Bull. Chem. Soc. Jpn., *62*, *1053—1056 (1989)*

Inversion and Deuteration at the Chiral Nitrogen Centers of [Co(acac or ox)$_2$(Me-en or Me$_3$en)]$^{+\text{or}-}$ (acac=2,4-Pentanedionate Ion; ox=Oxalate Ion; Me-en=*N*-Methylethylenediamine, Me$_3$en=*N,N,N'*-Trimethylethylenediamine)

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(Received July 15, 1988)

The rates of the base-catalyzed proton exchange (deuteration, k_D) and isomerization (epimerization, k_{ep}) at the chiral amine nitrogen centers of [Co(acac or ox)$_2$(Me-en or Me$_3$en)]$^{+\text{or}-}$ in aqueous solutions were measured at 34.0 °C, and the results were compared with one another and with those of related complexes. The deuteration rate is affected more by the nature of coexisting ligands than the overall charge on the complex. The uninegative ox complexes have larger k_D values than the unipositive acac complexes. The k_{ep} values of the ox complexes are ca. 10^4 times as large as those of the acac complexes. For both ox and acac complexes, the complexes with Me$_3$en have larger k_D and k_{ep} values than the complexes with Me-en. The deuteration rates are ca. 10^4—10^5 and ca. 10^2 times greater than the inversion rates for the acac and ox complexes, respectively.

In a previous paper,[1] we reported that the rates of OH$^-$-catalyzed isomerization (epimerization, k_{ep}) and proton exchange (deuteration, k_D) at the chiral nitrogen center of [Co(acac)$_2$(Me-en)]$^+$ are unusually slow, the rates being ca. 10^4 times as small as those of [Co(NH$_3$)$_4$(Me-en)]$^{3+}$.[2] The rates of the same reactions of the sarcosinate ion (sar) in [Co(sar)(Hbg)$_2$]$^{2+}$ (Hbg: biguanide=NH$_2$C(=NH)NHC(=NH)NH$_2$)[3] are also ca. 10^3—10^4 times as small as those of [Co(sar)(NH$_3$)$_4$]$^{2+}$.[4] These results suggest that the rates are largely affected by the nature of coexisting ligands, although deuteration rates at the coordinated amine nitrogen centers are known to increase with an increasing positive charge on the complex.[5] Thus it is interesting to compare the rates of [Co(acac)$_2$(diamine)]$^+$ with those of [Co(ox)$_2$(diamine)]$^-$; both complexes belong to the CoO$_4$N$_2$-type, but they have charge of different signs.

In this paper, we report the rates of epimerization and deuteration at chiral nitrogen centers of [Co(acac or ox)$_2$(Me-en or Me$_3$en)]$^{+\text{or}-}$. The paper also describes the preparation and some properties of oxalato complexes with related diamines.

Experimental

[Co(acac)$_2$(Me$_3$en)]ClO$_4$ (Me$_3$en=*N,N,N'*-trimethylethylenediamine) was prepared and separated into the two isomers, $\Lambda(R)\Delta(S)$ and $\Lambda(S)\Delta(R)$, as described previously.[6] Absorption and ^{1}H NMR spectra were measured on a Hitachi 323 spectrophotometer and a Hitachi R-90H spectrometer, respectively.

