November, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* **59,** *3505—3510 (1986)*

Inversion at Selenium in the Bis(β-diketonato)[2-(methylseleno)ethylamine]cobalt(III) Ion

Kiyohiko Nakajima, Masaaki Kojima, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa-ku, Nagoya 464

(Received June 10, 1986)

The selenide (selenoether) complexes, $[\mathrm{Co}(\beta\text{-dik})_2(\mathrm{CH_3SeCH_2CH_2NH_2})]^+$ (β-dik: acac=2,4-pentanedionate, Clacac=3-chloro-2,4-pentanedionate, Meacac=3-methyl-2,4-pentanedionate, and dbme=1,3-diphenyl-1,3-propanedionate) were prepared and separated into two racemic pairs of the diastereomers ($\Delta(R)\Lambda(S)$ and $\Delta(S)\Lambda(R)$ isomers). The complexes in solution epimerize by inversion at the selenium atom, and the rates were followed by high-performance liquid chromatography in the temperature range of 30.3—55.0 °C in 0.05 mol dm^{-3} $\mathrm{Na_2SO_4}$ (acac, Clacac, and Meacac complexes) or in methanol (dbme complex). The $\Delta G^{\ddagger}_{25\,°\mathrm{C}}$ values for inversion of $[\mathrm{Co}(\beta\text{-dik})_2(\mathrm{CH_3SeCH_2CH_2NH_2})]^+$ decrease in the order β-dik=Clacac(108)>acac(106)>dbme(104)>Meacac(100 kJ mol^{-1}), and the decrease in $\Delta G^{\ddagger}_{25\,°\mathrm{C}}$ comes mainly from a decrease in $\Delta H^{\ddagger}$. The effect of substituents is electronic and the Hammett relationship was found to hold for the inversion rates of the acac, Clacac, and Meacac complexes.

The selenium atom of a selenide (RSeR′) ligand becomes chiral on coordination to a metal ion. It has been reported that inversion at a coordinated selenide site is too rapid for the resolution in such complexes as $\mathrm{Pt^{II}}$, $\mathrm{Pt^{IV}}$, and $\mathrm{Pd^{II}}$.[1] In a previous paper, however, we reported that inversion at selenium in $[\mathrm{M^{III}}(\mathrm{RSeCH_2CH_2NH_2})(\mathrm{tren})]^{3+}$ ($\mathrm{M^{III}}$=Co, Rh; R=$\mathrm{CH_3}$, $\mathrm{CH_3CH_2}$, $\mathrm{C_6H_5CH_2}$; tren=tris(2-aminoethyl)amine=$\mathrm{N(CH_2CH_2NH_2)_3}$) is so slow that they can be resolved by conventional methods, and that the inversion rates are dependent on the steric crowding around the Se–R group of the complexes.[2]

In order to investigate the electronic effect on the inversion rate, we have prepared a series of $[\mathrm{Co}(\beta\text{-dik})_2(\mathrm{CH_3SeCH_2CH_2NH_2})]^+$ (β-dik: Clacac=3-chloro-2,4-pentanedionate, Meacac=3-methyl-2,4-pentanedionate, and dbme=1,3-diphenyl-1,3-propanedionate) and studied the inversion kinetics.

A part of this study has been reported briefly.[3,4]

Experimental

$[\mathrm{Co(acac)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{ClO_4}$. This complex was prepared from $[\mathrm{Co(acac)_2(H_2O)_2}]$ and $\mathrm{CH_3SeCH_2CH_2NH_2}$ by the same method as that for $[\mathrm{Co(acac)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{PF_6}$[3] except that $\mathrm{LiClO_4}$ was used instead of $\mathrm{NH_4PF_6}$. Yield: 42%. Found: C,31.71; H, 4.83; N, 2.27%. Calcd for $\mathrm{C_{13}H_{23}NClCoO_8Se}$: C, 31.56; H, 4.69; N, 2.83%.

