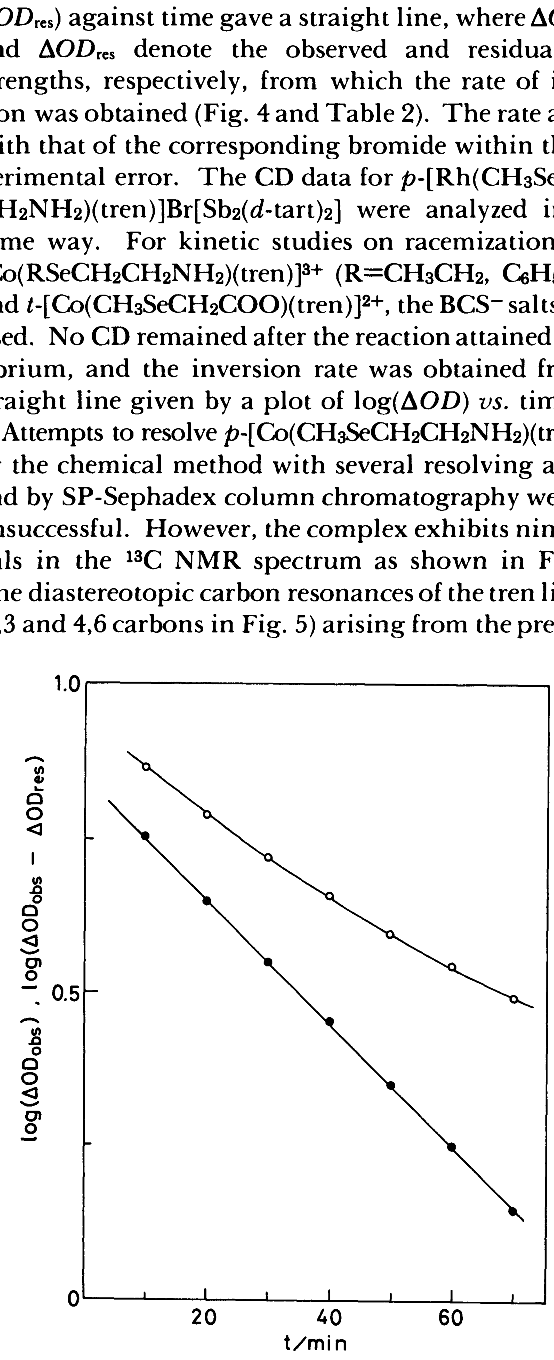


Fig. 4. Plots of log($\Delta OD_{\mathrm{obsd}}$) *vs.* *t* (○) and log ($\Delta OD_{\mathrm{obsd}} - \Delta OD_{\mathrm{res}}$) *vs.* *t* (●) for $(-)^{\mathrm{CD}}_{480}$-*t*-[Co($CH_3SeCH_2CH_2NH_2$)(tren)]Br[Sb_2(*d*-tart)$_2$] in water (I= 0.25, $NaClO_4$) at 28.25 °C.

TABLE 2. RATE CONSTANTS FOR INVERSION OF THE COMPLEXES

Complex	t/°C	k_{inv}/s^{-1}
t-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	19.30	$(0.58\pm0.01)\times10^{-4}$
	24.85	$(1.25\pm0.03)\times10^{-4}$
	29.25	$(2.19\pm0.05)\times10^{-4}$
	33.50	$(3.86\pm0.03)\times10^{-4}$
t-[Co(CH$_3$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	4.37	$(0.73\pm0.01)\times10^{-4}$
	8.10	$(1.24\pm0.01)\times10^{-4}$
	12.25	$(2.31\pm0.02)\times10^{-4}$
	15.80	$(3.84\pm0.02)\times10^{-4}$
t-[Co(C$_6$H$_5$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	0.25	$(0.75\pm0.02)\times10^{-4}$
	4.15	$(1.40\pm0.02)\times10^{-4}$
	8.15	$(2.44\pm0.03)\times10^{-4}$
	12.10	$(4.58\pm0.04)\times10^{-4}$
t-[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$	19.10	$(0.59\pm0.01)\times10^{-4}$
	24.12	$(1.16\pm0.01)\times10^{-4}$
	28.80	$(2.13\pm0.01)\times10^{-4}$
	32.83	$(3.62\pm0.02)\times10^{-4}$
p-[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	0.45	$(0.94\pm0.05)\times10^{-4}$
	4.10	$(1.80\pm0.04)\times10^{-4}$
	7.90	$(3.18\pm0.06)\times10^{-4}$
	11.90	$(5.51\pm0.08)\times10^{-4}$
p-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	*ca.*60	10 ± 1

