August, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 2547—2552 (1989) 2547

Substituent Group Electronic Effects on Inversion and Proton-Exchange Rates at Chiral Nitrogen Centers for a Series of Bis(β-diketonato)-(N-methylethylenediamine)cobalt(III) Complexes

Guilin Ma, Masaaki Kojima, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01

(Received April 3, 1989)

The rates of the base-catalyzed proton exchange (deuteration, k_D) and inversion (epimerization, k_{ep}) at chiral nitrogen centers of $[Co(Xacac)_2(Me\text{-}en)]^+$ (Xacac: NO_2acac=3-nitro-2,4-pentanedionate, Clacac=3-chloro-2,4-pentanedionate, CH_3acac=3-methyl-2,4-pentanedionate; Me-en=*N*-methylethylenediamine) in aqueous solutions have been measured at 34.0 °C, and the results were compared with one another and with those of the corresponding acac complex (acac=2,4-pentanedionate) in order to investigate the substituent influence on the rates. The k_D and k_{ep} values of the NO_2acac complex are ca. 10^4 and ca. 10^6 times, respectively, larger than those of the CH_3acac complex. The effect of substituents is electronic and the Hammett relationship was found to hold for both deuteration and epimerization rates. The reduction (Co^{3+}/Co^{2+}) half-wave potential, $E_{1/2}$ obtained by rotating glassy carbon electrode voltammetry increases from −0.59 V (vs. SCE) for the CH_3acac complex to −0.08 V for the NO_2acac complex. A linear dependence was observed between $E_{1/2}$ and the Hammett parameter.

The kinetics of inversion and proton exchange at chiral secondary amine nitrogen centers of metal complexes have been studied extensively.[1] However, factors influencing the rates are not clear yet. In a previous paper,[2] we measured the rates of base-catalyzed epimerization and deuteration of $[Co(acac\ or\ ox)_2(Me\text{-}en)]^{+or-}$ (ox=oxalate ion), and found that the rates of the uninegative ox complex are greater than those of the unipositive acac complex. The results indicate that the rates are largely affected by the electronic effect of coexisting ligands rather than the number of positive charges on the complex.[3]

In order to investigate the electronic effect on the rates of proton exchange and inversion in more detail, we have prepared a series of $[Co(Xacac)_2(Me\text{-}en)]^+$, in which the hydrogen atom at the 3-position of the acac ligand is replaced by a methyl, chloro, or nitro group.

Experimental

The $[Co(acac)_2(Me\text{-}en)]^+$ complex was prepared and separated into the two racemic pairs of diastereomers, $\Delta(R)\Delta(S)$ and $\Lambda(S)\Delta(R)$, as described previously.[4]

$[Co(CH_3acac)_3]$. To a solution of $CoCl_2\cdot 6H_2O$ (5 g, 21 mmol) in water (5 cm^3) was added 30% H_2O_2 (7.5 cm^3). This solution was added to an ice-cold slurry of $KHCO_3$ (15 g) in water (15 cm^3) with stirring. The resulting green solution of $[Co(CO_3)_3]^{3-}$[5] was filtered. To the filtrate was added 3-methyl-2,4-pentanedione[6] (7.2 g, 63 mmol) and the mixture was heated at 40 °C for 1.5 h to yield a green solid. The product was collected by filtration, washed with water, and recrystallized from chloroform by adding petroleum ether. Yield: 4.0 g. The ^{1}H NMR spectrum in $CDCl_3$ was identical with that reported by Brown et al.[7]