$\Lambda(R)\Delta(S)$-Na[Co(ox)$_2$(Me-en)]·H$_2$O, $\Lambda(S)\Delta(R)$-Na[Co(ox)$_2$(Me-en)]·H$_2$O, Na[Co(ox)$_2$(*N,N*-Me$_2$en)]·0.5NaCl·0.5H$_2$O (*N,N*-Me$_2$en=*N,N*-Dimethylethylenediamine), $\Lambda(RR)\Delta(SS)$-Na[Co(ox)$_2$(*N,N'*-Me$_2$en)]·2H$_2$O (*N,N'*-Me$_2$en=*N,N'*-Dimethylethylenediamine), $\Lambda(RS)\Delta(SR)$-Na[Co(ox)$_2$(*N,N'*-Me$_2$en)]·2H$_2$O, and $\Lambda(SS)\Delta(RR)$-Na[Co(ox)$_2$(*N,N'*-Me$_2$en)]. These complexes were prepared by a similar method to that for Na[Co(ox)$_2$(en)] (en=ethylenediamine).[7] Yield: 20—50%. For Me-en and *N,N'*-Me$_2$en complexes, the complexes were epimerized in dil Na$_2$CO$_3$ solution (pH 8—9) for 30 min at room temperature, and then the isomers were separated by Dowex 1×8 column chromatography (eluent: 0.05 mol dm^{-3} NaCl-0.01 mol dm^{-3} HCl). Anal. (C$_7$H$_{12}$N$_2$CoNaO$_9$=$\Lambda(R)\Delta(S)$- and $\Lambda(S)\Delta(R)$-Na[Co(ox)$_2$(Me-en)]·H$_2$O) C,H,N. (C$_8$H$_{13}$N$_2$Cl$_{0.5}$CoNa$_{1.5}$O$_{8.5}$=Na[Co(ox)$_2$(*N,N*-Me$_2$en)]·0.5NaCl·0.5H$_2$O) C,H,N. (C$_8$H$_{16}$N$_2$CoNaO$_{10}$=$\Lambda(RR)\Delta(SS)$- and $\Lambda(RS)\Delta(SR)$-Na[Co(ox)$_2$(*N,N'*-Me$_2$en)]·2H$_2$O) C,H,N. (C$_8$H$_{12}$N$_2$CoNaO$_8$=$\Lambda(SS)\Delta(RR)$-Na[Co(ox)$_2$(*N,N'*-Me$_2$en)]) C,H,N.

$\Lambda(R)\Delta(S)$-Na[Co(ox)$_2$(Me$_3$en)]·H$_2$O and $\Lambda(S)\Delta(R)$-Na[Co(ox)$_2$(Me$_3$en)]·3H$_2$O. To an aqueous solution (80 cm^3) of K$_3$[Co(ox)$_3$]·3H$_2$O (3.7 g, 9.4 mmol) was added an aqueous solution (20 cm^3) of Me$_3$en (1.35 g, 11.3 mmol). The mixture was stirred for 25 h at room temperature and then filtered. The purple filtrate was diluted with water (1 dm^3), and applied on a column (ϕ2.6 cm×20 cm) of Dowex 1×8 (200—400 mesh). By elution with 0.15 mol dm^{-3} NaCl, a purple, a pink (probably a cobalt(II)-ox complex), and a green ([Co(ox)$_3$]$^{3-}$) band developed in this order. From the purple eluate the complex (a mixture of the two isomers) was isolated as the sodium salt. Yield: 2.6 g (73%). The complex was epimerized and separated into the two isomers, $\Lambda(R)\Delta(S)$ and $\Lambda(S)\Delta(R)$, in the ratio of 5.2 : 1 by the same method as for the Me-en complex. Anal. (C$_9$H$_{16}$N$_2$CoNaO$_9$=$\Lambda(R)\Delta(S)$-Na[Co(ox)$_2$(Me$_3$en)]·H$_2$O) C,H,N. (C$_9$H$_{20}$N$_2$CoNaO$_{11}$=$\Lambda(S)\Delta(R)$-Na[Co(ox)$_2$(Me$_3$en)]·3H$_2$O) C,H,N.

Na[Co(ox)$_2$(Me$_4$en)]·4H$_2$O (Me$_4$en=*N,N,N',N'*-Tetramethylethylenediamine). This complex was prepared by a method similar to that described for the Me$_3$en complex in a yield of 37% (violet crystals). Anal. (C$_{10}$H$_{24}$N$_2$CoNaO$_{12}$) C,H,N.

