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Kinetics and Mechanism of Anation of *cis*-β-Diaqua(3,6-diazaoctane-1,8-diamine) Cobalt(III) in 30% (v/v) Ethanol-Water Medium

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Synopsis. The kinetics of the aqua-ligand substitution of the title complex [Co^{III}(trien)(H$_2$O)$_2$$^{3+}$] (trien=3,6-diazaoctane-1,8-diamine) with various substituting amino acid ligands L=glycine, DL-alanine, L-proline, DL-valine, and L-serine was studied spectrophotometrically as a function of incoming ligand concentration, pH (3.0—5.0) and temperature (45—60 °C). The results are consistent with an ion-pair dissociative mechanism.

We have reported earlier the substitution behavior of *cis*-diaqua-bis(ethylenediamine)cobalt(III) complex ion with a series of amino acid ligands.[1–3] Recently, in an effort to gain an insight in a general phenomena of aqua substitution of [Co^{III}(N$_4$)(H$_2$O)$_2$] system, we have undertaken the study of substitution reaction of H$_2$O in [Co^{III}(trien)(H$_2$O)$_2$]$^{3+}$, [Co^{III}(cyclam)(H$_2$O)$_2$]$^{3+}$, and [Co^{III}(salen)(H$_2$O)$_2$]$^{+}$ etc. with a series of bidentate (N,O) ligands viz amino acids, pyridine carboxylic acids. These complex species having terdentate ligand system are interesting for the following considerations. It may show the unusual cis-labilization effect of hydroxide ion[4,5] and conformational changes in the chelate ring during substitution process may produce much distortion in the transition state which in turn, labilizes the Co-OH$_2$ bond.[6] As a part of our studies, we report, herein, the kinetic behavior of *cis*-β-[Co(trien)(H$_2$O)$_2$]$^{3+}$ with glycine, DL-alanine, L-proline, DL-valine, and L-serine in aqua-organic medium.

Experimental

Meterials and Methods. *Cis*-β-[Co(trien)CO$_3$]ClO$_4$·H$_2$O **1** was prepared by following the published procedure[7] and characterized by elemental analysis, spectral data. For the kinetic experiments, *cis*-β-[Co(trien)(H$_2$O)$_2$]$^{3+}$ **2** was produced in the solution by treating **1** with calculated amount of 0.2 M HClO$_4$ (1 M=1 mol dm^{-3}) and spectral data of the solution agreed well with that of reported values.[7] The substituted reaction products [Co(trien)(L)](ClO$_4$)$_2$·*x*H$_2$O for the reaction between *cis*-β-[Co(trien)(H$_2$O)$_2$]$^{3+}$ and amino acid (L) was prepared, and characterized as chelated [Co(trien)(L)](ClO$_4$)$_2$·H$_2$O (where L=amino acid ligands) compounds. IR spectrum of each product complex shows a sharp peak at 1620±10 cm^{-1} indicating the presence of coordinated carboxylato group. No band at 1220—1020 cm^{-1} (due to C-N stretching of free amino group of amino acid) was observed in the spectra, whereas, appearance of N-H stretching band at 3200—3100 cm^{-1} confirms the coordination of two NH$_2$ groups and two NH groups of trien and one NH$_2$ group of amino acid ligand. However, IR spectroscopy is not the most reliable method for differentiating two complexes [Co(trien)(H$_2$O)(HL)](ClO$_4$)$_3$ and [Co(trien)-(L)](ClO$_4$)$_2$. Possibility of the formation of monoaqua substituted product was ruled out by one independent pH titration experiment with one of our reaction product [Co(trien)(L)]$^{2+}$ (L=glycine) in which we missed the hydrolysis step [Co(trien)(H$_2$O)(L)]$^{2+}$ → [Co(trien)(L)(OH)]$^{+}$+H^{+} which confirms that our reaction product is mixed chelate [Co(trien)(L)]$^{2+}$ complex.

All other chemicals used are in A.R. grade and double distilled water was used to prepare all solutions.