$\Delta(R)\Delta(S)$- and $\Delta(S)\Delta(R)$-$[Co(CH_3acac)_2(Me\text{-}en)]ClO_4$. Active charcoal (0.2 g) and a solution of Me-en (0.244 g, 3.3 mmol) in methanol (20 cm^3) were added to a solution of $[Co(CH_3acac)_3]$ (1.2 g, 3.0 mmol) in methanol (80 cm^3). The mixture was stirred for 45 min and then filtered. The purple filtrate was diluted with water (1 dm^3), and applied on a column (ϕ3 cm×20 cm) of SP-Sephadex C-25. By elution with 0.05 mol dm^{-3} NaCl, a purple and a red (probably $[Co(CH_3acac)(Me\text{-}en)_2]^{2+}$) band developed in this order. The eluate containing the purple band was collected and evaporated to a small volume under reduced pressure. To the concentrate sodium perchlorate was added to yield purple crystals, which were recrystallized from water (60 °C). Yield: 0.4 g. The crystals were a mixture of the two isomers, and they were separated by a column chromatographic method. About 0.15 g of the mixture was dissolved in water and the solution was applied on a column (ϕ2.2 cm×50 cm) of SE-Toyopearl HW-40[8] (fine). A recycling chromatographic technique with an eluent of 0.05 mol dm^{-3} NaCl was employed. After two times of recycling, two isomers, $\Delta(R)\Delta(S)$ and $\Delta(S)\Delta(R)$ were eluted separately in this order. From each eluate the perchlorate of the isomer was obtained by the same method as that described above. Found for the $\Delta(R)\Delta(S)$-isomer: C, 39.22; H, 6.12; N, 6.09%. Found for the $\Delta(S)\Delta(R)$-isomer: C, 39.36; H, 6.14; N, 6.18%. Calcd for $C_{15}H_{28}N_2O_8ClCo$: C, 39.27; H, 6.15; N, 6.11%.

$\Delta(R)\Delta(S)$- and $\Delta(S)\Delta(R)$-$[Co(Clacac)_2(Me\text{-}en)]ClO_4$. These complexes were prepared by chlorination of the corresponding isomers of $[Co(acac)_2(Me\text{-}en)]ClO_4$ with *N*-chlorosuccinimide by a method similar to that for $[Co(Clacac)(en)_2](ClO_4)_2$[9] (en=ethylenediamine). To a suspension of $\Delta(R)\Delta(S)$-$[Co(acac)_2(Me\text{-}en)]ClO_4\cdot 0.5H_2O$ (0.66 g, 1.54 mmol) in 0.01 mol dm^{-3} $HClO_4$ (8 cm^3) was added *N*-chlorosuccinimide (0.49 g, 3.67 mmol) little by little, and the mixture was stirred for 30 min at 50 °C. After cooling, the purple product was collected by filtration, and recrystallized from 0.01 mol dm^{-3}$HClO_4$. Yield: 0.26 g. The $\Delta(S)\Delta(R)$-isomer was obtained from $\Delta(S)\Delta(R)$-$[Co(acac)_2(Me\text{-}en)]ClO_4$ by the same method. Found for the $\Delta(R)\Delta(S)$-isomer: C, 31.14; H, 4.43; N, 5.57%. Found for the $\Delta(S)\Delta(R)$-isomer: C, 31.10; H, 4.40; N, 5.59%. Calcd for $C_{13}H_{22}N_2Cl_3CoO_8$: C, 31.25; H, 4.44; N, 5.61%.

$\Delta(R)\Delta(S)$- and $\Delta(S)\Delta(R)$-$[Co(NO_2acac)_2(Me\text{-}en)]ClO_4$. These complexes were prepared by nitration of the corresponding isomers of $[Co(acac)_2(Me\text{-}en)]ClO_4$ in a manner similar to that for $[Co(NO_2acac)_3]$.[10] A mixture of finely ground $Cu(NO_3)_2\cdot 3H_2O$ (1.93 g, 8.0 mmol) and acetic anhydride (60 cm^3) was stirred for 15 min at 0 °C. To the slurry was added $\Delta(R)\Delta(S)$-$[Co(acac)_2(Me\text{-}en)]ClO_4\cdot 0.5H_2O$ (0.6 g, 1.4 mmol).

The mixture was stirred for 3 h at 0 °C, and then for 1 h at room temperature. The blue solution was mixed with water (90 g) and ice (90 g), and the mixture was evaporated to a small volume under reduced pressure. To the concentrate was added sodium perchlorate to yield purple crystals. They were collected by filtration and recrystallized from 0.01 mol dm^{-3} $HClO_4$. Yield: 0.4 g. The $\Lambda(S)\Delta(R)$-isomer was obtained from $\Lambda(S)\Delta(R)$-[Co(acac)$_2$(Me-en)]ClO_4 by the same method. Found for the $\Lambda(R)\Delta(S)$-isomer: C, 30.29; H, 4.22; N, 10.76%. Found for the $\Lambda(S)\Delta(R)$-isomer: C, 29.86; H, 4.25; N, 10.83%. Calcd for $C_{13}H_{22}N_4ClCoO_{12}$: C, 29.99; H, 4.26; N, 10.76%.

