Stereospecific Deuteration of Chelated 2,2'-Thiodiacetate(tda) in $[Co(dien)(tda)]^+$ (dien = diethylenetriamine) Observed in the Acidic D_2O Solutions

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Stereospecific deuteration rates of 2,2'-thiodiacetate (tda) in *s-fac-* and *u-fac-*$[Co(dien)(tda)]^+$ were measured at 70.2 °C in D_2O (pD range 4.4 — 6.4). The observed rate constants (k') were proportional to the $[OD^-]$. The large $k'/[OD^-]$ value (ca. 3.8×10^6) shows that the protons on the chelated $-SCH_2COO^-$ ring are much more active than those on the chelated $-NHCH_2COO^-$ ring.

In the course of studies on cobalt(III) complexes, it was found that the α methylene protons in the $-NHCH_2COO^-$ moiety (glycinate ring) are stereospecifically deuterated in a basic D_2O solution,[1,2] and that the methylene protons neighboring to the coordinated thioether-S are active.[3,4] Though it is expected that the complexes containing the ligands which have the $-SCH_2COO^-$ moiety (thioglycolate ring) are also deuterated in D_2O solution, there are few reports about the deuteration rates of the thioglycolate rings.[3] Therefore, we designed a study on the deuteration rates of $[Co(dien)(tda)]^+$ (dien: diethylenetriamine; tda: 2,2'-thiodiacetate) isomers and obtained interesting result that the stereospecific deuteration of the chelated thioglycolate rings is much faster than that of the chelated glycinate rings.

The isomers of $[Co(dien)(tda)]^+$ were prepared by the method reported in the previous paper.[5] The *u-fac-*[Co(dien)(tda)]Cl isomer was newly optically resolved by the chromatographic method using an SP-Sephadex column (K^+ form; eluent: 0.1 mol·dm^{-3} $K_2[Sb_2(d\text{-tart})_2]$). $\Delta\varepsilon_{542} = -2.17$. Though the UV and CD spectral changes with time of the *u-fac* and *s-fac* isomers were followed under the same condition as the H—D exchange reactions (vide post), appreciable spectral changes were not observed. These results show that their racemization and isomerization reactions are not significant at 70 °C in the pD region 4.4 — 6.4. However, the *mer* isomer showed appreciable spectral change at 70 °C, suggesting that its isomerization was not negligible; accordingly, we must give up an estimation of the deuteration rate for the *mer* isomer.

The ^1H NMR spectra of the $[Co(dien)(tda)]^+$ isomers are given in Fig. 1. In the *s-fac* isomer, two $-SCH_2COO^-$ arms in the coordinated tda are equivalent, but the two protons in each arm are inequivalent. Therefore, the two protons appear as an AB quartet (δ = 3.67 and 4.03 ppm, J_{gem} = 18 Hz). The methylene protons in the facially coordinated tda are stereospecifically deuterated in neutral D_2O solution as shown in Fig. 1; a new singlet signal arising from -CHD- appeared between the two higher-field peaks (3.54 and 3.74ppm) with an intensity loss of the AB quartet and subsequently the new singlet signal disappeared with the formation of $-CD_2$-. Similar result was obtained for the α methylene protons in facially coordinated edma (*N*-carboxymethylethylenediamine).[1] In the edma complexes, it was pointed out that the rate of the inside α proton is slower than the outside proton. The application of this result to *s-fac-*$[Co(dien)(tda)]^+$ leads to the following conclusion; the two lower-field peaks of the AB quartet arise from the outside proton which is easily deuterated, while the two higher-field peaks arise from the inside proton.