The ionic strength of the solutions was adjusted with NaNO$_3$ and NaClO$_4$, and pH of the solution was maintained by adding NaOH and HClO$_4$. Infrared spectra were recorded on a Shimadzu IR-435 instrument for the characterization of the substituted products. The pH measurements were carried out with a Digisun pH meter with an accuracy of ±0.001 unit. Substitution reaction was followed spectrophotometrically by using Shimadzu UV-160 spectrophotometer equipped with TCC-240A temperature controller. Under the conditions selected, the reactions were all found to go to completion, and the pseudo-first-order plots of log $(A_\alpha - A_t)$ versus time, where A_α and A_t are the absorbances at infinite time (i.e. of [Co(trien)(L)]$^{2+}$) and time, *t*, respectively, were linear for at least 2 half-lives. The rate constant data are reproducible within ±4%.

Results and Discussion

The kinetics of the substitution reaction of *cis*-β-[Co(trien)(H$_2$O)$_2$]$^{3+}$ with a series of amino acid ligands were investigated by conventional mixing technique. The rate of formation of [Co(trien)L]$^{2+}$ at a fixed pH 3.0 and ionic strength 0.5 M (NaClO$_4$) was found to be first order with respect to complex (*cis*-β-[Co(trien)(H$_2$O)$_2$]$^{3+}$) concentration.

$$\mathrm{d[Co(trien)(L)^{2+}]}/\mathrm{d}t = k_{\mathrm{obs}}\ cis\text{-}\beta\text{-}\mathrm{[Co(trien)(H_2O)_2]^{3+}} \qquad (1)$$

The variation of pseudo-first order rate constant (k_{obs}) with substituting amino acid concentration is comparable to our earlier results for amino acid substitution of *cis*-diaqua-bis(ethylenediamine)cobalt(III).[1–3]

The observed saturation of k_{obs} at high ligand concentration for each ligand under study can be interpreted in terms of the mechanism outlined in Eqs. 2—4 for which the rate expression is given by Eqs. 5 and 6:

$$cis\text{-}\beta\text{-}\mathrm{[Co(trien)(H_2O)_2]^{3+} + HL} \underset{}{\overset{K_{\mathrm{E}}}{\rightleftarrows}} \mathrm{([Co(trien)(H_2O)_2]HL)^{3+}}\ \text{(ion-pair)} \qquad (2)$$

$$cis\text{-}\beta\text{-}\mathrm{([Co(trien)(H_2O)_2]HL)^{3+}} \xrightarrow{k_{\mathrm{a}}} \mathrm{[Co(trien)(H_2O)(HL)]^{3+} + H_2O} \qquad (3)$$

$$\mathrm{[Co(trien)(H_2O)(HL)]^{3+}} \xrightarrow{\text{fast}} \mathrm{[Co(trien)(L)]^{2+} + H_3O^{+}} \qquad (4)$$

Table 1. Values of Anation Rate Constant (k_{obs}) for the Reaction[a)]
$cis\text{-}\beta\text{-}[Co(trien)(H_2O)_2]^{3+}+HL \xrightarrow{k_a} [Co(trien)(L)]^{2+}+H_2O+H_3O^+$

Temp /°C	$k_a \times 10^4/s^{-1}$				
	Glycine	DL-Alanine	L-Proline	DL-Valine	L-Serine
45	2.22	1.92	2.13	1.82	2.01
50	5.21	4.85	5.07	4.77	4.92
55	10.27	9.89	10.11	9.31	9.76
60	21.60	20.00	21.10	18.80	19.20

a) $[cis\text{-}\beta\text{-}Co(trien)(H_2O)_2]^{3+}=5\times10^{-3}$ M, pH=4.2, μ=0.5 M ($NaClO_4$).

$$k_{obs}=\frac{k_aK_E[HL]}{1+K_E[HL]} \tag{5}$$

$$\frac{1}{k_{obs}}=\frac{1}{k_a}+\frac{1}{k_aK_E[HL]}. \tag{6}$$

The rate determinating loss of coordinated water molecule (Eq. 3) is preceeded by ion pairing (Eq. 2) and at higher amino acid concentration a limiting rate is attained due to completion of ion pair formation. Plot of $1/k_{obs}$ versus $1/[HL]$ (Eq. 6) were linear for each ligand under investigation and one such plot is depicted in Fig. 1. The values of k_a (calculated from intercept) at different temperatures are summarized in Table 1. K_E values calculated from slope are in the range 2.7—5.0 M^{-1}.