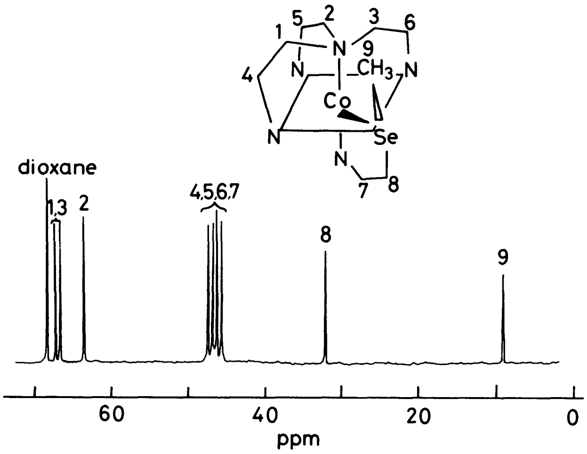


Fig. 5. ^{13}C NMR spectrum of p-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ in D$_2$O at room temperature.

of the chiral selenoether group are clearly resolved at room temperature, demonstrating the stability toward inversion on the NMR time scale. Thus it can be concluded that the inversion at selenium in the p-isomer is slow on the NMR time scale , but not so slow as to be resolved by conventional techniques. With a rise in temperature, the two signals of 1 and 3 carbons broaden and coalesce at *ca.* 60 °C (Fig. 6). Although activation parameters of the inversion could not be obtained because of the instability of the complex at elevated temperatures, the rate at the coalescence temperature (*ca.* 60 °C) is roughly estimated to be *ca.* 10 s^{-1}.

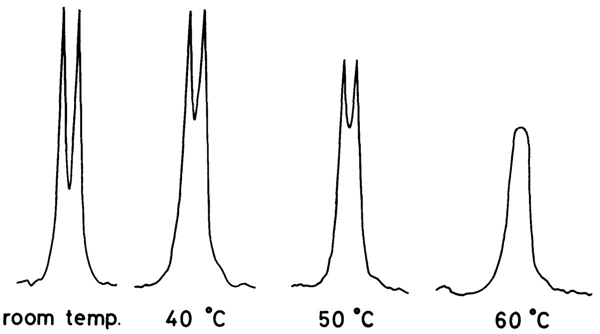


Fig. 6. Variable-temperature ^{13}C NMR spectra of the 1,3-carbon absorption region of p-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ in D$_2$O (See Fig. 5 for carbon numbers).

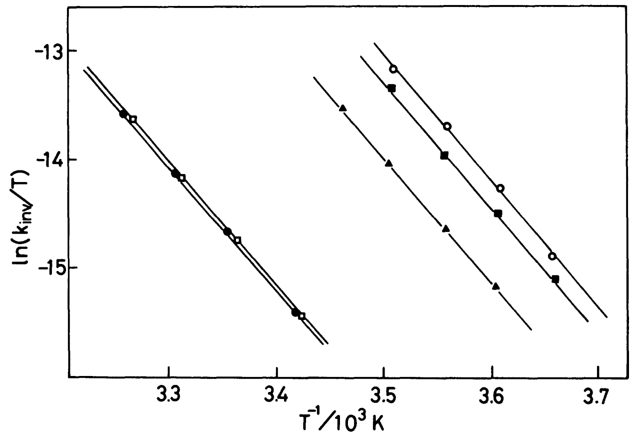


Fig. 7. Plot of log(k_{inv}/T) against T^{-1} for t-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ (●), t-[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$ (◇), t-[Co(CH$_3$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ (▲), t-[Co(C$_6$H$_5$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ (■), and p-[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ (○).

Eyring treatments of log(k_{inv}/T) *vs.* T^{-1} yielded activation parameters (Fig. 7 and Table 3). The rate constant of t-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ at 60 °C is calculated from the $\Delta H^{\ne}$ and $\Delta S^{\ne}$ values to be 8.5×10^{-3} s^{-1}. The value is smaller by a factor of 10^3 than that of the p-isomer at the same temperature. Jackson and Sargeson[3] studied the rates of sulfur inversion in t-[Co(CH$_3$SCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ and related complexes by the NMR method, and revealed that the rates are slow (k_{inv}<10 s^{-1}) on the NMR time scale at 25 °C, but

TABLE 3. THERMODYNAMIC PARAMETERS FOR INVERSION OF THE COMPLEXES

Complex	ΔS^*/J mol^{-1} K^{-1}	ΔH^*/kJ mol^{-1}	$\Delta G^{\ddagger}_{25\,^\circ C}$/kJ mol^{-1}
t-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	3.1±2.2	96.1±0.6	95.2±0.9
t-[Co(CH$_3$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	19.4±3.4	95.2±0.6	89.4±1.4
t-[Co(C$_6$H$_5$CH$_2$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	26.9±5.6	95.7±1.5	87.7±2.2
t-[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$	−0.2±2.2	95.1±1.7	95.1±1.0
p-[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$	35±13	97.6±4.4	87.2±5.9
p-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$			*ca.* 76 (60 °C)

exceeds 0.1 s^{-1}. For example, the ^{13}C NMR spectrum of t-[Co(CH$_3$SCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ showed clearly resolved diastereotopic carbon signals at 25 °C. On the other hand, the corresponding signals for the p-isomer were not resolved under the same conditions. These observations are consistent with our results that the inversion rate of the coordinated selenium atom is faster in the p-isomer than in the t-isomer. A similar trend was reported for sulfur inversion in p- and t-[Co{S(O)CH$_2$CH$_2$NH$_2$}(tren)]$^{2+}$.[14)]