Measurements. Absorption and ^{1}H NMR spectra were measured on a Hitachi 323 spectrophotometer and a Hitachi R-90H spectrometer, respectively. Electrochemical measurements were performed at 24 °C by using a Fuso HECS 321B potential sweep unit. Rotating disk experiments were carried out on a three-electrode system composed of glassy carbon rotating disk (2000 rev min^{-1}), platinum wire, and saturated calomel electrodes as the working, auxiliary, and reference electrodes, respectively. KCl was used as the supporting electrolyte at 0.1 mol dm^{-3} concentration.

Deuteration Studies. The rates of deuteration at the chiral amine nitrogen centers of the Clacac and CH_3acac complexes were measured in a phosphate buffer, pD 4.8—6.2 and pD 7.7—9.2, respectively at 34.0 °C, while those of the NO_2acac complex in a phthalate buffer (pD 2.4—3.1) at 34.0 °C. The empirical formula, pD=pH meter reading +0.4, was used to calculate [OD$^-$].[11] The complex perchlorates were converted into the more soluble chlorides with a Dowex 1X8 anion exchanger in the chloride form. The deuteration rates were followed by monitoring signal changes in the ^{1}H NMR spectra. The N-CH_3 doublet signal becomes a singlet by deuteration. All rates were followed for at least two half-lives. From the spectral changes, pseudo-first-order rate constants for deuteration, $k_{D(obsd)}$ were obtained as described previously.[12] For each complex, the $k_{D(obsd)}/[OD^-](=k_D)$ values are constant at 34.0 °C in the pD range measured, indicating that the reaction is first order in [OD$^-$]. Thus, the rate law was the same as that obtained previously for other amine complexes, $R=k_D$[complex][OD$^-$].[1]

Epimerization Studies. The rates of epimerization of the NO_2acac and the Clacac complexes were measured in a phosphate buffer (pH 6.4—7.2) and a borate buffer (pH 9.1—10.2), respectively, while that of the CH_3acac complex in 0.1 mol dm^{-3} NaOH (pH 12.6 at 34.0 °C) and a saturated aqueous solution of $Ca(OH)_2$ (pH 12.1 at 34.0 °C). The rates were followed by the same method as described previously.[12—14] It involves separation of two isomers of the complexes by a high-performance liquid chromatographic method. Analysis of chromatograms changed with reaction time gives the pseudo-first-order rate constant, $k_{ep(obsd)}$. The rate law for the epimerization reaction was the same as that for racemization (epimerization) of other chiral amine complexes, $R=k_{ep}$[complex][OH$^-$].[1] The runs starting from either of the isomers gave the same result within the experimental error. From these observations, the reaction can be expressed as

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

The forward and reverse second-order rate constants, k_1 and k_{-1} were obtained from k_{ep} ($k_{ep}=k_1+k_{-1}$) and the equilibrium constant ($K_{eq}=k_1/k_{-1}$).

Results and Discussion

Preparation and Characterization of the Complexes. The [Co(CH_3acac)$_2$(Me-en)]$^+$ complex was prepared by the reaction of [Co(CH_3acac)$_3$] with Me-en in the presence of active charcoal. Four stereoisomers, $\Lambda(R)$, $\Lambda(S)$, $\Delta(R)$, and $\Delta(S)$ are possible for the complex (Fig. 1). The isomers were separated into two racemic pairs of the diastereomers, $\Lambda(R)\Delta(S)$ and $\Lambda(S)\Delta(R)$ by column chromatography on SE-Toyopearl. The structures of the isomers were assigned from the chemical shift of the *N*-methyl group in ^{1}H NMR spectra taking a shielding effect by the CH_3acac chelate ring into consideration; an isomer which shows a doublet attributable to the *N*-methyl group at a higher magnetic field is assigned to the $\Lambda(S)\Delta(R)$ isomer (Fig. 1 and Table 1). The isomers ($\Lambda(R)\Delta(S)$ and $\Lambda(S)\Delta(R)$) of [Co(Clacac)$_2$(Me-en)]$^+$ and [Co(NO_2acac)$_2$(Me-en)]$^+$ were prepared by chlorination and nitration, respectively of the corresponding isomers of [Co(acac)$_2$(Me-en)]$^+$. The configurations of the parent complexes remained unchanged as verified by the ^{1}H NMR spectra.