Measurements of the deuteration rates of the present complexes were carried out as follows. A buffer solution (pD 4.4 — 6.4) was prepared by adding a proper amount of 0.1 mol·dm^{-3} CD_3COOD—D_2O to a solution containing 0.02 g of CD_3COONa in 10 ml of D_2O. About 0.3 g of *s-fac-*[Co(dien)(tda)]Cl was dissolved into the buffer solution and kept in a water bath at 70.2 °C. At prescribed time intervals, a portion of the reaction solution (ca. 0.5 ml) was taken out and put into an NMR tube and then quickly quenched in an ice bath. In each run, the pseudo-first-order rate constant of the outer proton ($k'_s(out)$) was estimated from the intensity decrease of the two peaks in the range 3.9 — 4.2 ppm (Fig. 1), and that of the inner proton ($k'_s(in)$) was from the intensity decrease of the signals in the range 3.5 — 3.8 ppm. The $k'_s/[OD^-]$ values ($k_s(out)$ and $k_s(in)$) are listed in Table 1, together with the observed k'_s values. The k_s values of the *s-fac* isomer are almost constant at 70.2 °C in the pD range 4.4 — 6.4. This result shows that the deuteration reaction is first-order in $[OD^-]$. Similar results were obtained for the base-catalyzed deuteration of

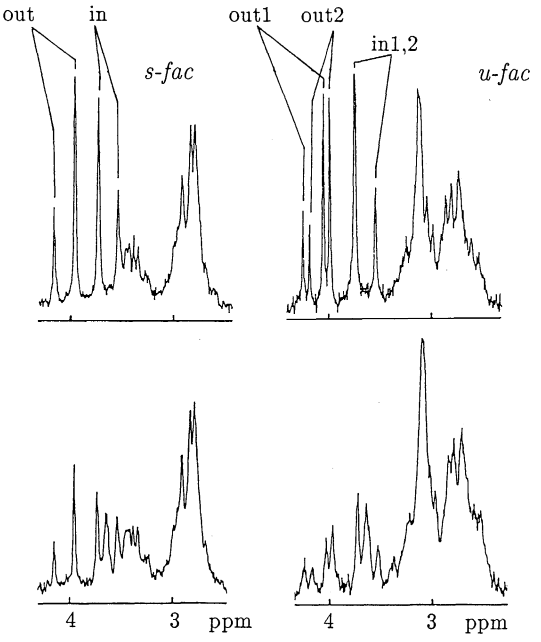

Figure 1. ^1H NMR Spectra (90 MHz) of *s-fac-* and *u-fac-*$[Co(dien)(tda)]^+$. upper: non-deuterated; and lower: partially deuterated.

Table 1. H—D Exchange Reaction Rates in D_2O (70.2 °C).

Complexes	pD	Observed Rate Constants (k'/ sec^{-1})		Second-Order Rate Constants[a] (k/ mol^{-1} dm^{-3} sec^{-1})	
$s-fac$-[Co(dien)(tda)]$^+$	4.4	$k'_s(out)$	1.5×10^{-4}	$k_s(out)$	3.8×10^{6}
		$k'_s(in)$	2.1×10^{-5}	$k_s(in)$	5.2×10^{5}
	4.9	$k'_s(out)$	5.2×10^{-4}	$k_s(out)$	4.1×10^{6}
	5.4	$k'_s(out)$	1.4×10^{-3}	$k_s(out)$	3.4×10^{6}
		$k'_s(in)$	1.9×10^{-4}	$k_s(in)$	4.7×10^{5}
	6.4	$k'_s(in)$	1.8×10^{-3}	$k_s(in)$	4.5×10^{5}
$u-fac$-[Co(dien)(tda)]$^+$	5.4	$k'_u(out1)$	1.6×10^{-3}	$k_u(out1)$	4.0×10^{6}
		$k'_u(out2)$	2.2×10^{-3}	$k_u(out2)$	5.4×10^{6}

[a] k values were calculated by the following equations: $k = k'/[OD^-]$

the α-methylene protons in the chelated glycinate ring.[1] The $k_S(out)/k_S(in)$ values are about 7 (at 70 °C) in *s-fac*-[Co(dien)(tda)]$^+$. These $k_S(out)/k_S(in)$ values are similar in maginitude to those observed in the facially coordinated tridentates containing glycinate ring (e. g., some isomers of [Co(edma)$_2$]$^+$). The above mentioned results show that the chelated thioglycolate ring resembles the chelated glycinate ring in regard to deuteration of α methylene. However, they differ to each other in the magnitude of deuteration rate. That is, the $k_S(out)$ values of *s-fac*-[Co(dien)(tda)]$^+$ are about 10^2 times larger than those of edma in *C_i-trans(O)*-[Co(edma)$_2$]$^+$ at 70 °C. The $k_S(in)$ values of the former are at least 10^2 times larger than those of the latter. This difference shows that the methylene protons on the chelated thioglycolate ring are much more active than those on the chelated glycinate ring.