Studies of the variable-temperature NMR spectra of Pt^{II}-thioether and -selenoether complexes revealed the presence of coupling between ^{195}Pt and ^{1}H even above the coalescence temperature.[15,16)] The result suggests that the inversion does not involve breaking of the Pt–S and Pt–Se bonds; pyramidal inversion mechanism is proposed, which proceeds *via* a trigonal planar intermediate.[17)] Although such argument on couplings may not be applied on the present selenoether Co^{III} and Rh^{III} complexes, the facts that the rates of racemization are independent of pH and the presence of resolving agent strongly suggest that the racemization takes place intramolecularly by pyramidal inversion at the selenium atom. If the racemization would proceed by this mechanism, the difference in rate of inversion between the two isomers of [Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ seems to stem from a difference in structure around the Se–R group. Molecular models of [Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ show that the p-isomer involves fairly large steric interactions between the methyl group and the tren chelate ring, whereas the t-isomer does not have such large steric interactions around the Se–CH$_3$ group. In the trigonal planar transition state, on the other hand, both p- and t-isomers seem to have a similar structural situation involving no particular steric interaction around the Se–CH$_3$ group. Accordingly, the p-isomer will have a lower energy barrier for the inversion than that of the t-isomer, and racemizes faster than does the t-isomer.

The ΔG^* values for inversion of t-[Co(RSeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ decrease in the order CH$_3$>CH$_3$CH$_2$>C$_6$H$_5$CH$_2$. The decrease in ΔG^* value comes from an increase in positive ΔS^*, the ΔH^* values being almost constant (95—97 kJ mol^{-1}) in these complexes. It seems that the entropy change associated with inversion arises from the gain of ratational freedom of the substituent on selenium upon going from the ground state to the transition state. Although the t-isomer is sterically preferred in the ground state, the steric interaction in this isomer increases with an increasing size of the substituent, CH$_3$<CH$_3$CH$_2$<C$_6$H$_5$CH$_2$ to reduce the degree of rotational freedom of the substituent on the selenium atom in the ground state (Fig. 8). In the transition state, however, the substituent is far away from the tren chelate ring, and can rotate more easily than in the ground state (Fig. 8). Thus, the difference in degree of freedom between the ground and the transition states becomes larger with an increasing size of the substituent, which is reflected on the ΔS^* values (Table 3).

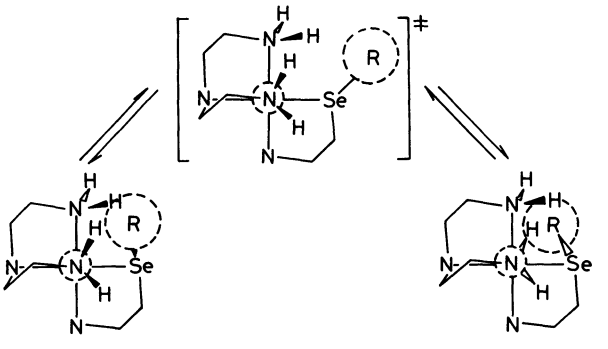


Fig. 8. A proposed mechanism for inversion of t-[Co(RSeCH$_2$CH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ viewed from the p-N-Co-p-N bond axis.

It is to be noted that the activation parameters of t-[Co(CH$_3$SeCH$_2$COO)(tren)]$^{2+}$ are nearly the same as those of t-[Co(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$. The effect of nature of the donor atom cis to selenium on the inversion barriers (cis effect) seems to be small in the present complexes. Similarly equivocal results for the cis effect on sulfur and selenium inversion barriers have been reported on *fac*-[Pt^{IV}XMe$_3${MeE(CH$_2$)$_n$EMe}] (X=Cl, Br, I; E=S, Se; n=2, 3).[18)]

The inversion rate of p-[Rh(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ is calculated to be *ca.* 2.3×10^{-1} s^{-1} at 60 °C from the ΔH^* and ΔS^* values, the rate being much smaller than that of the corresponding cobalt(III) complex (*ca.* 10 s^{-1}) at the same temperature. The difference can be explained by both steric and electronic factors. The M–Se and M–N bond distances should be longer in the Rh^{III} complex than in the Co^{III} complex,[2)] and thus smaller steric interactions are expected for the Rh^{III} complex between the ligands to increase the activation energy for the inversion. The inversion is also related with the M–Se bond strength; the weaker the bond becomes, the faster the inversion occurs.[16)] p-[M(CH$_3$SeCH$_2$CH$_2$NH$_2$)(tren)]$^{3+}$ (M=Co, Rh) seems to be the case; the Rh–Se bond is expected to be stronger than the Co–Se bond because a soft selenium donor atom will prefer Rh^{III} to Co^{III}.

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