The distributions of the isomers at equilibrium (34 °C) were analyzed by the reversed-phase high-performance liquid chromatographic technique, and the results are given in Table 1. The difference in stability is very small between the isomers for each complex. Table 1 also gives the absorption spectral data for the [Co(Xacac)$_2$(Me-en)]$^+$ complexes, and the spectra are shown in Fig. 2. The $\Lambda(S)\Delta(R)$ isomers, in which the *N*-methyl group is situated over one of the Xacac chelate rings exhibit the first d-d absorption

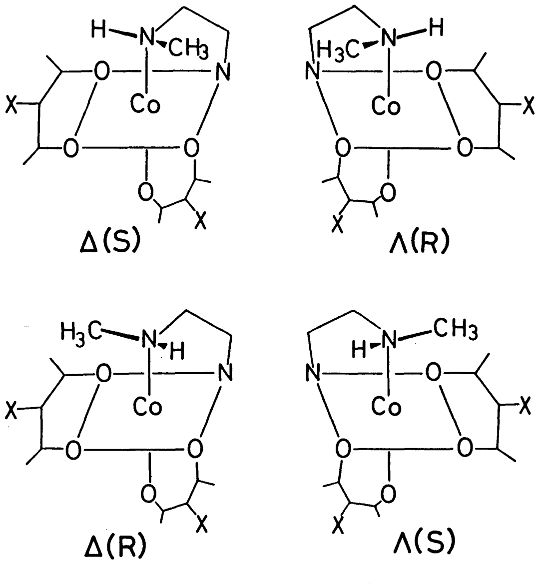

Fig. 1. The four stereoisomers of [Co(Xacac)$_2$(Me-en)]$^+$.

Table 1. ^{1}H NMR and Absorption Spectral Data for [Co(Xacac)$_2$(Me-en)]$^+$ and the Distributions of the Isomers at Equilibrium (34 °C)

Xacac	Isomer	^{1}H NMR (δ)		Absorption$^{c)}$ $\tilde{\nu}_{max}/10^3$ cm^{-1} (log ε)			Relative abundance/%
		NCH$_3$	N$\underline{H}$ (CH$_3$)				
NO$_2$acac	$\Lambda(S)\Delta(R)$	2.03d	7.50$^{a)}$	18.79(2.19)	30.77(3.81)	40.49(3.03)	44
	$\Lambda(R)\Delta(S)$	2.43d	6.50$^{a)}$	18.87(2.20)	30.86(3.82)	40.82(3.05)	56
Clacac	$\Lambda(S)\Delta(R)$	2.00d	6.65$^{a)}$	18.32(2.20)	28.99(3.75)	40.00(4.45)	40
	$\Lambda(R)\Delta(S)$	2.15d	5.45$^{a)}$	18.38(2.25)	28.99(3.83)	40.00(4.45)	60
acac	$\Lambda(S)\Delta(R)$	1.80d	5.70$^{b)}$	18.32(2.16)	30.77(3.80)	40.65(4.41)	45
	$\Lambda(R)\Delta(S)$	2.10d	5.25$^{b)}$	18.38(2.17)	30.77(3.80)	40.65(4.43)	55
CH$_3$acac	$\Lambda(S)\Delta(R)$	1.77d	5.55$^{b)}$	18.12(2.25)	28.99(3.83)	40.16(4.40)	45
	$\Lambda(R)\Delta(S)$	1.92d	5.00$^{b)}$	18.21(2.30)	29.07(3.87)	40.32(4.43)	55

a) In D$_2$O-DCl. b) In D$_2$O. c) In 0.01 mol dm^{-3} HClO$_4$.

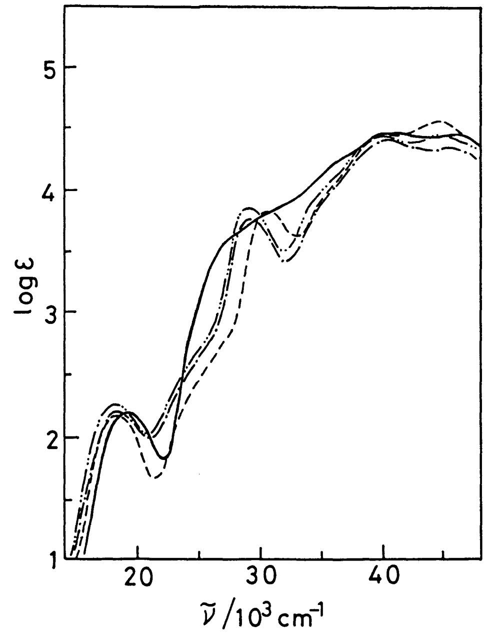

Fig. 2. Absorption spectra of $\Lambda(S)\Delta(R)$-[Co(Xacac)$_2$(Me-en)]$^+$ in 0.01 mol dm^{-3} HCl, Xacac=NO$_2$acac (——), Clacac (—•—), acac (----), and CH$_3$acac (—••—).

band at lower energy than that of the $\Lambda(R)\Delta(S)$ isomers. The first absorption band shifts to lower energy as Xacac is changed from NO$_2$acac through Clacac and acac to CH$_3$acac. The shift will be related with the electronic effect of the X substituent on acac, since no steric interaction seems to occur among the X substituent and other ligands.