$[\mathrm{Co(Clacac)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{ClO_4}$. This complex was prepared by chlorination of $[\mathrm{Co(acac)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{ClO_4}$ with *N*-chlorosuccinimide by a method similar to that for $[\mathrm{Co(Clacac)(en)_2}](\mathrm{ClO_4})_2$.[5] To a methanol solution (15 cm^3) of *N*-chlorosuccinimide (0.041 g, 3.07×10^{-4} mol) was added $[\mathrm{Co(acac)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{ClO_4}$ (0.050 g, 1.01×10^{-4} mol), and the solution was stirred for ca. 4 h at room temperature. The reaction mixture was diluted with water (20 cm^3) and applied on a column (ϕ 1.1 cm×6 cm) of SE-Toyopearl HW-40 (fine).[6] The adsorbed product was washed with water and eluted with 0.05 mol dm^{-3} $\mathrm{Na_2SO_4}$. The column showed two green bands. The faster-moving band (minor product) seemed to contain $[\mathrm{Co(Clacac)(acac)(CH_3SeCH_2CH_2NH_2)}]^+$ on the basis of the absorption spectrum, but this complex was not isolated. The eluate containing the slower-moving band (major product) was collected and mixed with $\mathrm{LiClO_4}$ (ca. 5 g), and the complex was extracted with chloroform (50 cm^3×3). The chloroform layer was dried with anhydrous $\mathrm{MgSO_4}$ and evaporated under reduced pressure to dryness. The deep green residue was dissolved in acetone (0.4 cm^3)–water (1.6 cm^3), and the solution was evaporated slowly in a desiccator over $\mathrm{P_2O_5}$ to yield deep green crystals, which were collected by filtration, washed with cold water, and air dried. Yield: 0.03 g (53%). Found: C, 27.71; H, 3.76; N, 2.49%. Calcd for $\mathrm{C_{13}H_{21}NCl_3CoO_8Se}$: C, 27.96; H, 3.53; N, 2.20%.

$[\mathrm{Co(Meacac)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{ClO_4}$. To a cold aqueous solution (7 cm^3) of NaOH (0.70 g, 1.75×10^{-2} mol) was slowly added 3-methyl-2,4-pentanedione[7] (2.0 g, 1.75×10^{-2} mol). The solution was then added dropwise to an aqueous solution (10 cm^3) of $\mathrm{CoCl_2\cdot6H_2O}$ (2.1 g, 8.83×10^{-3} mol). A yellow powder precipitated was collected quickly by filtration. This product was believed to be crude $[\mathrm{Co(Meacac)_2(H_2O)_2}]$ and was used without purification. It is not stable even in the solid state; the color changes from yellow to green. To a hot (ca. 50 °C) ethanol solution (20 cm^3) containing $\mathrm{CH_3SeCH_2CH_2NH_2\cdot HCl}$ (0.10 g, 5.73×10^{-4} mol) and LiOH (0.014 g, 5.8×10^{-4} mol) was added freshly prepared $[\mathrm{Co(Meacac)_2(H_2O)_2}]$ (0.20 g, 6.2×10^{-4} mol). The color of the solution turned deep green immediately. The mixture was heated at 50 °C with stirring for 30 min. After cooling to room temperature, the solution was mixed with 3 mol dm^{-3} $\mathrm{LiClO_4}$ (10 cm^3), and the complex was extracted with chloroform (200 cm^3×2). The chloroform layer was evaporated to dryness under reduced pressure, the deep green residue was dissolved in water, and then the solution was applied on a column (ϕ 2.2 cm×8 cm) of SP-Sephadex C-25. After washing the column with water the adsorbed product was eluted with 0.05 mol dm^{-3} $\mathrm{Na_2SO_4}$. The column showed a green and a brown band. From the eluate containing the faster-moving green band the complex was isolated as the perchlorate by the same method as that for the Clacac complex, and recrystallized from water. Yield: 0.063 g (21%). Found: C, 34.80; H, 5.47; N, 2.89%. Calcd for $\mathrm{C_{15}H_{27}NClCoO_8Se}$: C, 34.47; H, 5.21; N, 2.68%.

$[\mathrm{Co(dbme)_2(CH_3SeCH_2CH_2NH_2)}]\mathrm{ClO_4\cdot H_2O}$. To an ethanol solution (10 cm^3) of LiOH (0.12 g, 5.0×10^{-3} mol) was added slowly 1,3-diphenyl-1,3-propanedione (1.125 g, 5.0×10^{-3} mol). The resulting yellow suspension was added dropwise to an ethanol solution (6 cm^3) of $CoCl_2\cdot6H_2O$ (0.595 g, 2.5×10^{-3} mol). The mixture containing a yellow-orange precipitate was mixed with water (10 cm^3), stirred for 30 min at room temperature, and then the precipitate was collected by filtration. It was dissolved in hot ethanol (65 cm^3)-chloroform (35 cm^3), and the solution was evaporated to a volume of ca. 30 cm^3 and cooled to give fine orange crystals, which were collected by filtration and air dried. Yield: 1.30 g. This product was believed to be [Co(dbme)$_2$(H_2O)$_2$] and was used to prepare [Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ without analysis. To an *N,N*-dimethylformamide (DMF) solution (40 cm^3) of [Co(dbme)$_2$(H_2O)$_2$] (1.00 g, 1.85×10^{-3} mol) was added a DMF solution (10 cm^3) containing $CH_3SeCH_2CH_2NH_2\cdot HCl$ (0.322 g, 1.85×10^{-3} mol) and triethylamine (0.187 g, 1.85×10^{-3} mol). Acetic acid (2 cm^3) and PbO_2 (0.221 g, 9.25×10^{-4} mol) were added to the solution, the mixture was stirred for about 30 min at 30—40 °C, and then filtered. The filtrate was mixed with 0.5 mol dm^{-3} $NaClO_4$ (200 cm^3) with vigorous stirring to yield a green precipitate, which was recrystallized from chloroform by adding hexane. Yield: 1.04 g (74%). Found: C, 52.19; H, 3.97; N, 2.00%. Calcd for $C_{33}H_{33}NClCoO_9Se$: C, 52.09; H, 4.37; N, 1.84%.

