Metal Complexes of Amino Acids. XII.[1] The Deuteration of α-Hydrogen Atoms in Cobalt(III) Complexes Containing α-Amino Carboxylates

Tomoharu AMA,* Hiroshi KAWAGUCHI, Makoto KANEKIYO, and Takaji YASUI
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
(Received June 29, 1979)

The second-order rate constants (rate=$k_{D(base)}$[Complex][OD^-]) for the deuterium exchange of α-methylene or α-methine protons in the amino carboxylato complexes, *trans(O)*-, C_1-*cis(O)*-, and C_2-*cis(O)*-$[Co(gly)_2(en)]^+$ and -$[Co(gly)_2(tn)]^+$, $[Co(gly)(NH_3)_4]^{2+}$, $[Co(gly)(en)_2]^{2+}$, $[Co(gly)(tn)_2]^{2+}$, $[Co(sar)(en)_2]^{2+}$, and *Λ*- and *Δ*-$[Co(L\text{-}ala)(en)_2]^{2+}$, were determined by the ^1H-NMR measurement. The major factors determining the deuteration rate of α-hydrogens in the amino carboxylate chelate are the geometry and charge of the complex, and the nature of the substituent bonded to the chelate ring to be deuterated; the minor factor is the chelate-ring size of the ligands other than amino carboxylate in a complex molecule.

It is well-known that the metal ions increase the reactivity of α-methylene protons in α-amino carboxylate. Since the magnitude and specificity of the effect were first shown by Williams and Busch[2] through a ^1H-NMR study of cobalt(III) complexes containing glycinate, alaninate, and ethylenediaminetetraacetate, a large number of studies involving the deuteration of the cobalt(III) complexes have been undertaken.[3-14] Many of these studies have treated polyamino carboxylato complexes. On the other hand, few studies have been made of the α-amino carboxylato complexes. It had been found that the deuteration rate of the glycinate methylene proton in the polyamino carboxylato complex is related to the chelate-ring strain; *i.e.*, the methylene protons of out-of-plane glycinate (less strained) in $[Co(edta)]^-$ are more rapidly deuterated than those of in-plane glycinate (strained).[2] However, factors (the charge and geometry of the complex and substituent in the ligand, and so on) other than the ring strain must also be related to the deuteration rate. In order to determine these factors, a study using α-amino carboxylato complexes is more profitable than one using polyamino carboxylato complexes because then we can exclude the effect of the chelate-ring strain.

In the present paper, we will evaluate the deuteration rates of α-protons in several types of cobalt(III) complexes containing the chelated glycinate, L-alaninate, and sarcosinate; we will also discuss the relation between the deuteration rate and the geometry of the complex, the charge of the complex ion, and the nature of the substituent in a ligand.

Experimental

Preparation of the Complexes. Synthesis and Separation of the Isomers of Bis(glycinato)(trimethylenediamine)cobalt(III) Chloride: A solution containing 10 g of cobalt(II) chloride hexahydrate in 10 ml of water was added to a solution containing 5 g of trimethylenediamine and 6.4 g of glycine in 30 ml of water. Lead dioxide (10 g) was then gradually added to the solution on a water bath, after which the solution was mechanically stirred at 55 °C for about 30 min. The precipitates were filtered off, and the filtrate was kept in a refrigerator overnight. The precipitates were filtered off again, and the filtrate was poured into a column containing a cation-exchange resin (Dowex 50W×8, 200—400 mesh, K^+ form). The column was flushed with water to sweep out any nonelectrolytic or anionic complexes, and then the adsorbed band was developed with a 0.2 M aqueous solution of potassium chloride. Two bands appeared: a violet one (lower) and a red-violet one (upper). It was confirmed from their absorption spectra that the early- and late-eluted solutions contain *trans(O)* and *cis(O)* (mixture of C_1-*cis(O)* and C_2-*cis(O)*) isomers respectively. Each eluted solution was evaporated to a small volume using a rotary evaporator, a small amount of ethanol was added to the concentrated solution, and the potassium chloride was filtered off. A crude product of the *trans(O)* isomer was obtained from the above solution (early eluate) on the addition of more ethanol. The C_1-*cis(O)* isomer was deposited as columnar crystals by the further addition of a small amount of ethanol to the above ethanolic solution (late eluate) and by then keeping the solution in a refrigerator overnight. After the C_1-*cis(O)* isomer had been removed by filtration, a large amount of ethanol was added to the filtrate. A crude product of the C_2-*cis(O)* isomer was obtained as fine needle crystals. Each isomer was recrystallized from water by the addition of ethanol. Found for the *trans(O)* isomer: C, 25.91; H, 6.14; N, 17.15%. Calcd for $[Co(gly)_2(tn)]Cl\cdot 0.5H_2O$: C, 25.81; H, 5.88; N, 17.20%. Found for the C_1-*cis(O)* isomer: C, 25.20; H, 6.13; N, 16.85%. Calcd for $[Co(gly)_2(tn)]Cl\cdot H_2O$: C, 25.12; H, 6.02; N, 16.74%. Found for the C_2-*cis(O)* isomer: C, 24.63; H, 6.29; N, 16.08%. Calcd for $[Co(gly)_2(tn)]Cl\cdot 1.5H_2O$: C, 24.46; H, 6.11; N, 16.30%.