Electrochemistry and ^{1}H NMR Spectra. Electrochemistry is very useful for measuring electronic effects of substituents on the ligand in metal complexes. Rotating glassy carbon electrode voltammograms of the [Co(Xacac)$_2$(Me-en)]$^+$ complexes were measured in 0.1 mol dm^{-3} KCl vs. a saturated calomel electrode (SCE), and the results are summarized in Table 2. The complexes show a quasi-reversible reduction wave assignable to the Co^{3+}/Co^{2+} couple. The half-wave potentials ($E_{1/2}$ values) range from −0.08 V to −0.59 V. The difference in $E_{1/2}$ between the isomers is small in each complex. The $E_{1/2}$'s are plotted as a function of the Hammett σ_p parameter for the X substituent in [Co(Xacac)$_2$(Me-en)]$^+$ (Fig.3). A linear relationship between them indicates that the electronic effect of a substituent at the 3-position of the acac ligand is transmitted through the ligand to the metal ion in these complexes. It has been demonstrated that polarographic reduction potentials of Cr(III) and Ru(III) β-diketonates correlate well with the substituent electronic effects as measured by Hammett substituent effects.[15,16]

If the electronic effect is transmitted further to the amine nitrogen atoms, it should be reflected on the properties of the amine group. This is especially true for ^{1}H NMR spectroscopy, where an increase

Table 2. Electrochemical Data for the Reduction of [Co(Xacac)$_2$(Me-en)]$^+$ (vs. SCE) at 24 °C$^{a)}$

Xacac	Substituent parameter/σ_p	Isomer	$E_{1/2}$/V	$\lvert E_{3/4}-E_{1/4}\rvert$/V$^{b)}$
NO$_2$acac$^{c)}$	+0.78	$\Lambda(S)\Delta(R)$	−0.08	0.095
		$\Lambda(R)\Delta(S)$	−0.08	0.095
Clacac	+0.23	$\Lambda(S)\Delta(R)$	−0.28	0.095
		$\Lambda(R)\Delta(S)$	−0.27	0.095
acac	0	$\Lambda(S)\Delta(R)$	−0.47	0.100
		$\Lambda(R)\Delta(S)$	−0.47	0.105
CH$_3$acac	−0.17	$\Lambda(S)\Delta(R)$	−0.59	0.090
		$\Lambda(R)\Delta(S)$	−0.56	0.100

a) By glassy carbon rotating disk experiments (in water containing 0.1 mol dm^{-3} KCl with a 0.01 V s^{-1} scan rate; 2000 rev min^{-1}). b) $E_{3/4}$ and $E_{1/4}$ are potentials at three-fourth and one-fourth of the limiting current value, respectively. c) Adjusted to pH 4 with dil HClO$_4$.

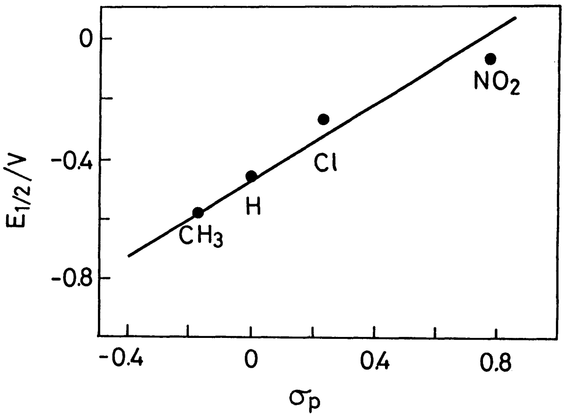

Fig. 3. Plot of the reduction half-wave potentials ($E_{1/2}$) vs. the Hammett parameter σ_p for [Co(Xacac)$_2$(Me-en)]$^+$ (Xacac=NO$_2$acac, Clacac, acac, and CH$_3$acac).