Deuteration Studies. The rates of deuteration at the chiral nitrogen centers of [Co(ox)$_2$(Me-en)]$^-$, [Co(ox)$_2$(Me$_3$en)]$^-$, and [Co(acac)$_2$(Me$_3$en)]$^+$ were followed by monitoring N-CH$_3$ signal changes in the ^{1}H NMR spectra as described previously.[1] [Co(acac)$_2$(Me$_3$en)]ClO$_4$ was converted into the more soluble chloride with a Dowex 1×8 anion exchanger in the chloride form. The rates for [Co(ox)$_2$(Me-en)]$^-$ and [Co(acac)$_2$(Me$_3$en)]$^+$ were measured in a phosphate buffer (pD 5.7—7.1) at 34.0 °C, while that for [Co(ox)$_2$(Me$_3$en)]$^-$ in a phthalate buffer (pD 4.3—6.5) at 34.0 °C. The empirical formula, pD=pH meter reading+0.4, was used to calculate

[OD$^-$].[8]

Epimerization Studies. The rates of epimerization for [Co(ox)$_2$(Me-en)]$^-$, [Co(ox)$_2$(Me$_3$en)]$^-$, and [Co(acac)$_2$(Me$_3$en)]$^+$ in aqueous solutions at 34.0 °C were followed by the same method as that described previously.[1,9] It involves separation of two isomers of the complexes by a high-performance liquid chromatographic method, and analysis of chromatograms changed with reaction time.

Results and Discussion

Two, three, and two isomers (racemic pairs of diastereomers) are possible for [Co(ox)$_2$(Me-en)]$^-$, [Co(ox)$_2$(*N*,*N*′-Me$_2$en)]$^-$, and [Co(ox)$_2$(Me$_3$en)]$^-$, respectively (Fig. 1). All these isomers were separated by Dowex 1X8 column chromatography under acidic conditions. The aqueous solutions should be kept acidic to avoid isomerization (inversion at the chiral nitrogen centers, vide infra). The structures of the complexes were assigned on the basis of the ^{1}H NMR spectra taking magnetic anisotropy of the carboxyl group into consideration; a complex which shows a doublet attributable to the *N*-methyl group at a higher magnetic field is assigned to the Λ(*S*)Δ(*R*)-isomer (Table 1).

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. Table 1 also gives the absorption spectral data for the complexes. Both distributions of the isomers and positions of the d-d absorption bands seem to be related with the steric crowding involved in the isomers. For example, the Λ(*S*)Δ(*R*)-isomer of [Co(ox)$_2$(Me-en)]$^-$, in which the *N*-methyl group is situated over one of the ox ligands and larger steric crowding will be involved than the Λ(*R*)Δ(*S*)-isomer, is formed less and exhibits the d-d absorption bands at lower energy than the Λ(*R*)Δ(*S*)-isomer (Fig. 1 and Table 1). The [Co(ox)$_2$(Me$_4$en)]$^-$ complex exhibits the d-d absorption bands at the lowest energy in the present complexes (Table 1). The low ligand field strength of the Me$_4$en ligand was also reported for [Co(acac)$_2$(Me$_4$en)]$^+$ and was ascribed to the steric crowding which occurs in the complex.[6,10]

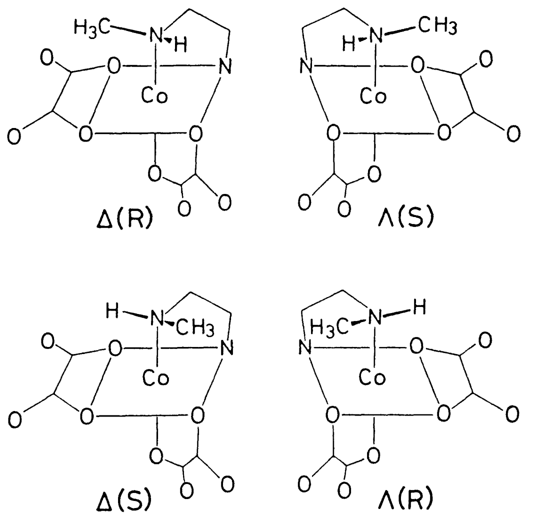

Fig. 1. The four possible isomers of [Co(ox)$_2$(Me-en)]$^-$.

