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# Hydrolysis Kinetics of *trans*(*O*)-Bromo, Chloro or Nitro-(3,6,9-Triazaundecanedioato)cobalt(III) Complex

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For the acid-uncatalyzed aquation of *trans*(*O*)-[Co(taud)X] at the ionic strength ($\mu$) of 0.1 ($NaClO_4$), the first order rate constant ($k_{aq}$) is $9.6\times10^{-5}$ $s^{-1}$ at 25 °C, $\Delta H^{\ddagger}=93$ kJ mol$^{-1}$, $\Delta S^{\ddagger}=-10$ J K$^{-1}$ mol$^{-1}$, $\Delta V^{\ddagger}=-3.2$ cm$^3$ mol$^{-1}$ with $X=Cl^-$; and $k_{aq}$ is $4.6\times10^{-4}$ $s^{-1}$ at 25 °C, $\Delta H^{\ddagger}=91$ kJ mol$^{-1}$, $\Delta S^{\ddagger}=-4$ J K$^{-1}$ mol$^{-1}$, $\Delta V^{\ddagger}=-2.3$ cm$^3$ mol$^{-1}$ with $X=Br^-$. Here taud stands for the quinquedentate $^-OOCCH_2NH(CH_2)_2NH(CH_2)_2NHCH_2COO^-$. These magnitudes of $\Delta V^{\ddagger}$ are slightly different from the expected values. For the acid-catalyzed aquation of *trans*-(*O*)-[Co(taud)$NO_2$], $k_{aq}$/s$^{-1}$ depends on the [H$^+$]/M of the solution: $k_{aq}=1.3\times10^{-4}[H^+]+3.09\times10^{-3}[H^+]^2$ at 45.6 °C and $\mu=0.5$ (M = mol dm$^{-3}$). For the base hydrolysis of *trans*(*O*)-[Co(taud)X] at $\mu=1.0$ ($NaClO_4$), the second order rate constant ($k_2$) is 104 M$^{-1}$ s$^{-1}$ at 25 °C, $\Delta H^{\ddagger}=77$ kJ mol$^{-1}$, $\Delta S^{\ddagger}=12$ J K$^{-1}$ mol$^{-1}$ with $X=Cl^-$; and $k_2$ is 760 M$^{-1}$ s$^{-1}$ at 25 °C, $\Delta H^{\ddagger}=79$ kJ mol$^{-1}$, $\Delta S^{\ddagger}=36$ J K$^{-1}$ mol$^{-1}$ with $X=Br^-$. The $\Delta V^{\ddagger}$ 's at $\mu\approx0$ are 19.1 cm$^3$ mol$^{-1}$ with $X=Cl^-$ and 19.7 cm$^3$ mol$^{-1}$ with $X=Br^-$. In the base hydrolysis with excess NaOH at $\mu=1.0$, the pseudo-first-order rate constant ($k_{obsd}$) departs slightly positively from the proportionality to the [OH$^-$] at 0.3 M < [OH$^-$]. This type of nonlinearity has rarely been reported for the base hydrolysis of a cobalt(III) complex. The magnitudes of the activation volume for the base hydrolysis are in line with the $S_N1$ CB mechanism. Therefore, the mechanism may be the $S_N1$ CB mechanism, where an additional minor pathway via the second deprotonation from the taud ligand or via a hydroxide adduct formation to the carbonyl group of the taud ligand also participates.

In our previous reports, we have described the preparation of *trans*(*O*)-[Co(taud)$NO_2$], *trans*(*O*)-[Co(taud)$H_2O$]$ClO_4$, *trans*(*O*)-[Co(taud)Cl]·0.5$H_2O$, *trans*(*O*)-[Co(taud)Br], *trans*(*O*)-[Co(taud)NCS], and *trans*(*O*)-[Co(taud)$NH_3$]$ClO_4$, where the taud stands for 3,6,9-triazaundecanedioate $^-OOCCH_2NH(CH_2)_2NH(CH_2)_2NHCH_2COO^-$.[1,2] In these complexes, the taud acts as a quinquedentate ligand with the two oxygen atoms occupying the trans positions of the coordination octahedron. In the present report, we study the acid and base hydrolysis velocities of *trans*(*O*)-[Co(taud)Cl] and *trans*(*O*)-[Co(taud)Br] at normal and high pressures up to 1600 bar. We also study the acid hydrolysis of *trans*(*O*)-[Co(taud)$NO_2$] at normal pressure and 45.6 °C. Kinetic studies of the hydrolysis reactions of various cobalt(III) complexes have been extensively carried out. However, most of the works have treated positively charged complexes. The hydrolysis velocity of a nonelectrolytic cobalt(III) complex has not been studied often.[3,4] In this report, we are interested in the hydrolyses of the title nonelectrolytic complexes, especially in the pressure effect on these hydrolyses velocities.