In the *u-fac*-[Co(dien)(tda)]$^+$, the chemical environments of the two methylenes in the facially coordinated tda are inequivalent: *trans* position to one of the two thioglycolate carboxyl-O is occupied by secondary amino-N of dien and that to another carboxyl-O is primary amino-N. Therefore, the signals for two pairs of four α protons are observable as two AB quartets (3.4 — 4.3 ppm; Fig. 1). These protons are stereospecifically deuterated in a manner similar to that of *s-fac*-[Co(dien)(tda)]$^+$. The $k'_u(out1)$ and $k'_u(out2)$ values (deuteration rates observed for the outer protons of facially coordinated tda in *u-fac*-[Co(dien)(tda)]$^+$) were estimated from the intensity decreases at 3.98 and 4.18 and at 4.05 and 4.25 ppm, respectively. (It was difficult to estimate the $k'_u(in1)$ and $k'_u(in2)$ values (the rates for the inner protons) because of the overlapping of the NMR signals.) The $k'_u(out1)/k'_u(out2)$ value is about 1.3, showing that the deuteration rates of the two outer protons do not differ so largely. Similarly to the case of *s-fac*-[Co(dien)(tda)], the second-order rate constants of the tda outer α protons of *u-fac*-[Co(dien)(tda)] are also much larger than those of the edma α protons in the [Co(edma)$_2$]$^+$ isomers.

The experiments to estimate the deuteration rate of tda in the [Co(tda)$_2$]$^-$ isomers were designed. However, because of significantly faster isomerization reactions, we could not obtain the reliable deuteration rate constants.

The neutral H_2O solution of *s-fac*-[Co(dien)(tda)]Cl showed 4 peaks in the $^{13}C\{^1H\}$ NMR spectra; 42.0, 45.5 52.6 and 182.8 ppm. However, in its neutral D_2O solution, the peaks at 42.0 and 182.8 ppm split to multiplets and their intensities decreased; accordingly, their signal heights were very low. This observation is attributed to the fast H—D exchange on the α-methylene protons of coordinated tda in neutral D_2O. The *u-fac* isomer exhibited eight $^{13}C\{^1H\}$ NMR signal peaks in H_2O solution; 42.0, 42.3, 42.4, 44.9, 54.2, 55.8, 182.8, and 183.1ppm. However, the heights of the signals at 42.0, 42.4, 182.8, and 183.1ppm were extremely low in its D_2O solution. In the ^{13}C NMR measurements of the neutral D_2O solution of the [Co(dien)(tdp)]$^+$ isomers[5] (tdp = $S(CH_2CH_2COO^-)_2$), such intensity decreases as observed in the [Co(dien)(tda)]$^+$ isomers were not observed. In [Co(aeaps)(tacn)]$^+$ (aeaps: 1,6-diamino-4-thiahexane; tacn: 1,4,7-triazacyclononane), the H—D exchange in -SCH_2CH_2- moiety was observed in 1 mol·dm^{-3} NaOD solution,[4] however, the second order rate constants are much smaller than those of the present complexes. These results indicate that the methylene protons present between the coordinated thioether-S and carboxyl groups are much more active than that between another methylene and the coordinated thioether-S groups.

References and Notes

1 T. Ama, H. Kawaguchi, T. Yasui, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **58**, 2561 (1985).

2 P. F. Coleman, J. I. Legg, and J. Steele, *Inorg. Chem*, **9**, 937 (1970); D. J. Radanovic and B. E. Douglas, *Inorg. Chem.*, **14**, 6 (1975); D. H. Williams and D. H. Busch, *J. Amer. Chem. Soc.*, **87**, 4644 (1965); J. L. Sudmeier and G. Occupati, *Inorg. Chem.*, **7**, 2524 (1968).

3 M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 2958 (1983).

4 P. Kofod, E. Larsen, C. H. Petersen, and J. Springborg, *Acta Chem. Scand.*, **46**, 1149 (1992).

5 K. Kanamori, T. Sudani, K. Kawai, *Bull. Chem. Soc. Jpn.*, **49**, 2739 (1976).