[Co(Bracac)$_2$($CH_3SeCH_2CH_2NH_2$)]ClO_4. This complex was obtained from the acac complex by a method similar to that for the corresponding Clacac complex using *N*-bromosuccinimide instead of *N*-chlorosuccinimide. Yield: 30%. Found: C, 23.91; H, 3.13; N, 2.25%. Calcd for $C_{13}H_{21}NBr_2ClCoO_8Se$; C, 23.93; H, 3.24; N, 2.15%. This complex is stable in the solid state but decomposes gradually in aqueous solution (ca. 5% in a day at room temperature).

[Co(NO_2acac)$_2$($CH_3SeCH_2CH_2NH_2$)]ClO_4. This complex was prepared by nitration of [Co(acac)$_2$($CH_3SeCH_2CH_2NH_2$)]ClO_4 in a manner similar to that for [Co(NO_2acac)$_3$].[8] Yield: 42%. The complex is not stable even in the solid state and was not analyzed; the color of the complex changed from purple to brown on storage in a vial. The complex in water was estimated to decompose by ca. 10% in a day on the basis of the absorption spectrum.

Separation of the Diastereomers. The complexes [Co(Clacac)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ and [Co(Meacac)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ were separated into two racemic pairs of the diastereomers (Δ(*R*)Λ(*S*) and Δ(*S*)Λ(*R*)) by column chromatography on SE-Toyopearl (eluent: 0.05 mol dm^{-3} Na_2SO_4) in the same manner as that for [Co(acac)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$.[3] The column showed two green bands, but the diastereomers were not isolated because they are likely to epimerize. Each eluate was kept in a freezer at ca. −20 °C for kinetic studies. The diastereomers do not interconvert detectably over a period of at least 1 month under the given conditions.

[Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ was separated into the diastereomers by fractional crystallization of the perchlorate salt. [Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$ClO_4\cdot H_2O$ (0.14 g, 1.84×10^{-4} mol) was dissolved in chloroform (3 cm^3), and hexane (4 cm^3) was added dropwise. After cooling the solution in an ice bath, the crystals which deposited were collected. Almost pure (purity>95%) Δ(*S*)Λ(*R*) isomer (0.05 g) was obtained by repeated (4 times) recrystallization from chloroform–hexane by the same method as above. The purity was checked by a high-performance liquid chromatographic method (vide infra). The Δ(*S*)Λ(*R*) isomer (purity>95%) was also obtained by slow evaporation of a methanol solution of the perchlorate salt at room temperature.

Partial Resolution of [Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)].$^+$ Partial resolution of [Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ was achieved by column chromatography. About 5 mg of [Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$ClO_4\cdot H_2O$ dissolved in a small amount of methanol was applied on a column of D-TA(ES)-Toyopearl[6] (ϕ1.7 cm×30 cm; eluent: 0.02 mol dm^{-3} sodium (*R,R*)-tartrate in 70% methanol–30% water). A recycling chromatographic technique was employed. After three times of recycling, the first and the last fractions of the band showed CD spectra almost mirror image of each other in the region of 340—600 nm, indicating partial resolution of the complex.

Kinetic Studies. Kinetics of epimerization of [Co(dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ was studied by a method similar to those for [Co(acac, Clacac, or Meacac)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$.[3,4] Since the complex is insoluble in water, methanol was used as the solvent. Portions of the reaction mixture were withdrawn at intervals, and chromatographed with a column (ϕ 0.46 cm×15 cm) of JASCO Finepack SIL $C_{18}S$ and 0.1 mol dm^{-3} sodium dodecyl sulfate in 72.5% CH_3CN–27.5% H_2O as the eluent. The chromatography was carried out with a JASCO TRI ROTAR V system at a flow rate of 1.0 cm^3 min^{-1}, the Δ(*R*)Λ(*S*) isomer being eluted faster. The two isomers (Δ(*R*)Λ(*S*) and Δ(*S*)Λ(*R*)) were detected at 315 nm where they give the same molar absorption coefficient and no detectable change in absorbance was observed during the epimerization reaction.