## Experimental

The complex samples *trans*(*O*)-[Co(taud)Cl]·0.5$H_2O$, *trans*(*O*)-[Co(taud)Br], *trans*(*O*)-[Co(taud)$NO_2$] and *trans*(*O*)-[Co(taud)$H_2O$]$ClO_4$ were described in previous works.[1,2] Ionic strength ($\mu$) was adjusted using $NaClO_4$ (Kanto, G). The base hydrolysis kinetics at a normal pressure were studied using a temperature controlled (±0.1 °C) Unisoku RS-450 stopped flow apparatus. Equal volumes of the complex solution ($\mu=1.0$) and the alkaline solution ($\mu=1.0$) were mixed. The change of the optical density was followed after the mixing during about five half-lives of the reaction and was treated according to the first-order rate law. The alkaline solution was prepared by dilution of 4 M NaOH (Nacalai) and 4 M $NaClO_4$. It was checked by the addition of a drop of aqueous $Ba(OH)_2$ that aqueous 4 M NaOH and 4 M $NaClO_4$ solutions and distilled water were $CO_2$-free.[5] The concentrations of the alkaline solutions were checked by titration with aqueous $HClO_4$ standardized with tris (Nacalai, GR). A JEOL-GSX-270-FT-NMR instrument and a Shimadzu UV-2200 UV-vis spectrophotometer were used. High pressure kinetics were studied using a Hawley–Chase type sapphire cell as described elsewhere.[6] The experimental rate constants given in the Tables are mean values of triplicate independent runs unless otherwise indicated.

## Results and Discussion

**Aquation.** The UV-vis absorption spectrum of an acidic aqueous solution of *trans*(*O*)-[Co(taud)X] changes with time ($X=Cl^-$, $Br^-$, $NO_2^-$). Isosbestic points are maintained at 369, 428, and 504 nm for $X=Cl^-$; at 432 and 517 nm for $X=Br^-$, and at 466 nm for $X=NO_2^-$. The final spectra coincide with that of *trans*(*O*)-[Co(taud)$H_2O$]$^+$.[2] Therefore, the aquations proceed with retention of the configuration.

$$trans(O)\text{-}[Co(taud)Cl]+H_2O\rightarrow trans(O)\text{-}[Co(taud)H_2O]^++Cl^- \quad (1)$$

$$trans(O)\text{-}[Co(taud)Br]+H_2O\rightarrow trans(O)\text{-}[Co(taud)H_2O]^++Br^- \quad (2)$$

$$trans(O)\text{-}[Co(taud)NO_2] + H_2O \rightarrow trans(O)\text{-}[Co(taud)H_2O]^+ + NO_2^- \qquad (3)$$

The absorption intensity was followed at a certain wavelength and was analyzed according to the first-order rate law. The resultant rate constants ($k_{aq}$) are summarized in Tables 1 and 2. The activation volume ($\Delta V^\ddagger$) was estimated from the pressure dependence of the $k_{aq}$ by $\Delta V^\ddagger = -RT(\mathrm{d}\ln k_{aq}/\mathrm{d}P)$, where a linear dependence of $\ln k_{aq}$ on $P$ was assumed. The activation parameters are summarized in Table 5. The $k_{aq}$ 's of reactions 1 and 2 are independent of the $[H^+]$ of the solution, whereas that of reaction 3 depends on the $[H^+]$. This is in line with the general tendency for the acid hydrolysis of a cobalt(III) complex that the chloride or bromide liberation is not catalyzed by acid, whereas nitrite liberation is catalyzed by acid.[3] In the acid hydrolysis of $[Co(NO_2)(NH_3)_5]^{2+}$, the rate constant depends approximately linearly on the $[H^+]$.[7] This was explained by a mechanism through two routes; one not acid-catalyzed and the other via a protonated complex species $[Co(NO_2H)(NH_3)_5]^{3+}$.[7] The experimental $k_{aq}/s^{-1}$ of reaction 3 is expressed as a function of the $[H^+]$:

$$k_{aq} = 1.3 \times 10^{-4}[H^+] + 3.09 \times 10^{-3}[H^+]^2$$

Table 2. Aquation Rate Constant ($10^4 k_{aq}/s^{-1}$) of *trans*($O$)-[Co(taud)X] at High Pressures