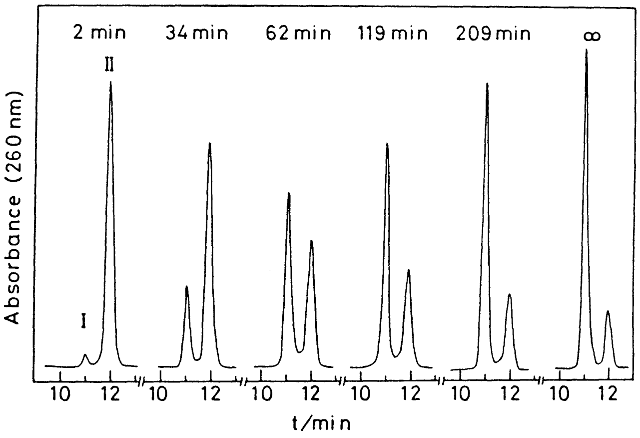

Fig. 2. Change in the elution curve during the epimerization of Λ(*S*)Δ(*R*)-[Co(ox)$_2$(Me$_3$en)]$^-$ at pH 6.03 and 34.0 °C (I: Λ(*R*)Δ(*S*) isomer, II: Λ(*S*)Δ(*R*) isomer). Chromatographic conditions: column, JASCO Finepack SIL C$_{18}$, ϕ 0.46 cmX25 cm; eluent, 5X10^{-3} mol dm^{-3} Bu$_4$NCl in CH$_3$CN-H$_2$O (11:89 v/v); flow rate, 2.0 cm^3 min^{-1}; UV detection, 260 nm.

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

L	Assignment	^{1}H NMR (δ)		Absorption (d-d bands)	Relative
		CH$_3$	N$\underline{\text{H}}$(CH$_3$)	$\tilde{\nu}_{\text{max}}$/10^3 cm^{-1} (log ε)	abundance/%
en				18.52 (2.11) 26.11 (2.31)[c]	
Me-en	Λ(*R*)Δ(*S*)	2.25d	5.50[a]	18.35 (2.12) 25.91 (2.31)[d]	68
	Λ(*S*)Δ(*R*)	1.87d	5.92[a]	18.32 (2.11) 25.84 (2.31)[d]	32
N,*N*′-Me$_2$en	Λ(*RR*)Δ(*SS*)	2.20d	5.83[a]	18.18 (2.12) 25.71 (2.32)[d]	58
	Λ(*RS*)Δ(*SR*)	2.23d, 1.80d	5.96, 6.22[a]	18.15 (2.11) 25.64 (2.31)[d]	33
	Λ(*SS*)Δ(*RR*)	1.84d	6.29[a]	18.12 (2.10) 25.64 (2.31)[d]	9
N,*N*-Me$_2$en		2.36s, 1.88s[b]		17.89 (2.11) 25.45 (2.29)[c]	
Me$_3$en	Λ(*R*)Δ(*S*)	2.33s, 2.19d, 1.86s	5.96[a]	17.73 (2.12) 25.25 (2.32)[d]	82
	Λ(*S*)Δ(*R*)	2.35s, 1.82d, 1.86s	6.45[a]	17.70 (2.06) 25.19 (2.26)[d]	18
Me$_4$en		2.33s, 1.87s[b]		17.30 (2.13) 24.63 (2.31)[c]	

a) In D$_2$O-DCl. b) In D$_2$O. c) In H$_2$O. d) In 10^{-2} mol dm^{-3} HCl.