Measurements. Absorption and circular dichroism (CD) spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40CS spectropolarimeter, respectively. ^{1}H NMR spectra in $CDCl_3$ solutions were measured with a JEOL PMX-60 spectrometer using TMS as an internal reference.

Results and Discussion

Preparation and Characterization of the Complexes. Metal–acac complexes are known to be susceptible to electrophilic substitutions such as halogenation, nitration, or acetylation at the central methine of the acac chelate.[9] The [Co(acac)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ complex was halogenated (chlorinated, brominated) and nitrated, respectively, by *N*-halosuccinimide and a mixture of copper(II) nitrate and acetic anhydride. The ^{1}H NMR spectra verified the substitutions at the methine of the acac ligand. The resonances due to the methine protons in the spectrum of the parent complex disappeared completely on halogenation or nitration. The Bracac and NO_2acac complexes were unstable in solution, and the kinetics of epimerization reactions could not be studied. [Co(Meacac or dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ was prepared by oxidizing a mixture of [Co(Meacac or dbme)$_2$(H_2O)$_2$] and $CH_3SeCH_2CH_2NH_2$. The Meacac complex was easily oxidized on exposure to the air, while the dbme complex was not formed under similar conditions and PbO_2 was used as an oxidizing agent.

Four stereoisomers, Δ(*R*), Δ(*S*), Λ(*R*), and Λ(*S*) are possible for the present complexes (Fig. 1). The complexes were separated into two isomers (racemic pairs of the diastereomers), Δ(*R*)Λ(*S*) and Δ(*S*)Λ(*R*), by column chromatography on SE-Toyopearl or by fractional crystallization. The structures of the isomers were assigned on the basis of the ^{1}H NMR spectra. Table 1 lists the ^{1}H NMR spectral data. In the Δ(*R*)Λ(*S*) isomer, the Se-methyl group is placed over one of the two acac chelate rings and the methyl protons will be shielded by the acac ring. Thus, the isomer whose Se-methyl signal is observed at a higher magnetic field is assigned to the Δ(*R*)Λ(*S*) isomer.

The absorption spectral data for [Co(acac, Clacac, Meacac, or dbme)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ are given in Table 2, and the spectra are shown in Fig. 2. The spectral difference between the isomers is very small in each complex.

The absorption spectra of the acac, Clacac, and Meacac complexes are similar to that of [Co(acac)$_2$(en)]$^+$ [10,11] (en=ethylenediamine) except a strong band at 32000—33000 cm^{-1} assignable to an Se-to-Co^{III} charge transfer transition.[2,12,13] The present complexes show the first absorption band, $^1A_{1g}\rightarrow{}^1T_{1g}$ (O_h) around 17000 cm^{-1}, and a shoulder in the region of 23000—24000 cm^{-1}. [Co(acac)$_2$(en)]$^+$ also shows a shoulder at ca. 24000 cm^{-1} and it has been assigned to the second d-d absorption band, $^1A_{1g}\rightarrow{}^1T_{2g}$ (O_h).[10,11] The first d-d absorption band of [Co(β-dik)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ shifts to lower energies as β-dik is changed from acac (17100 cm^{-1}) through Clacac (16800 cm^{-1}) to Meacac (16600 cm^{-1}). It has been reported that the intensities of the first absorption band of cobalt(III)-acac complexes increase on halogenation.[5] [Co(acac)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ is the case.

The bands observed at energies higher than 32000 cm^{-1} in the spectra of the acac, Clacac, and

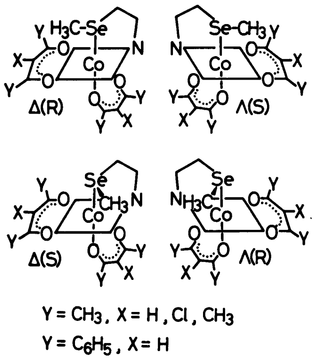

Fig. 1. The four stereoisomers of [Co(β-dik)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$.