$C$=0.5 mM. $\mu$=0.1 ($HClO_4$).

| | | $P$/bar | | | | |
|---|---|---|---|---|---|---|
| X | $t$/°C | 50 | 400 | 800 | 1200 | 1600 |
| $Cl^-$ a) | 40.0 | 6.28 | 6.26 | 6.68 | 7.05 | 7.51 |
| $Br^-$ a) | 30.3 | 8.60 | 8.85 | 9.17 | 9.48 | 9.89 |

a) $\lambda$=290 nm. b) $\lambda$=315 nm.

where the contribution of the acid uncatalyzed component is negligible. This quadratic dependence cannot be explained by assuming only a route via the protonated species *trans*($O$)-$[Co(taud)(NO_2H)]^+$. Another route through the acid-catalyzed nitro–nitrito linkage isomerization might also participate.[8]

$$trans(O)\text{-}[Co(taud)NO_2] \xrightarrow{(H^+)} trans(O)\text{-}[Co(taud)ONO] \xrightarrow{2H^+} trans(O)\text{-}[Co(taud)H_2O]^+ + NO^+$$

Generally the activation volume reflects the electrostatic aspects of the activation process.[9] The $\Delta V^\ddagger$ 's for the aquation of 2+ charged chlorocobalt(III) complexes are −8—−2 $cm^3\ mol^{-1}$ and those of 1+ charged ones are −2—+2 $cm^3\ mol^{-1}$.[10,11] This trend is explained if the liberation of an anion from a 2+ charged complex causes solvational volume contraction more remarkably than that from a 1+ charged complex and accords with the dissociative nature of the activation process. The electrostatic solvational volume $V_{el}$ around an octahedral metal complex ion of charge $Z$ is estimated as

$$V_{el} = -2.5Z^2\ cm^3\ mol^{-1}$$

on experimental grounds.[12] Therefore, in the limiting dissociative mechanism, the liberation of a −1 charged anion from the 2+, 1+, and 0 charged complex causes solvational volume contraction around the complex, amounting to $2.5(3^2-2^2)=12.5\ cm^3\ mol^{-1}$; $2.5(2^2-1^2)=7.5\ cm^3\ mol^{-1}$ and $2.5(1^2-0^2)=2.5\ cm^3\ mol^{-1}$ respectively. According to this estimation, activation volume of ca. 5 $cm^3\ mol^{-1}$ may be expected for the aquation of a nonelectrolytic chloro or bromo cobalt(III) complex through the limiting dissociative mechanism. Taking account of the interchange character of the mechanism, the dependence of the solvational volume contraction on $Z$ may not be so remarkable as estimated

Table 1. Aquation Rate Constant ($10^4 k_{aq}/s^{-1}$) of *trans*($O$)-[Co(taud)X] at the Normal Pressure

Concentration of the complex ($C$)=0.5 mM. $\mu$ = 0.1 unless otherwise indicated.

X=$Cl^-$.
The wavelength($\lambda$) where the reaction was followed=290 nm.

| [$HClO_4$]/mM<br>$t$/°C | 1 | 10 | 100 | 500 |
|---|---|---|---|---|
| 31.8 | | 2.29 | | |
| 36.8 | | 4.05 | | |
| 41.2 | 7.07 | 7.04 | 6.93 | 7.00$^{a)}$ |
| 46.7 | | 13.1 | | |

X=$Br^-$. $\lambda$=315 nm.

| [$HClO_4$]/mM<br>$t$/°C | 1 | 10 | 100 | 500 |
|---|---|---|---|---|
| 21.0 | | 2.75 | | |
| 25.7 | | 4.99 | | |
| 30.3 | 8.85 | 8.86 | 8.67 | 8.88$^{a)}$ |
| 35.4 | | 16.3 | | |