The other cobalt(III) complexes examined here were prepared by the published methods[15-21] and were found to be analytically pure.

Measurements of Deuteration Rate. The deuteration runs were carried out under a flow of nitrogen in order to avoid a decrease in the pD by the absorption of CO_2 in air. Each complex (1 mmol) was dissolved in 9 ml of D_2O. The sample solution was kept at 30.0, 40.0, or 50.0 °C (±0.05 °C) in a thermostat, and then 20 μl of *t*-butyl alcohol and 1 ml of a 1 M Na_2CO_3–D_2O solution (or a 0.5 M Na_2CO_3–0.5 M $NaDCO_3$–D_2O solution) were added to the sample solution. The deuteration of the methylene protons of chelated glycinate began immediately after the Na_2CO_3–D_2O solution was added to the sample solution. At prescribed time intervals, 0.5-ml aliquot sample solutions were taken out from the container, kept in a thermostat. The exchange reaction was immediately stopped by adding the sample solution to 0.05 ml (or 0.038 ml) of 2 M DCl and by then cooling the mixture to 0 °C. The pD of the sample solution in the container was measured by the use of a pH meter (Beckman LABOMATE II) with a combination electrode. The pD=pH+0.4[22] and $[OD^-]=3.0\times 10^{-15}[D^+]^{-1}$ formulae were used to evaluate $[D^+]$ and $[OD^-]$ re-

spectively.

The ^{1}H-NMR spectra of the neutralized solutions were recorded at 100 MHz using a JEOL MH-100 NMR spectrometer at room temperature. The intensities of the ^{1}H-NMR signals of the methylene protons in the chelated glycinate were estimated by comparing them with that of *t*-butyl alcohol as a standard. The ^{1}H-NMR data are given with the chemical shifts *vs.* DSS.

Results and Discussion

trans(O), C_1-cis(O), and C_2-cis(O) Isomers of $[Co(gly)_2(en)]^+$. The ethylene proton signals arising from the chelated ethylenediamine were unchanged throughout the experiment. In addition, on developing the residual solution of each deuteration run in the cation-exchange column (SP-Sephadex), only one band was observed; no complexes resulting from decomposition or isomerization were detected. The neutralized solution used for the ^{1}H-NMR measurement did not show any change in its NMR intensity or spectral pattern for at least one day at room temperature.

The resonance peaks of the methylene protons of chelated glycinate appeared in the range of 3.4—3.7 ppm. The two glycinate methylenes in the C_2-*cis(O)* and *trans(O)* isomers are equivalent, but those in the C_1-*cis(O)* isomer are not. Figure 1 shows the resonance patterns which are to be expected from the symmetries of these isomers. Yoneda *et al.*[23] assigned the methylene signal at 3.60 ppm to the $H_a(H_a')$ of glycinate and that at 3.44 ppm to $H_b(H_b')$ (Fig. 1).