Table 1. ^{1}H NMR Data for [Co(β-dik)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$ in $CDCl_3$

β-dik	Assignment	Chemical shift (Se-methyl, δ)
acac	Δ(*R*)Λ(*S*)	1.63
	Δ(*S*)Λ(*R*)	1.94
Clacac	Δ(*R*)Λ(*S*)	1.60
	Δ(*S*)Λ(*R*)	1.96
Bracac	Δ(*R*)Λ(*S*)	1.61
	Δ(*S*)Λ(*R*)	1.98
Meacac	Δ(*R*)Λ(*S*)	1.53
	Δ(*S*)Λ(*R*)	1.90—2.00[a]
dbme	Δ(*R*)Λ(*S*)	1.49
	Δ(*S*)Λ(*R*)	1.93
NO_2acac	Δ(*R*)Λ(*S*)	1.71
	Δ(*S*)Λ(*R*)	2.08

a) Overlapping with the *C*-methyl signals.

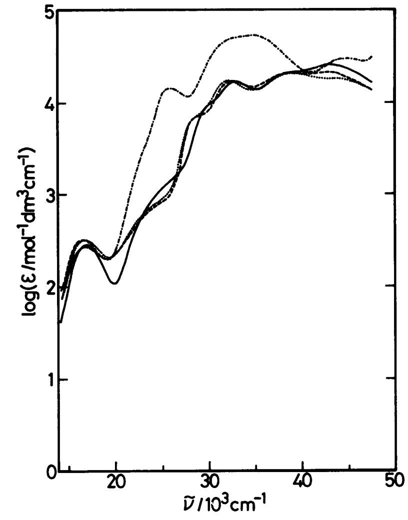

Fig. 2. Absorption spectra of [Co(β-dik)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$, β-dik=acac(——, in H_2O), Clacac(····, in H_2O), Meacac(- - -, in H_2O), and dbme(—·—, in CH_3OH).

Table 2. Absorption Spectral Data for [Co(β-dik)$_2$($CH_3SeCH_2CH_2NH_2$)]$^+$

β-dik	$\tilde{\nu}_{max}/10^3$ cm^{-1} (log (ε/mol^{-1} dm^3 cm^{-1}))		
acac[a]	17.1(2.46)	24(sh, 2.93)	30(sh, 3.97)
	32.9(4.23)	39.2(4.32)	43.3(4.40)
Clacac[a]	16.8(2.51)	23(sh, 2.79)	29(sh, 3.87)
	32.1(4.23)	38.9(4.30)	44(sh, 4.25)
Meacac[a]	16.6(2.52)	23(sh, 2.75)	29(sh, 3.86)
	32.6(4.24)	38.6(4.31)	42.7(4.32)
dbme[b]	16.8(2.43)	23(sh, 3.48)	25.9(4.16)
	32(sh, 4.68)	34.5(4.73)	44.8(4.48)

Solvent, a): H_2O, b): CH_3OH.

Meacac complexes can be assigned to the π-π^* transitions of the β-diketonate ligand[14,15] and an N-to-Co^{III} charge transfer transition. $[Co(dbme)_2(CH_3SeCH_2CH_2NH_2)]^+$ shows the first d-d absorption band at nearly the same position as that for the Clacac complex. The absorption bands observed at energies higher than 22000 cm^{-1} for the dbme complex are more intense than those for the other complexes probably because of overlapping of the intense phenyl group transitions.

Inversion at the Coordinated Selenium Atom. In a previous paper,[3] we have shown that the epimerization of $[Co(acac)_2(CH_3SeCH_2CH_2NH_2)]^+$ is caused by the inversion at the selenium atom. The related complexes, Clacac and Meacac complexes, are expected to epimerize by the same way, and the dbme complex is also suggested to epimerize in a similar way on the basis of the CD spectrum. The dbme complex was partially resolved into the enantiomers by column chromatography. The CD spectra changed only slightly during epimerization. In general, the optical activity of a metal complex is explained by the superposition of the configurational (chiral arrangement of ligands around the metal ion) and the vicinal (chiral ligand) effects, the former being larger.[16,17] These observations suggest that the small CD change is caused by inversion at the selenium atom and that the configuration around the cobalt(III) ion remains unchanged. Thus, all the complexes studied here are believed to epimerize by selenium inversion.