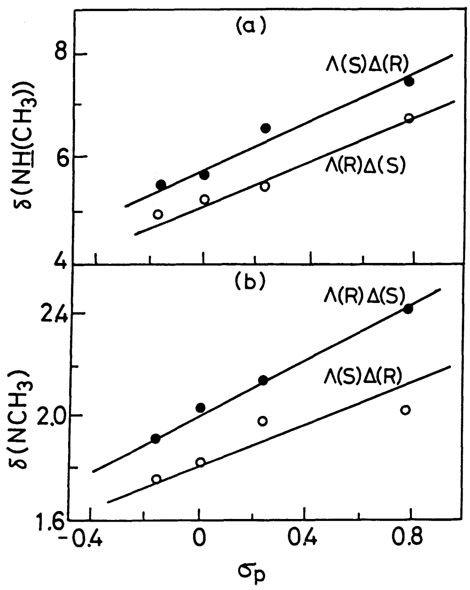

Fig. 4. Correlation of the ^{1}H NMR chemical shifts with the Hammett parameter, σ_p: δ(N$\underline{H}$(CH$_3$)) vs. σ_p (a) and δ(NCH$_3$) vs. σ_p (b).

(decrease) in electron density on a particular proton will lead to a high (low) field shift for that proton. The chemical shift data of the N$\underline{H}$(CH$_3$) and NCH$_3$ indicate this electronic effect (Table 1). For example, the N$\underline{H}$(CH$_3$) signal of $\Lambda(S)\Delta(R)$-[Co(NO$_2$acac)$_2$(Me-en)]$^+$ is shifted 1.95 ppm downfield from its position in the spectrum of the corresponding CH$_3$acac complex. The nitro group withdraws electron density from the *N*-methyl nitrogen atom to cause the downfield shift of the amine proton signal. Plots of the chemical shifts of the N$\underline{H}$(CH$_3$) and NCH$_3$ protons vs. the Hammett substituent constants (σ_p) were linear (Fig. 4).

Deuteration and Eqimerization Reactions. Table 3 gives the rate constants for deuteration, k_D at chiral nitrogen centers of the [Co(Xacac)$_2$(Me-en)]$^+$ complexes. The k_D value of the NO$_2$acac complex is ca. 10^4 times as large as that of the CH$_3$acac complex. A decrease in electron density on the amine nitrogen should labilize the hydrogen to promote H-D exchange. A linear relationship holds as shown in Fig. 5, where the logarithms of the deuteration rate constants for the Xacac complexes relative to that for the acac complex are plotted against the Hammett σ_p values. Although such a Hammett relationship has been reported to hold for deuteration of [Co(X-acac)$_2$(en)]$^+$ (Xacac=NO$_2$acac, Bracac, acac) in a D$_2$O-DMSO-d_6 mixture (weight ratio 1 : 3.9), the NO$_2$acac complex was deuterated faster than the acac complex only by a factor of 12.[16] The factor of the present Me-en complex in D$_2$O is 1600.

The rate constants for epimerization, k_{ep} of the [Co(Xacac)$_2$(Me-en)]$^+$ complexes are given in Table 3. Electronic contributions of the X substituents induce pronounced effect on the rates. For example, the epimerization rate of the NO$_2$acac complex is ca. 10^6 times greater than that of the CH$_3$acac complex. There also exists a linear Hammett relationship as

Table 3. A Comparison of Data for the Deuteration and Inversion at Chiral Nitrogen Centers of [Co(Xacac)$_2$(Me-en)]$^+$ at 34.0 °C

Xacac	Isomer	k_D/M^{-1} s^{-1} b)	k_{ep}/M^{-1} s^{-1}	(k_1 or k_{-1})/M^{-1} s^{-1}	r=(k_1 or k_{-1})/k_D
NO$_2$acac	$\Lambda(S)\Delta(R)$	1.4×10^7	6.6×10^3	k_1: 3.7×10^3	2.6×10^{-4}
	$\Lambda(R)\Delta(S)$	2.1×10^6		k_{-1}: 2.9×10^3	1.4×10^{-3}
Clacac	$\Lambda(S)\Delta(R)$	9.1×10^4	4.2	k_1: 2.5	2.8×10^{-5}
	$\Lambda(R)\Delta(S)$	1.7×10^4		k_{-1}: 1.7	1.0×10^{-4}
acac$^{a)}$	$\Lambda(S)\Delta(R)$	8.9×10^3	1.3×10^{-1}	k_1: 7.1×10^{-2}	7.7×10^{-6}
	$\Lambda(R)\Delta(S)$	c)		k_{-1}: 5.9×10^{-2}	
CH$_3$acac	$\Lambda(S)\Delta(R)$	7.9×10^2	2.9×10^{-3}	k_1: 1.6×10^{-3}	2.0×10^{-6}
	$\Lambda(R)\Delta(S)$	1.5×10^2		k_{-1}: 1.3×10^{-3}	8.3×10^{-6}

a) From Ref. 12. b) 1 M=1 mol dm^{-3}. c) The data could not be obtained because of the overlapping of the N-CH$_3$ and C-CH$_3$ signals.