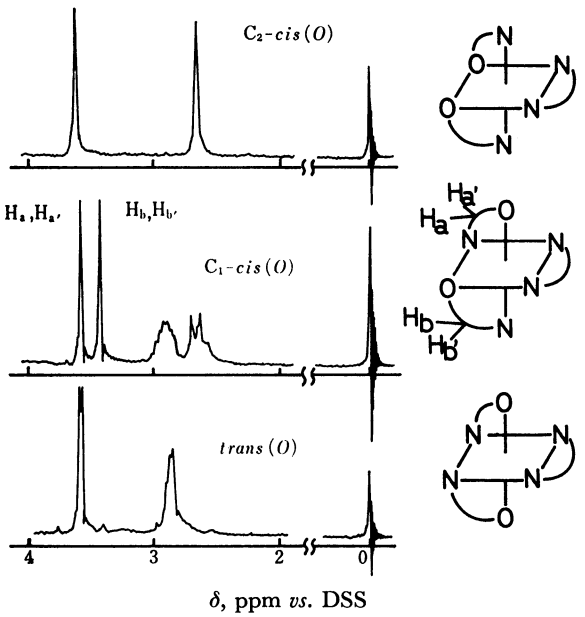

Fig. 1. ^{1}H-NMR spectra of C_2-*cis(O)*-, C_1-*cis(O)*-, and *trans(O)*-$[Co(gly)_2(en)]^+$ complex ions.

Plots of log *I vs.* the deuteration time at a constant pD yield straight lines, where *I* denotes the relative NMR intensities of the glycinate methylenes to the *t*-butyl alcohol methyls, the internal standard (Fig. 2). Accordingly, the deuteration rate at a constant pD

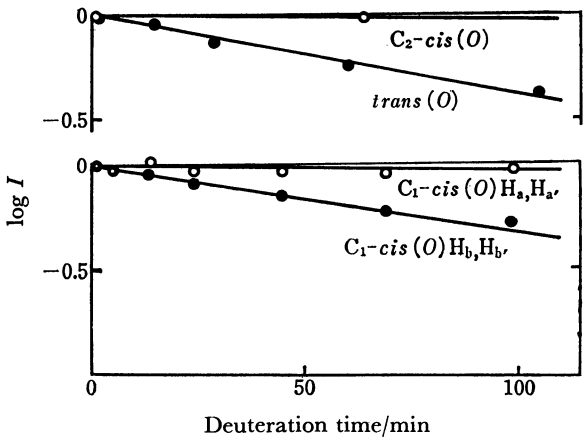

Fig. 2. Plots of log *I* (*I* denotes the relative NMR intensity of α-hydrogens) *vs.* deuteration time of three isomers in $[Co(gly)_2(en)]^+$ complex ion. pD=11.7; Temperature, 30.0 °C.

can be expressed as:

$$-\frac{d[complex]}{dt} = k'_{D(base)}[complex],$$

where $k'_{D(base)}$ is the apparent rate constant for the base-catalyzed deuteration at a constant pD. This result agrees with that obtained from the study of EDDA–Co(III) complexes by Sudmeier and Occupati.[5] The rate constants of the deuterium exchange of methylene protons in the chelated glycinate are given in Table 1. Sudmeier and Occupati showed, in their study of the base-catalyzed deuterium exchange of EDDA–Co(III) complexes, that the reaction was first-order in $[OD^-]$. Our present result coincides with their result; *i.e.*, the $k'_{D(base)}[OD^-]^{-1}$ values of the present complexes are constant at a given temperature.

The deuteration rates of the methylene protons in the chelated glycinate at 50 °C decrease in this order; *trans(O)*$\geq H_b(H_b')$ of C_1-*cis(O)*$>C_2$-*cis(O)*$\geq H_a(H_a')$ of C_1-*cis(O)*. Dabrowiak and Cooke[24] studied the reaction of acetaldehyde with cobalt(III) complexes containing chelated glycinate. They showed that the order of reactivity is: $[Co(gly)(en)_2]^{2+}$>*trans(O)*-$[Co(gly)_2(en)]^+$ >C_1-*cis(O)*-$[Co(gly)_2(en)]^+$>C_2-*cis(O)*-$[Co(gly)_2(en)]^+$. This order agrees with that of the deuteration rate determined in the present study. The fact that the rates are different among the geometrical isomers of the present complexes with the same 1+ charge suggests that the geometry of the complex is one of the most important factors affecting the deuteration rate.