The epimerization of $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$ was studied in the temperature range of 30.3—55.0 °C. $\Delta(S)\Lambda(R)$-[Co(acac, Clacac, or Meacac)$_2$(CH$_3$SeCH$_2$CH$_2$NH$_2$)]$^+$ was epimerized in 0.05 mol dm^{-3} Na_2SO_4, and $\Delta(S)\Lambda(R)$-$[Co(dbme)_2(CH_3SeCH_2CH_2NH_2)]^+$ was done in methanol since the complex is insoluble in water. The rates were followed by high-performance liquid chromatography. This method has the great advantages of a short elution time and micro quantities of samples. Figure 3 shows a typical set of elution curves obtained at intervals after $\Delta(S)\Lambda(R)$-$[Co(dbme)_2(CH_3SeCH_2CH_2NH_2)]ClO_4\cdot H_2O$ had been dissolved in methanol at 40.0 °C. The area of band I ($\Delta(R)\Lambda(S)$ isomer) increases whereas that of band II ($\Delta(S)\Lambda(R)$ isomer) decreases with time as the result of epimerization:

$$\Delta(R)\Lambda(S) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \Delta(S)\Lambda(R)$$

where k_1 and k_{-1} denote the forward and reverse rate constants, respectively. In each kinetic run, the plot of $\ln[S_t^{II}/(S_t^I+S_t^{II})-S_\infty^{II}/(S_\infty^I+S_\infty^{II})]$ vs. time gave a straight line for at least three half-lives (S_t^I, S_t^{II}, S_∞^I, and S_∞^{II}

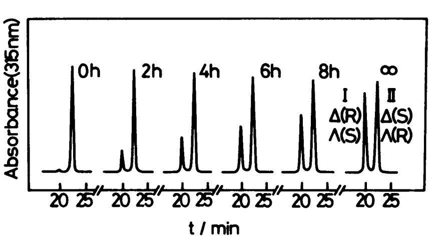

Fig. 3. Change in the elution curve during the epimerization of $\Delta(S)\Lambda(R)$-$[Co(dbme)_2(CH_3SeCH_2CH_2NH_2)]ClO_4\cdot H_2O$ in methanol at 40.0 °C. Chromatographic conditions: column, JASCO Finepack SIL C$_{18}$S, ϕ0.46 cm × 15 cm; eluent, 0.1 mol dm^{-3} sodium dodecyl sulfate in 72.5% CH$_3$CN–27.5% H$_2$O; flow rate, 1.0 cm^3 min^{-1}; UV detection, 315 nm.

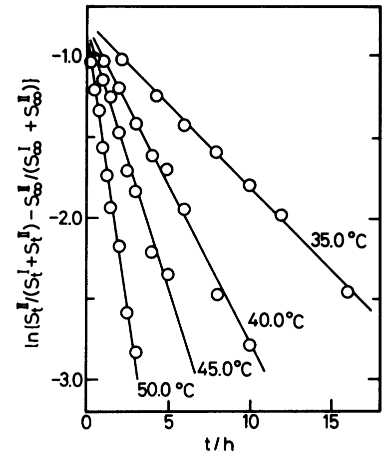

Fig. 4. The plots of $\ln[S_t^{II}/(S_t^I+S_t^{II})-S_\infty^{II}/(S_\infty^I+S_\infty^{II})]$ against time for the epimerization of $\Delta(R)\Lambda(S)$-$[Co(dbme)_2(CH_3SeCH_2CH_2NH_2)]^+$ at 35.0, 40.0, 45.0, and 50.0 °C (S_t^I, S_t^{II}, S_∞^I, and S_∞^{II} denote the areas of bands I and II at time t and at infinite time).

Table 3. Rate Constants for Epimerization of $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$ and Equilibrium Constants of the Isomers

$$\Delta(R)\Lambda(S) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \Delta(S)\Lambda(R) \quad k_{obsd}=k_1+k_{-1} \quad K_{eq}=k_1/k_{-1}$$

β-dik (K_{eq})	t/°C	$k_{obsd}/10^{-5}\ s^{-1}$	$k_1/10^{-5}\ s^{-1}$	$k_{-1}/10^{-5}\ s^{-1}$
acac[a)]	40.0	3.39±0.09	1.78±0.06	1.61±0.06
(K_{eq}=1.1)	45.5	7.18±0.14	3.76±0.10	3.42±0.10
	50.4	14.2 ±0.04	7.44±0.03	6.76±0.03
	55.0	25.8 ±0.06	13.5 ±0.04	12.3 ±0.04
Clacac[a)]	35.0	0.63±0.03	0.39±0.02	0.24±0.02
(K_{eq}=1.6)	40.0	1.29±0.05	0.80±0.03	0.50±0.03
	45.0	2.67±0.09	1.64±0.06	1.03±0.06
	50.0	6.01±0.15	3.70±0.11	2.31±0.11
Meacac[a)]	30.3	5.87±0.16	3.56±0.11	2.31±0.11
(K_{eq}=1.5)	35.1	11.01±0.19	6.68±0.14	4.33±0.14
	40.2	20.03±0.31	12.14±0.22	7.89±0.22
	45.2	37.60±0.74	22.80±0.53	14.80±0.53
dbme[b)]	35.0	2.79±0.07	1.53±0.05	1.26±0.05
(K_{eq}=1.2)	40.0	5.38±0.14	2.94±0.10	2.43±0.10
	45.0	8.80±0.27	4.82±0.19	3.98±0.19
	50.0	18.48±0.39	10.12±0.28	8.36±0.28