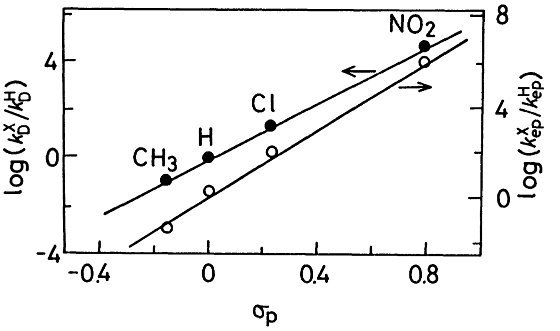

Fig. 5. Plot of $\log(k_D{}^X/k_D{}^H)$ vs. the Hammett σ_p for $\Delta(S)\Delta(R)$-[Co(Xacac)$_2$(Me-en)]$^+$ (●) and plot of $\log(k_{ep}{}^X/k_{ep}{}^H)$ vs. the Hammett σ_p for [Co(Xacac)$_2$(Me-en)]$^+$ (○).

shown in Fig. 5. We assume here that the proton-exchange and epimerization reactions proceed by Eqs. 1—3.[1,18]

$$\Delta(S)\text{-}[\mathrm{Co(Xacac)_2(NH(CH_3)CH_2CH_2NH_2)}]^+ + \mathrm{OH}^- \underset{k_{+\mathrm{H}^+}}{\overset{k_{-\mathrm{H}^+}}{\rightleftarrows}} \Delta(S)\text{-}[\mathrm{Co(Xacac)_2({}^-N(CH_3)CH_2CH_2NH_2)}]+\mathrm{H_2O} \qquad (1)$$

$$\Delta(S)\text{-}[\mathrm{Co(Xacac)_2({}^-N(CH_3)CH_2CH_2NH_2)}] \underset{k'_i}{\overset{k_i}{\rightleftarrows}} \Delta(R)\text{-}[\mathrm{Co(Xacac)_2({}^-N(CH_3)CH_2CH_2NH_2)}] \qquad (2)$$

$$\Delta(R)\text{-}[\mathrm{Co(Xacac)_2({}^-N(CH_3)CH_2CH_2NH_2)}] + \mathrm{H_2O} \underset{k'_{-\mathrm{H}^+}}{\overset{k'_{+\mathrm{H}^+}}{\rightleftarrows}} \Delta(R)\text{-}[\mathrm{Co(Xacac)_2(NH(CH_3)CH_2CH_2NH_2)}]^+ + \mathrm{OH}^- \qquad (3)$$

The actual rate of inversion of the amido complex is k_i (k'_i) and is pH independent.[19] The measured rate constant for epimerization (k_{ep}) is pH dependent since the rate depends on the amount of amido complex present. The ratio, $r=(k_1$ or $k_{-1})/k_D$, which is determined by partitioning the deprotonated intermediate between inversion and reprotonation, becomes a direct measure of the actual rate of inversion if the reprotonation rate is constant (diffusion controlled). This is the case when the pK_a values of [Co(Xacac)$_2$(Me-en)]$^+$ exceed 14, as has been estimated for other cobalt(III)-amine complexes.[1,20] A plot of $\log(r^X/r^H)$ against σ_p is found to be linear (reaction constant $\rho=+2.2$), where r^X and r^H denote the r values of the Xacac and acac complexes, respectively (Fig. 6).

The selenium atom of a selenide (RSeR′) ligand becomes chiral on coordination to a metal ion. We have studied the inversion at the selenium atom in [Co(Xacac)$_2$(CH$_3$SeCH$_2$CH$_2$NH$_2$)]$^+$ and found that the Hammett relationship holds for the rates of the Clacac, acac, and CH$_3$acac complexes, where the reaction constant ρ is -2.9, a negative value.[21] The first step of inversion at a chiral nitrogen center will be the abstraction of the coordinated secondary amine proton by OH$^-$ to yield a pyramidal center (Eq. 1).