Table 2. A Comparison of Data for the Deuteration and Inversion at Chiral Nitrogen Centers of $[Co(ox)_2L]^-$ (L=Me-en, Me$_3$en) and $[Co(acac)_2L]^+$ at 34.0 °C

Complex	Isomer	$k_D/M^{-1}\,s^{-1}$ b)	$k_{ep}/M^{-1}\,s^{-1}$	$(k_1 \text{ or } k_{-1})/M^{-1}\,s^{-1}$	$k_D/(k_1 \text{ or } k_{-1})$
$[Co(ox)_2(Me\text{-}en)]^-$	$\Lambda(R)\Delta(S)$	2.2×10^4	8.4×10^2	k_{-1}: 2.7×10^2	8.1×10
	$\Lambda(S)\Delta(R)$	1.8×10^5		k_1: 5.7×10^2	3.2×10^2
$[Co(ox)_2(Me_3en)]^-$	$\Lambda(R)\Delta(S)$	1.2×10^5	1.2×10^4	k_{-1}: 2.1×10^3	5.7×10
	$\Lambda(S)\Delta(R)$	8.1×10^5		k_1: 9.9×10^3	8.2×10
$[Co(acac)_2(Me\text{-}en)]^+$ a)	$\Lambda(R)\Delta(S)$	c)	1.3×10^{-1}	k_{-1}: 5.9×10^{-2}	
	$\Lambda(S)\Delta(R)$	8.9×10^3		k_1: 7.1×10^{-2}	1.3×10^5
$[Co(acac)_2(Me_3en)]^+$	$\Lambda(R)\Delta(S)$	2.4×10^3	1.0	k_{-1}: 3.4×10^{-1}	7.1×10^3
	$\Lambda(S)\Delta(R)$	1.1×10^4		k_1: 6.6×10^{-1}	1.7×10^4

a) From Ref. 1. b) 1M=1 mol dm^{-3}. c) The data could not be obtained because of the overlapping of the $N\text{-}CH_3$ and $C\text{-}CH_3$ signals.

Kinetic studies of reversible isomerization (epimerization) between the two isomers of $[Co(ox)_2(Me\text{-}en)]^-$, $[Co(ox)_2(Me_3en)]^-$, and $[Co(acac)_2(Me_3en)]^+$ were performed in aqueous solutions at 34.0 °C by observing the change in chromatograms with reaction time. Figure 2 shows a typical set of elution curves obtained at intervals after $\Lambda(S)\Delta(R)$-$[Co(ox)_2(Me_3en)]^-$ had been dissolved in water at pH 6.03 and 34.0 °C. The pseudo-first-order rate constant, $k_{ep(obsd)}$ was obtained by the method described previously.[1,9] The $k_{ep(obsd)}/[OH^-]$ ($=k_{ep}$) values are constant at 34.0 °C in the pH range 5.7—6.7 indicating that the reaction is first order in $[OH^-]$. Thus, the rate law was the same as that for racemization (epimerization) of other chiral amine complexes, $R=k_{ep}[\text{complex}][OH^-]$.[11] 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

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

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 ($K_{eq}=k_1/k_{-1}$) as given in Table 2.

The rates of deuteration at chiral amine nitrogen centers of $[Co(ox)_2(Me\text{-}en)]^-$, $[Co(ox)_2(Me_3en)]^-$, and $[Co(acac)_2(Me_3en)]^+$ were followed by monitoring siganl changes in the ^{1}H NMR spectra. From the changes, the pseudo-first-order rate constants for deuteration, $k_{D(obsd)}$ were obtained by a method similar to that for epimerization. The rate law for the deuteration reaction was the same as that obtained previously for other amine complexes, $R=k_D[\text{complex}][OD^-]$.[11] The k_D values are given in Table 2.