It is obvious from Table 1 and Fig. 2 that the two non-equivalent glycinates in the bis(glycinato) complex differ in their deuteration rates; *i.e.*, the rate of the deuterium exchange of $H_b(H_b')$ in C_1-*cis(O)*-$[Co(gly)_2(en)]^+$ is larger than that of $H_a(H_a')$. It is known that the deuteration of the "out-of-plane" glycinate protons in $[Co(edta)]^-$ is far more rapid than those of any other CH_2 protons in the complex. Williams and Busch[2] suggested that such a difference between the two non-equivalent glycinates in $[Co(edta)]^-$ is a function of the ring strain. In the present complex, C_1-*cis(O)*-$[Co(gly)_2(en)]^+$, no such chelate-ring strain as in

TABLE 1. RATE CONSTANTS FOR THE DEUTERIUM-EXCHANGE REACTION OF GLYCINATE α-HYDROGENS IN *trans(O)*-, C_2-*cis(O)*-, AND C_1-*cis(O)*-$[Co(gly)_2(en)]^+$ COMPLEX IONS

Species	Temp °C	$k'_{D(base)}$ (10^{-4} s^{-1})	[OD⁻] (mol/l)	$k_{D(base)}$ ($k'_{D(base)}$/[OD⁻])
trans(O)	20.0	0.29±0.01	0.19×10^{-2}	0.015±0.0006
	30.0	1.53±0.03	0.15×10^{-2}	0.100±0.0018
	50.0	1.26±0.13	0.61×10^{-4}	2.1 ±0.21
C_2-*cis(O)*	30.0	0.14±0.01	0.77×10^{-3}	0.018±0.0013
	40.0	0.66±0.03	0.74×10^{-3}	0.089±0.0036
	50.0	2.44±0.21	0.75×10^{-3}	0.325±0.0280
C_1-*cis(O)* H_b	30.0	1.12±0.03	0.17×10^{-2}	0.066±0.0016
	40.0	2.47±0.13	0.87×10^{-3}	0.29 ±0.015
	50.0	2.62±0.27	0.19×10^{-3}	1.4 ±0.14
	50.0	6.35±0.34	0.42×10^{-3}	1.5 ±0.08
C_1-*cis(O)* H_a	30.0	0.18±0.04	0.17×10^{-2}	0.011±0.0023
	40.0	0.46±0.04	0.87×10^{-3}	0.053±0.0049
	50.0	0.58±0.23	0.19×10^{-3}	0.31 ±0.12
	50.0	1.22±0.12	0.42×10^{-3}	0.29 ±0.028

TABLE 2. ACTIVATION PARAMETERS FOR THE BASE-CATALYZED DEUTERATION OF GLYCINATO α-HYDROGENS IN *trans(O)*-, C_2-*cis(O)*-, AND C_1-*cis(O)*-$[Co(gly)_2(en)]^+$ COMPLEX IONS

Species	ΔG^*(50 °C) (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})
trans(O)	77±8	131±4	168±14
C_2-*cis(O)*	82±10	120±5	117±16
C_1-*cis* (*O*) $H_b(H_b')$	78±13	128±6	154±20
C_1-*cis* (*O*) $H_a(H_a')$	82±11	139±5	176±18

$[Co(edta)]^-$ can be expected between the two non-equivalent glycinates. Nevertheless, the rate constant of $H_b(H_b')$ is about five times as large as that of $H_a(H_a')$. This suggests that, in the bis(glycinato) complexes, there are factors other than the chelate-ring strain.