X=$NO_2^-$. $\lambda$=327 nm. Mean of duplicate runs.

| [$HClO_4$]/mM$^{a)}$<br>$t$/°C | 0 | 101 | 202 | 316 | 408 | 510 |
|---|---|---|---|---|---|---|
| 45.6 | 0$^{b)}$ | 0.54 | 1.64 | 3.71 | 5.55 | 8.40 |

a) $\mu$ = 0.5. b) Spectral change was undetectable during 24 h.

above and activation volume of ca. 2 $cm^3\ mol^{-1}$ may be expected for reactions 1 and 2.[13] In this regard, the present experimental $\Delta V^\ddagger$ 's of $-3.2$ and $-2.3$ $cm^3\ mol^{-1}$ for reactions 1 and 2 are slightly away from the expected value, for which we have no convincing explanation at present.

**Base Hydrolysis.** When an aqueous solution of *trans*(*O*)-[Co(taud)X] is mixed with aqueous NaOH, a rapid decrease of the UV absorption can be observed ($X=Cl^-$, $Br^-$). The final UV-vis absorption spectrum does not coincide with the assumed spectrum $\lambda_{max}$/nm ($\varepsilon$)=384 (82), 517 (127) of *trans*(*O*)-[Co(taud)OH], where the latter spectrum was obtained by mixing an aqueous solution of *trans*(*O*)-[Co(taud)$H_2O$]$ClO_4$ with equivalent NaOH. With excess NaOH, the time dependent decrease of the UV absorption follows the first-order rate law strictly. Therefore, we considered that this spectral change corresponds to the base hydrolysis.

$$trans(O)\text{-}[Co(taud)Cl] + OH^- \rightarrow [Co(taud)OH] + Cl^- \quad (4)$$

$$trans(O)\text{-}[Co(taud)Br] + OH^- \rightarrow [Co(taud)OH] + Br^- \quad (5)$$

where the geometrical configuration of the product is unspecified. The pseudo first-order rate constant $k_{obs}$ at $\mu=1.0$ are summarized in Table 3. As shown in Fig. 1, the $k_{obs}$ is proportional to the $[OH^-]$ at low $[OH^-]$, but it departs slightly positively from the proportionality at 0.3 M$<[OH^-]$. This kind of positive departure has rarely been reported for the base hydrolysis of a cobalt(III) complex.[4] Since these reactant complexes are nonelectrolytic, the ion pair formation mechanism is irrelevant, but the $S_N1$ CB mechanism may be relevant to reactions 4 and 5.

Table 3. Base Hydrolysis Rate Constant of *trans*(*O*)-[Co(taud)X] at the Normal Pressure

$C$=0.25 mM. $\mu$=1.0. Mean of four runs.

| $X=Cl^-$. $\lambda$=285 nm. | | |
|---|---|---|
| [NaOH]/mM | $t$/°C | $k_{obs}/s^{-1}$ |
| 5 | 20.4 | 0.327 |
| 10 | 4.9 | 0.101 |
| 10 | 12.6 | 0.265 |
| 10 | 20.4 | 0.666 |
| 10 | 30.4 | 1.83 |
| 10 | 40.1 | 4.75 |
| 50 | 20.4 | 3.47 |
| 100 | 20.4 | 7.01 |
| 200 | 20.4 | 14.6 |
| 300 | 20.4 | 22.5 |
| 400 | 20.4 | 30.5 |
| 500 | 20.4 | 39.7 |
| $X=Br^-$. $\lambda$=305 nm. | | |
| [NaOH]/mM | $t$/°C | $k_{obs}/s^{-1}$ |
| 5 | 10.0 | 0.698 |
| 10 | 4.6 | 0.681 |
| 10 | 9.7 | 1.22 |
| 10 | 10.0 | 1.43 |
| 10 | 15.6 | 2.60 |
| 10 | 20.4 | 4.54 |
| 50 | 10.0 | 7.80 |
| 100 | 10.0 | 16.1 |
| 200 | 10.0 | 33.5 |
| 300 | 10.0 | 51.5 |
| 400 | 10.0 | 71.1 |
| 500 | 10.0 | 93.1 |