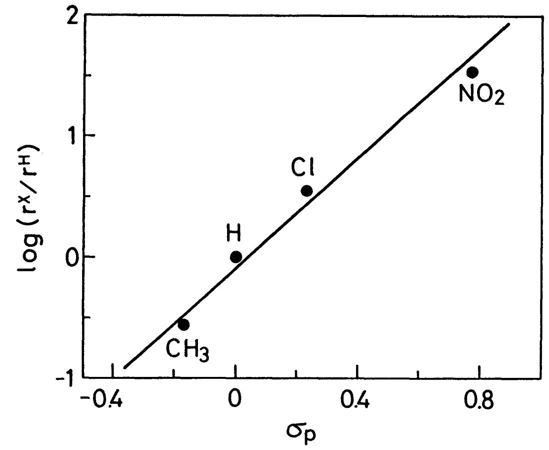

Fig. 6. Plot of $\log(r^X/r^H)$ vs. the Hammett σ_p for [Co(Xacac)$_2$(Me-en)]$^+$.

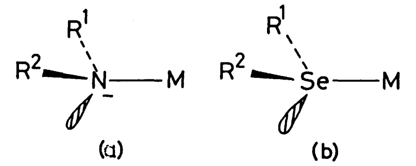

Fig. 7. Structures of the pyramidal amide intermediate (a) and the coordinated selenide (b).

The structure of the pyramidal amide intermediate will be similar to that of the coordinated selenide (Fig. 7), but inverse electronic effect was found. For a pyramidal atomic inversion, it is usually observed that an electronegative substituent on the central atom decreases the rate of inversion.[22] The Se inversion of the cobalt-selenides is the case.

The reason for the inverse electronic effect of the N inversion of [Co(Xacac)$_2$(Me-en)]$^+$ is difficult to explain. The cobalt-amide intermediates possess a formal negative charge on nitrogen, and the electronic effect of the charge might play an important role in controlling the stereochemistry to affect the inversion rate. The importance of electrostatic effect (electron repulsion effect) as a rate-controlling factor for an atomic inversion was pointed out by Anet et al.[23] They studied the rates of the N inversion of (CH$_2$)$_2$NX and those of the C inversion of R$_2$C$^-$X. The effect of the group X on the negatively charged carbanion system was found to differ from that on the neutral aziridine system. The lack of correlation between the two systems was ascribed to the difference in electrostatic effect between them. A similar discussion might be made for the cobalt-amide intermediates, since they are isoelectronic with cobalt-selenides as carbanions are with amines.

The present work was supported by a Grant-in-Aid for Scientific Research No. 61430013 from the Ministry of Education, Science and Culture.

References

1) W. G. Jackson and A. M. Sargeson, "Rearrangement in Coordination Complexes," in "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 2, p. 273, and references therein.

2) G. Ma, T. Hibino, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **62**, 1053 (1989).

3) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960); F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

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

5) M. Shibata, *Nippon Kagaku Zasshi*, **87**, 771 (1966).

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

7) A. J. Brown, O. W. Howarth, and P. Moore, *J. Am. Chem. Soc.*, **100**, 713 (1978).

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

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

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

11) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1964).

12) M. Kojima, T. Hibino, Y. Ouyang, and J. Fujita, *Inorg. Chim. Acta*, **117**, 1 (1986).

13) K. Nakajima, M. Kojima, M. Fujita, and J. Fujita, *J. Chromatogr.*, **301**, 241 (1984); K. Nakajima, M. Kojima, and J. Fujita, *ibid.*, **362**, 281 (1986).

14) K. Nakajima, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **59**, 3505 (1986).

15) G. S. Patterson and R. H. Holm, *Inorg. Chem.*, **11**, 2285 (1972).

16) R. F. Handy and R. L. Lintvedt, *Inorg. Chem.*, **13**, 893 (1974).

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

18) J. B. Goddard and F. Basolo, *Inorg. Chem.*, **8**, 2223 (1969).

19) T. P. Pitner and R. B. Martin, *J. Am. Chem. Soc.*, **93**, 4400 (1971).

20) R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

21) K. Nakajima, M. Kojima, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **59**, 3505 (1986).

22) J. B. Lambert, *Top. Stereochem.*, **6**, 19 (1971) and references therein.

23) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 357 (1967).