The activation parameters of these isomers are given in Table 2. Both the enthalpy and the entropy of activation for these isomers increase in this order: C_2-*cis(O)*< $H_b(H_b')$ of C_1-*cis(O)*<*trans(O)*<$H_a(H_a')$ of C_1-*cis(O)*. The order of ΔH^* and ΔS^* is different from the order of the deuteration rate.

trans*(O)*, C_1-cis*(O)*, *and* C_2-cis*(O) Isomers of* $[Co(gly)_2(tn)]^+$. The ^{1}H-NMR spectra of these complexes are shown in Fig. 3. The methylene resonances of the glycinates in the *trans(O)* and C_2-*cis(O)* isomers were observed at 3.57 and 3.58 ppm respectively. The methylene resonances of the C_1-*cis(O)* isomer appeared as singlet peaks at 3.57 ppm (assigned to H_a and H_a' on the basis of the theory proposed by Yoneda *et al.*)[23] and 3.35 ppm (assigned to H_b and H_b'). These isomers did not decompose or isomerize under the given conditions, and the neutralized solution used for the ^{1}H-NMR measurement did not indicate any change in NMR intensity and spectral shape for at least one day at room temperature.

The deuteration rates of the methylene protons of glycinates decrease in this order: $H_b(H_b')$ of C_1-*cis(O)*≳ *trans(O)*>C_2-*cis(O)*>$H_a(H_a')$ of C_1-*cis(O)* (at 50 °C; Table 3). This order is almost the same as that of the isomers of $[Co(gly)_2(en)]^+$. The difference in the deuteration rate between the two non-equivalent glycinates in the C_1-*cis(O)* isomer is obvious, as has been shown for the C_1-*cis(O)* isomer of the $[Co(gly)_2(en)]^+$ complex. The trimethylenediamine and ethylenediamine complexes indicated a nearly equal deuteration rate for each corresponding isomer.

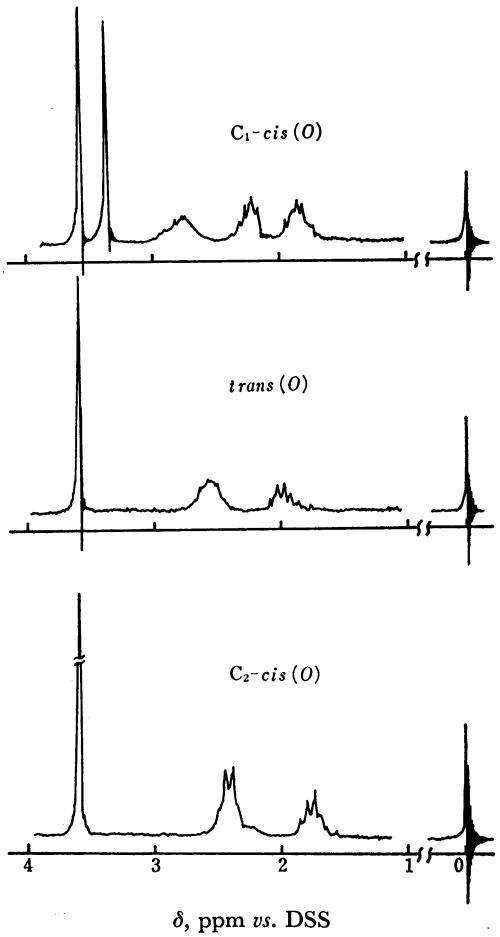

Fig. 3. ^{1}H-NMR spectra of C_1-*cis(O)*-, *trans(O)*-, and C_2-*cis(O)*-$[Co(gly)_2(tn)]^+$ complex ions.