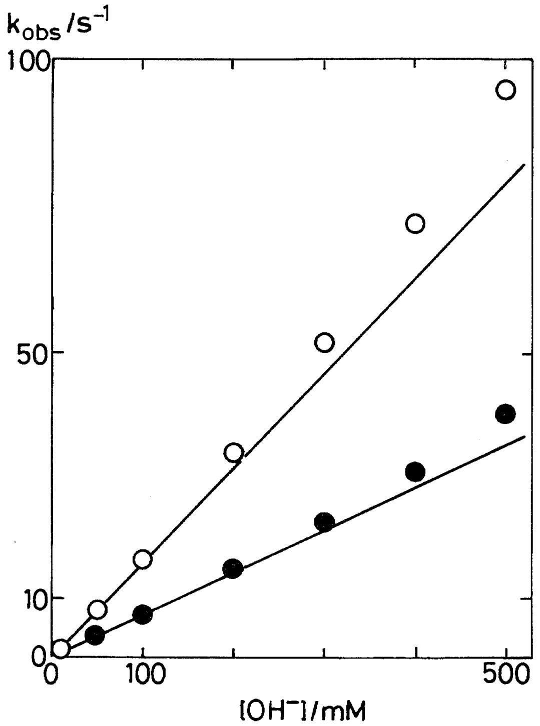

Fig. 1. The correlation between the $k_{obs}$ for the base hydrolysis and the $[OH^-]$. Closed circle: *trans*(*O*)-[Co(taud)Cl] at 20.4 °C and $\mu=1.0$; $k_{obs}=67.1[OH^-]+24.8[OH^-]^2$. Open circle: *trans*(*O*)-[Co(tand)Br] at 10.0 °C and $\mu=1.0$; $k_{obs}=148.3[OH^-]+78.1[OH^-]^2$.

$$trans(O)\text{-}[Co(taud)X] + OH^- \overset{K}{\rightleftharpoons} trans(O)\text{-}[Co(taud\text{-}H)X]^- + H_2O \quad (6)$$

$$trans(O)\text{-}[Co(taud\text{-}H)X]^- \xrightarrow{k} [Co(taud\text{-}H)] + X^- \quad (7)$$

$$[Co(taud\text{-}H)] + H_2O \xrightarrow{\text{fast}} [Co(taud)OH]$$

where the taud-H stands for the deprotonated taud ligand and X for Cl or Br.

$$k_{obs} = \frac{kK[OH^-]}{1+K[OH^-]} \quad (8)$$

Equation 8 predicts that $k_{obs}$ is proportional to the $[OH^-]$ at low $[OH^-]$ and departs negatively from the proportionality at high $[OH^-]$. Therefore, the observed positive departure at high $[OH^-]$ (Fig. 1) cannot be explained only by reactions 6 and 7. We cannot give a convincing explanation for this positive departure. One possible explanation is that an additional minor pathway via the second deprotonation from the taud ligand or via a hydroxide adduct formation to the carboxyl group of the taud ligand contributes.[4] The base hydrolysis was also studied in CHES buffers at high pressures (Table 4). The activation volumes of reactions 4 and 5 were estimated from the pressure dependence of the $k_{obs}$, where the approximately linear dependence of $k_{obs}$ on the $[OH^-]$ was assumed and the pressure induced variations of the $[OH^-]$ and of the

Table 4. Base Hydrolysis Rate Constant ($10^4$ $k_{obs}/s^{-1}$) of *trans*(*O*)-[Co(taud)X] at High Pressures

CHES=2-(Cyclohexylamino)ethanesulfonic acid.

| X | $t$ | [CHES] | [CHESNa] | pH[a)] | $\mu$ | $C$ | $P$/bar | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | °C | mM | mM | | | mM | 50 | 400 | 800 | 1200 | 1600 |
| $Cl^-$ | 20.3 | 14.0 | 6.0 | 9.01 | 0.006 | 0.4 | 7.50 | 8.09 | 8.52 | 9.13 | 9.54 |
| $Br^-$ | 10.4 | 16.0 | 4.0 | 8.77 | 0.004 | 0.4 | 7.79 | 8.27 | 8.91 | 9.24 | 8.99 |

a) At the normal pressure.