Solvent, a): 0.05 mol dm^{-3} Na_2SO_4, b): CH_3OH.

denote the areas of bands I and II at time t and at infinite time). The slope gave the first-order rate constant, k_{obsd} (Fig. 4). The rate constants for the epimerization were calculated from the equilibrium constant, K_{eq}, and the observed rate constant:

$$K_{eq} = k_1/k_{-1} = S^{II}_{\infty}/S^{I}_{\infty}$$

$$k_{obsd} = k_1 + k_{-1}.$$

The K_{eq} value was constant for each complex in the temperature range of 30.3—55.0 °C. The values of k_1 and k_{-1} are given in Table 3.

The racemization of $[Co(CH_3SeCH_2CH_2NH_2)(tren)]^{3+}$ and related complexes has been suggested to take place intramolecularly by pyramidal inversion at the selenium atom which proceeds via a trigonal intermediate.[2] The epimerization of $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$ also seems to proceed intramolecularly, since the rates are independent of pH.

Eyring treatments of $\ln(k_1/T)$ and $\ln(k_{-1}/T)$ vs. T^{-1} (Fig. 5) yielded activation parameters given in Table 4. The $\Delta G^{\ddagger}_{25\,°C}$ values for inversion of $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$ decrease in the order β-dik=Clacac>acac>dbme>Meacac. This order coincides with the decreasing order of $\Delta H^{\ddagger}$ values. The decrease in $\Delta G^{\ddagger}_{25\,°C}$ values comes mainly from a decrease in $\Delta H^{\ddagger}$, the $\Delta S^{\ddagger}$ values making relatively small contributions. Examination of molecular models indicates that the substituents (Cl, Me, Ph) on a β-diketonate chelate ring do not induce a large steric effect on the inversion at the selenium atom. Thus the enthalpy change associated with the inversion seems to arise from the electronic influence of the substituents on β-diketonate chelate rings. This view is supported by the Hammett correlation shown in Fig. 6, where logarithms of the observed rate constants at 40 °C for the Clacac and Meacac complexes relative to that for the acac complex are plotted against the Hammett σ_p values. The aromatic character of the coordinated acac is known.[18] The data follow a straight line with a slope equal to −2.9. The result shows that the Cl (or Me) substituent of the Clacac (or Meacac) complex, which is at the para position to the central metal, withdraws (or releases) the electron on the selenium atom via the central metal to decrease (or increase) the rate. For the inversion rates at sulfur of organic sulfonium ions, it is well-known that substituents more electronegative than carbon slow the rate.[19] The Hammett relationship was also reported to hold for the proton-exchange rate of ethylenediamine of $[Co(acac, Bracac, or NO_2acac)_2(en)]^+$.[20]

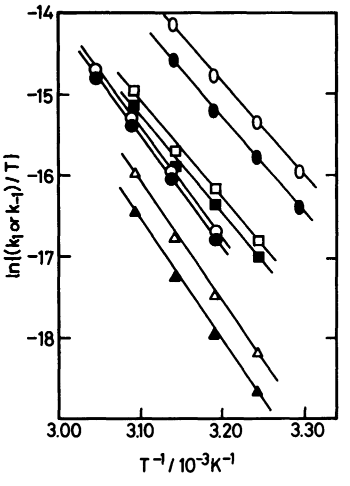

Fig. 5. Eyring treatments of $\ln(k_1/T)$ vs. T^{-1} and $\ln(k_{-1}/T)$ vs. T^{-1} for $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$, β-dik=acac(○,●) Clacac (△,▲), Meacac(0,◖), and dbme(□,■).