$[Co(gly)(en)_2]^{2+}$, $[Co(gly)(tn)_2]^{2+}$, and $[Co(gly)$-

Table 3. Rate constants at 50 °C for the deuterium-exchange reaction of amino carboxylato α-hydrogens in various complex ions

Species	$k_{D}'_{(base)}$ (10^{-4} s^{-1})	[OD^-] (mol/l)	$k_{D(base)}$ ($k_{D}'_{(base)}$/[OD^-])
trans(*O*)-[$Co(gly)_2(tn)]^+$	8.7 ±0.2	0.48×10^{-3}	1.8 ±0.047
C_1-*cis*(*O*)-[$Co(gly)_2(tn)]^+$ $\{H_b(H_b')$	10.1 ±0.3	0.50×10^{-3}	2.0 ±0.067
$\{H_a(H_a')$	2.0 ±0.1	0.50×10^{-3}	0.40±0.022
C_2-*cis*(*O*)-[$Co(gly)_2(tn)]^+$	2.8 ±0.1	0.60×10^{-3}	0.47±0.024
$[Co(gly)(NH_3)_4]^{2+}$	0.56±0.1	0.31×10^{-4}	1.8 ±0.39
$[Co(gly)(en)_2]^{2+}$	1.2 ±0.2	0.49×10^{-4}	2.4 ±0.51
$[Co(gly)(tn)_2]^{2+}$	1.5 ±0.3	0.38×10^{-4}	3.9 ±0.71
$[Co(sar)(en)_2]^{2+}$	3.0 ±0.7	0.48×10^{-4}	6.3 ±1.5
Δ-[Co(L-ala)$(en)_2]^{2+}$	0.34±0.03	0.35×10^{-4}	0.97±0.08
Λ-[Co(L-ala)$(en)_2]^{2+}$	0.32±0.02	0.34×10^{-4}	0.93±0.065

$(NH_3)_4]^{2+}$ Complexes. In the present study, we measured the deuteration rates of several 2+ charged complexes (Table 3). The rate constant of the bis(trimethylenediamine) complex is larger than that of the bis(ethylenediamine) complex, while that of the tetraammine complex is smaller than those of the bis(ethylenediamine) and bis(trimethylenediamine) complexes. The order of the rate constants is parallel to the basicity of these amines. However, the change in the deuteration rate caused by replacing four ammines with two ethylenediamines or two trimethylenediamines is not so large as that caused by the variation in the geometrical structures.

Norman *et al.*[14] and McClarin *et al.*[11] have suggested that the charge of a complex is one of the most important factors determining the deuteration rate. Their suggestions lead one to expect that the deuteration rate constant of neutral or negative-charged complex is smaller than that of a positive-charged one. In fact, the *cis*(*O*)*cis*(*N*) and *cis*(*O*)*trans*(*N*) isomers of the [Co(gly)$_2$(acac)]^0 complex and the [Co(gly)$(acac)_2]^0$ complex were deuterated very slowly under the conditions of the present study (accompanied by some isomerization or decomposition), although we were unsuccessful in all our attempts to estimate the rate constants with accuracy. The anionic complex, $[Co(gly)_2(NO_2)_2]^-$, was scarcely ever deuterated, and the C_1-*cis*(*O*)-[Co(gly)$_2$(ox)]$^-$ anion was deuterated very slowly, accompanies by a gradual decomposition, under the same conditions.

However, among the positive-charged complexes, we could not recognize any remarkable difference in the rate constants between 1+ and 2+ charged complex ions (Table 3). The rate constants for the 2+ charged complex ions, $[Co(gly)(tn)_2]^{2+}$ and $[Co(gly)(en)_2]^{2+}$, are nearly equal to those of the 1+ charged complex ions, *trans*(*O*)-[Co(gly)$_2$(tn)]$^+$, *trans*(*O*)-[Co(gly)$_2$(en)]$^+$, and $H_b(H_b')$ of C_1-*cis*(*O*)-[Co(gly)$_2$(tn)]$^+$ and -[Co(gly)$_2$-(en)]$^+$. In addition, the rate constant of the $[Co(gly)(NH_3)_4]^{2+}$ complex ion is comparable with those of these 1+ charged complexes. These results suggest that, for the positive complex ions, there are present important factors other than the charge of the complex which determines the deuteration rate.

Substituent Effect on Deuteration Rate. The rate constants of the deuteration for the methine protons in *Λ*- and *Δ*-[Co(L-ala)$(en)_2]^{2+}$ complexes are given in Table 3. The rate constants of the two diastereomers are nearly equal to each other. These data imply that the effect on the deuteration rate of the dissymmetry around Co(III) is fairly small. This result agrees with that obtained by Buckingham *et al.*[4] in their study of the equilibrium rate between $(-)_{589}$-[Co(L-ala)$(en)_2]^{2+}$ and $(-)_{589}$-[Co(D-ala)$(en)_2]^{2+}$ complexes.