Table 5. Activation Parameters and Rate Constants at 25 °C for Aquation and Base Hydrolysis of *trans*(*O*)-[Co(taud)X]

| X | Aquation | | | | Base hydrolysis | | | |
|---|---|---|---|---|---|---|---|---|
| | $k_{aq}$ (25 °C)[a)] | $\Delta H^\ddagger$ [a)] | $\Delta S^\ddagger$ [a)] | $\Delta V^\ddagger$ [b)] | $k_2$ (25 °C)[c)] | $\Delta H^\ddagger$ [d)] | $\Delta S^\ddagger$ [d)] | $\Delta V^\ddagger$ [e)] |
| | $s^{-1}$ | $kJ\,mol^{-1}$ | $J\,K^{-1}\,mol^{-1}$ | $cm^3\,mol^{-1}$ | $M^{-1}\,s^{-1}$ | $kJ\,mol^{-1}$ | $J\,K^{-1}\,mol^{-1}$ | $cm^3\,mol^{-1}$ |
| $Cl^-$ | $9.6\times10^{-5}$ | 93±2 | −10±5 | −3.2±0.2 | 104 | 77±1 | 12±3 | 19.1±0.3 |
| $Br^-$ | $4.6\times10^{-4}$ | 91±0 | −4±1 | −2.3±0.1 | 760 | 79±3 | 36±10 | 19.7±0.4 |

a) $[HClO_4]$=10 mM. b) $[HClO_4]$=0.1 M. c) Estimated at [NaOH]=10 mM by $k_{obs}$ (25 °C)/[NaOH]. d) [NaOH]=10 mM. e) In CHES buffers.

activity coefficient were taken into account.[5,14,15)] The activation parameters are summarized in Table 5. The $\Delta V^\ddagger$ for the reaction 4 or 5 is significantly smaller than the $\Delta V^\ddagger$=28—35 $cm^3\,mol^{-1}$ for the base hydrolysis of 2+ charged cobalt(III) complex or with the $\Delta V^\ddagger$=20—25 $cm^3\,mol^{-1}$ for those of 1+ charged cobalt(III) complex.[10,14)] This parallels the small estimated reaction volume for the preequilibrium 6. In the $S_N1$ CB mechanism the $\Delta V^\ddagger$ is expressed as

$$\Delta V^\ddagger = \Delta V(K) + \Delta V^\ddagger(k) \tag{9}$$

where $\Delta V(K)$ is the reaction volume of preequilibrium 6 and $\Delta V^\ddagger(k)$ is the activation volume of reaction 7.[5)] The reaction volume of the preequilibrium is estimated as 22, 17, and 12 $cm^3\,mol^{-1}$, for the 2+, 1+, and 0 charged cobalt(III) complexes referring to the experimental reaction volumes for the neutralization of a series of acidic octahedral transition metal complexes.[12)] Thus, $\Delta V^\ddagger(k)$ is deduced as 7.1 and 7.7 $cm^3\,mol^{-1}$ for reaction 7 with X=$Cl^-$ and $Br^-$ respectively. These magnitudes of $\Delta V^\ddagger(k)$ are slightly larger than the $\Delta V^\ddagger$=3.2 $cm^3\,mol^{-1}$ for the aquation of a uninegatively charged $[Co(edda)Cl_2]^-$ ($H_2edda$=ethylenediamine−*N*,*N*′−diacetic acid).[11)] This may be explained if the mechanism of reaction 7 is more dissociative than the aquation of $[Co(edda)Cl_2]^-$ by analogy with the larger activation volume ca. 10 $cm^3\,mol^{-1}$ for the aquation of $[CoY(NH_2)(NH_3)_4]^+$ compared with that ca. 5 $cm^3\,mol^{-1}$ for the aquation of *cis*-$[CoY(OH)(NH_3)_4]^+$ (Y=$Cl^-$, $Br^-$, and $NO_3^-$).[16)] The taud-H ligand in $[Co(taud\text{-}H)X]^-$ contributes strong labilizing power to the complex and $X^-$ can leave the first coordination sphere without stimulation by the entering $H_2O$ ligand. On the other hand, the nonlabile $Cl^-$ ligand in $[Co(edda)Cl_2]^-$ contributes moderate labilizing power to the complex and the labile $Cl^-$ can leave it only after the stimulation by the entering $H_2O$ ligand. The activation volume for the latter is small, owing to the incorporation of the entering $H_2O$ into the first coordination sphere of the complex in the transition state. The dissociative character of reaction 7 is also consistent with the general understanding that the ligand liberation in the $S_N1$ CB mechanism proceeds through the limiting dissociative mechanism.[4)]