Table 4. Thermodynamic Parameters for Epimerization of $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$

$$\Delta(R)\Lambda(S) \underset{(2)\ k_{-1}}{\overset{(1)\ k_1}{\rightleftharpoons}} \Delta(S)\Lambda(R)$$

β-dik		$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{25\,°C}$/kJ mol^{-1}
acac	(1)	113.2±1.8	25.2±5.6	105.7±2.5
	(2)	113.3±1.8	25.1±5.7	105.8±2.5
Clacac	(1)	121.3±2.2	44.8±6.9	107.9±3.0
	(2)	121.3±2.1	40.9±6.7	109.1±2.9
Meacac	(1)	96.9±1.9	−10.8±6.0	100.1±2.6
	(2)	97.0±2.5	−14.0±7.9	101.2±3.4
dbme	(1)	99.3±2.9	−15.2±9.1	103.8±4.0
	(2)	99.4±2.9	−16.3±9.1	104.3±4.0

If we take the pK_a value of a substituted Hacac in the enol form (Hacac: 8.23, HMeacac: 9.2, Hdbme: 9.1)[21] as a measure of the electronic effect of the substituent, then the order of $\Delta G^{\ddagger}_{25\,°C}$ and $\Delta H^{\ddagger}$ values should be related to that of the pK_a values. The $\Delta G^{\ddagger}_{25\,°C}$ and $\Delta H^{\ddagger}$ values of $[Co(\beta\text{-dik})_2(CH_3SeCH_2CH_2NH_2)]^+$ decrease in the order β-dik=acac>dbme>Meacac. The order is in accord with that of electron-

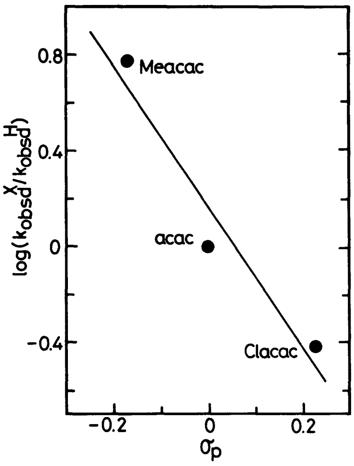

Fig. 6. Hammett's relationship for the inversion rate of $[Co(acac, Clacac, or Meacac)_2(CH_3SeCH_2CH_2NH_2)]^+$.

withdrawing tendency of the substituents predicted from the pK_a values. That the dbme and Meacac ligands increase electron density on the selenium atom via the central metal is also suggested by ^{1}H NMR spectra; for example, the CH_3Se- signal of the dbme complex is observed at a higher field than that of the acac complex (Table 1). Thus, the difference in inversion rate among the present complexes is explained by the difference in electron density on the selenium atom which is induced by the substituent on the β-diketonate skeleton. The inversion rate of $[Co(NO_2acac)_2(CH_3SeCH_2CH_2NH_2)]^+$, which has highly electron-withdrawing NO_2- groups (σ_p=0.78), is expected to be very slow. Unfortunately, the complex was so unstable that we could not determine the rate.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 58470032 from the Ministry of Education, Science, and Culture.

References

1) E. W. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, **32**, 1 (1984) and the references cited therein.

2) K. Nakajima, K. Tozaki, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **58**, 1130 (1985).

3) K. Nakajima, M. Kojima, M. Fujita, and J. Fujita, *J. Chromatogr.*, **301**, 241 (1984).

4) K. Nakajima, M. Kojima, and J. Fujita, *J. Chromatogr.*, **362**, 281 (1986).

5) K. Kuroda, K. Yoshitani, K. Kunigita, Y. Kamiiba, and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **49**, 2445 (1976).

6) M. Fujita, Y. Yoshikawa, and H. Yamatera, *Chem. Lett.*, **1982**, 437.

7) A. W. Johnson, E. Markham, and R. Prince, *Org. Synth.*, Coll. Vol. V, 785 (1973).

8) J. P. Collman and W. L. Young, III, *Inorg. Synth.*, VII, 205 (1963).

9) J. P. Collman, "Transition Metal Chemistry," ed by R. L. Carlin, Marcel Dekker, Inc., Vol. 2, New York (1966), p. 35, and the references cited therein.

10) L. J. Boucher, *Inorg. Chem.*, **9**, 1202 (1970).

11) Y. Ouyang, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **57**, 3574 (1984).

12) T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **57**, 3104 (1984).

13) T. Konno, K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **58**, 1119 (1985).

14) C. A. Fleming and D. A. Thornton, *J. Mol. Struct.*, **25**, 271 (1975).

15) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265 (1969); D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961).

16) C. T. Liu and B. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); B. Douglas, *ibid.*, **4**, 1813 (1965).

17) K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1965).

18) J. P. Collman, R. L. Marchall, and W. L. Young, III, *Chem. Ind. (London)*, **1962**, 1380.

19) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971).

20) K. Ito, H. Isono, E. Iwamoto, and Y. Yamamoto, *Inorg. Chem.*, **23**, 850 (1984).

21) M. P. Rumph and R. L. Riviere, *C. R. Acad. Sci. Paris*, **244**, 902 (1957).