In the deuteration reactions, the term in $[OD^-]$ is interpreted as removal of H^+ from the coordinated amine to leave a pyramidal center.[4,11] The pyramidal nitrogen center is followed by formation of a trigonal planar amide which leads to the inversion of the nitrogen center (epimerization of the complex).[4,11] Thus the k_{ep} values will be related to both the rate of deuteration and the stability of the trigonal planar amide in the transition state. The k_D values for the $\Lambda(S)\Delta(R)$ isomers of the present complexes are ca. 5—8 times as large as those for the $\Lambda(R)\Delta(S)$ isomers. The rate differences can be attributed to a difference in steric effect between the isomers. As is seen in Fig. 1 the secondary amine hydrogen in the $\Lambda(R)\Delta(S)$ isomer, which is situated over one of the ox ligands, will be more effectively hindered by the ox ring from atacking of OH^- than the hydrogen in the $\Lambda(S)\Delta(R)$ isomer. The same interpretation is given for the rate difference between the isomers of $[Co(acac)_2(Me_3en)]^+$.

For both ox and acac complexes, the complexes with Me$_3$en have larger k_D values than the complexes with Me-en. The result seems to be related with a difference in electron density on the secondary amine hydrogen atoms as suggested in the ^{1}H NMR spectra. For example, as one goes from $\Lambda(S)\Delta(R)$-$[Co(ox)_2(Me\text{-}en)]^-$ to $\Lambda(S)\Delta(R)$-$[Co(ox)_2(Me_3en)]^-$, the amine proton signal ($N\underline{H}(CH_3)$) is shifted from δ 5.92 to 6.45, suggesting a decrease in electron density at the hydrogen atom in line with the increase in k_D value (Tables 1 and 2). The k_{ep} values for the Me$_3$en complexes are also larger than those for the Me-en complexes.

It is known that deuteration rates increase with an increasing positive charge on the complex (ca. 10-fold for each unit of charge).[5] Thus the unipositive acac complexes are expected to give larger k_D values than the uninegative ox complexes. However, the inverse has been found. The difference in k_{ep} values between the ox and acac complexes is much more pronounced; the k_{ep} values for the ox complexes are ca. 10^4 times as large as those for the corresponding acac complexes. Kawaguchi et al.[3] reported that $[Co(sar)(Hbg)_2]^{2+}$ also gives much smaller k_D (ca. 10^4 mol^{-1} dm^3 s^{-1} at 39.6 °C) and k_{rac} ($=k_{ep}$, 13.8 mol^{-1} dm^3 s^{-1} at 35.0 °C) values than those ($k_D=1.2\times10^8$ mol^{-1} dm^3 s^{-1} and $k_{rac}=3.3\times10^4$ mol^{-1} dm^3 s^{-1} at 33.3 °C) of the corresponding ammine complex $[Co(sar)(NH_3)_4]^{2+}$.[4] These results suggest that the reactivity of coordinated secondary amine nitrogen center is affected more by the kind of coexisting ligands than the overall charge on the complex. The reason for the small rates of the acac and Hbg complexes remains unknown. However, it is worth noting that both acac and Hbg ligands form a chelate ring with delocalized π-electrons.

The $k_D/(k_1$ or $k_{-1})$ ratios (retention ratios) for $[Co(acac)_2(Me\text{-}en\ or\ Me_3en)]^+$ (ca. 10^4—10^5) are similar to that for $[Co(NH_3)_4(Me\text{-}en)]^{3+}$ (2.5×10^5 at 34.3 °C),[2] and the values imply that the configuration about the chiral nitrogen atom (pyramidal configuration) is retained most of the time that the proton is off the quarternary N site. On the other hand, the retention ratios for $[Co(ox)_2(Me\text{-}en\ or\ Me_3en)]^-$ (ca. 10^2) and $[Co(sar)(Hbg)_2]^{2+}$ (10^2—10^3) are small. The smaller retention ratios may result from an increased stabilization of the trigonal planar amide in the transition state.[2,12] However, the factors governing the retention ratio for the above complexes are not clear at the moment. More kinetic data will be needed to elucidate the effect of coexisting ligands on the reactivity of coordinated amine nitrogen center.

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

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