***trans*(*O*)-[Co(taud)($H_2O$)]$^+$ in alkaline solution.** In the connection with the final state of the base hydrolysis, we were interested in the variation of the UV-vis spectrum of *trans*(*O*)-$[Co(taud)H_2O]^+$ with addition of NaOH. Two isosbestic points $\lambda$/nm ($\varepsilon$)=380 (81) and 500 (121) are maintained with NaOH up to the equivalence. On further addition of NaOH, the UV spectrum ($\lambda$ <310 nm) remains unaltered, but the visible spectrum gets gradually away from these isosbestic points. For example, the $\lambda_{max}$/nm ($\varepsilon$)'s are 378(127) and 526(130) at 36 equivalents of NaOH. Thus the solution with excess NaOH contains unspecified complex species perhaps involving a taud ligand with one opened glycinate ring. The irreversibility of this change with excess NaOH was checked by the NMR spectral behavior on the reacidification. When an aqueous solution of *trans*(*O*)-$[Co(taud)H_2O]^+$ with the equivalent NaOH is reacidified, the glycinate ring proton resonance spectrum returns to the original one. On the other hand, on the reacidification of the solution with excess NaOH it does not return to the original one. Therefore, we presume that the above-mentioned disagreement of the final spectrum of the base hydrolysis with that of *trans*(*O*)-[Co(taud)OH] is partly due to the formation of this ring opened species. The aqueous solution (10 mM, 10 $cm^3$) of *trans*(*O*)-$[Co(taud)H_2O]^+$ was titrated by 0.1 M NaOH. For the protonic dissociation

$$trans(O)\text{-}[Co(taud)H_2O]^+ = trans(O)\text{-}[Co(taud)OH] + H^+$$

$pK_a$=8.14 was obtained at 25 °C. This magnitude is rather large compared with $pK_a$ values 5.0—7.5 of analogous cobalt(III) complexes.[3,12)]

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## References

1) K. Watanabe, K. Maeda, H. Shimizu, and Y. Kitamura, *Nippon Kagaku Kaishi*, **1990**, 1406.

2) K. Watanabe, H. Muneta, K. Maeda, and Y. Kitamura, *Nippon Kagaku Kaishi*, **1992**, 28.

3) D. A. House, *Coord. Chem. Rev.*, **23**, 223 (1977).

4) M. L. Tobe, *Adv. Inorg. Bioinorg. Mech.*, **2**, 1 (1983).

5) Y. Kitamura, R. van Eldik, and H. Kelm, *Inorg. Chem.*, **23**, 2038 (1984).

6) Y. Kitamura, T. Takamoto, and K. Yoshitani, *Inorg. Chem.*, **27**, 1382 (1988).

7) G. C. Lalor, *J. Chem. Soc. A*, **1966**, 1.

8) A. D. Harris, R. Stewart, D. Hendrickson, and W. L. Jolly, *Inorg. Chem.*, **6**, 1052 (1967).

9) Y. Kitamura, Y. Fujie, and M. Minakawa, *Rev. Phys. Chem. Jpn.*, **1990**, 95.

10) Y. Kitamura, S. Matsuzaki, and T. Butou, *Polyhedron*, **10**, 1449 (1991).

11) Y. Kitamura, T. Takamoto, and K. Kuroda, *Inorg. Chim. Acta*, **159**, 181 (1989).

12) Y. Kitamura and R. van Eldik, *Ber. Bunsenges. Phys. Chem.*, **88**, 418 (1984).

13) Y. Kitamura, *Inorg. Chem.*, **24**, 2 (1985).

14) Y. Kitamura, G. A. Lawrance, and R. van Eldik, *Inorg. Chem.*, **28**, 333 (1989).

15) Y. Kitamura and T. Itoh, *J. Solution Chem.*, **16**, 715 (1987).

16) Y. Kitamura, T. Itoh, and M. Takeuchi, *Inorg. Chem.*, **25**, 3887 (1986).