The deuteration rates of these L-alaninato complexes are smaller than that of $[Co(gly)(en)_2]^{2+}$. On the other hand, the rate of $[Co(sar)(en)_2]^{2+}$ is about 2.5 times larger than that of $[Co(gly)(en)_2]^{2+}$. These results suggest that the *C*-methyl and *N*-methyl have opposite effects. It is difficult to explain such different effects on the basis of the sterical interaction of methyl groups. Here, it seems reasonable to consider that the stability of the carbanion intermediate which is formed by deprotonation is different between the L-alaninato and sarcosinato complexes. This consideration leads to the prediction that the deuteration of the ligand which has the $-CH_2-NH-CH_2-COO^-$ group is faster than that of the chelated glycinate. This prediction was confirmed by the experimental finding that the deuteration rate of α-hydrogen is about ten times larger in *trans*(*O*)-[Co(edda)$(en)]^+$ [4] than in *trans*(*O*)-[Co(gly)$_2$(en)]$^+$. In addition, it can be expected from the above prediction that the out-of-plane α-hydrogens in [Co(edta)]$^-$ undergo deuteration much faster than the glycinate α-hydrogens in C_1-*cis*(*N*)-[Co(gly)$_2$(ox)]$^-$ do.

The conclusion obtained from this work is as follows: the most important factor in determining the deuteration rate of α-hydrogen may be the chelate-ring strain for the polyamino carboxylato complex, but for the bidentate amino acidato complex, the geometry and charge of the complex and the substituent in the chelate ring to be deuterated are the major factors. The chelate-ring size of the ligands other than the amino carboxylate also affect the deuteration rate, but the effect is a minor.

References

1) Part XI of this series: T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, **52**, 79 (1979).

2) D. H. Williams and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 4644 (1965).

3) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966).
4) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5133 (1967).
5) J. L. Sudmeier and G. Occupati, *Inorg. Chem.*, **7**, 2524 (1968).
6) D. H. Williams, J. R. Angus, and J. Steele, *Inorg. Chem.*, **8**, 1374 (1969).
7) B. B. Smith and R. H. Betts. *Inorg. Chem.*, **9**, 2585 (1970).
8) P. F. Coleman, J. I. Legg, and J. Steele, *Inorg. Chem.*, **9**, 937 (1970).
9) J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, **10**, 90 (1971).
10) G. L. Blackmer and J. L. Sudmeier, *Inorg. Chem.*, **10**, 2019 (1971).
11) J. A. McClarin, L. A. Dressel, and J. I. Legg. *J. Am. Chem. Soc.*, **98**, 4150 (1976).
12) W. E. Keyes, R. E. Caputo, R. D. Willett, and J. I. Legg, *J. Am. Chem. Soc.*, **98**, 6939 (1976).
13) W. E. Keyes and J. I. Legg, *J. Am. Chem. Soc.*, **98**, 4970 (1976).
14) P. R. Norman and D. A. Phipps, *Inorg. Chim. Acta*, **28**, L161 (1978).
15) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **40**, 1868 (1967).
16) S. H. Laurie, *Aust. J. Chem.*, **21**, 679 (1968).
17) Y. Fujii and T. Ejiri, *Bull. Chem. Soc. Jpn.*, **45**, 283 (1972).
18) M. B. Celap, T. J. Janjic, and D. J. Radanovic, *Inorg. Synth.*, Vol. IX, 173 (1967).
19) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 458 (1975).
20) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).
21) T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, **49**, 472 (1976).
22) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).
23) H. Yoneda, U. Sakaguchi, and Y. Nakashima, *Bull. Chem. Soc. Jpn.*, **48**, 209 (1975).
24) J. C. Dabrowiak and D. W. Cooke, *Inorg. Chem.*, **14**, 1305 (1975).