In the pH range 3.0 to 5.0 an increase in rate was observed with increasing pH. The dipolar nature as well as the reactivity of amino acid ligands selected for the substitution reaction are not altered appreciably in the studied range of pH (3.0—5.0).[8)] The effect of hydrogen ion concentration on the observed rate constant can be explained in terms of the following acid-dissociation equalibrium

$$cis\text{-}\beta\text{-}[Co(trien)(H_2O)_2]^{3+} \overset{K_1}{\rightleftarrows} cis\text{-}\beta\text{-}[Co(trien)(H_2O)(OH)]^{2+}+H^+ \tag{7}$$

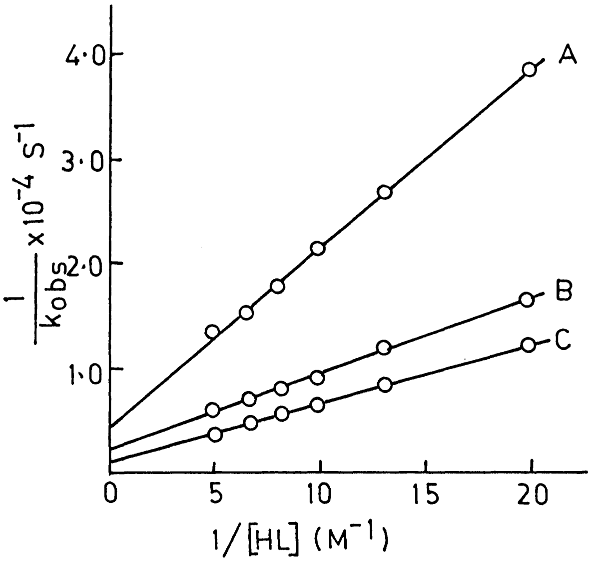

Fig. 1. Plot of $1/k_{obs}$ versus $1/[HL]$ at (a) 45 °C, (b) 50 °C, and (c) 55 °C, (HL=H-gly).

for which the rate expression is given in Eq. 8

$$k_{obs}=k_1+k_2K_1[H^+]^{-1}, \tag{8}$$

where k_1 is the observed rate constant when reacting species is diaqua complex and k_2 is the observed rate constant for the hydroxoaqua complex. The pK_1 value at 40 °C determined by us by using pH titration technique is 5.2, which agrees well with the reported value (5.9 at 25 °C).[9)] Plot of k_{obs} versus $[H^+]^{-1}$ were linear in each case and one such plot is depicted in Fig. 2. As the pH of the medium is raised the concentration of aquahydroxo complex in solution increases. *Cis*-labilization effect of hydroxide ion makes the aquahydroxo complex more reactive towards substitution than its diaquo analogue.

The effect of $[NO_3^-]$ and $[ClO_4^-]$ on the substitution rate were studied at high ligand concentration (40

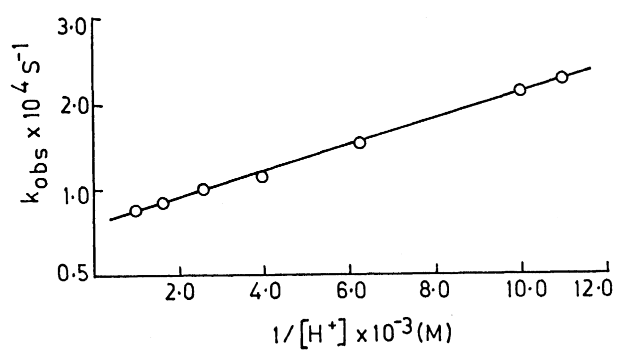

Fig. 2. Plot of k_{obs} versus $1/[H^+]$ at 50 °C, [Complex 2]=5×10^{-3} M, [H-gly]=0.075 M, μ=0.5 M ($NaClO_4$).

Table 2. Effect of $[NO_3^-]$ on k_{obs} for the Reaction[a)]
$cis\text{-}\beta\text{-}[Co(trien)(H_2O)_2]^{3+}+HL \xrightarrow{k_a} [Co(trien)L]^{2+}+H_2O+H_3O^+$

$[ClO_4^-]$/M	$k_{obs}/10^4$ s^{-1}	$[NO_3^-]$/M	$k_{obs}/10^4$ s^{-1}
0.5	1.42	0.5	1.85
0.6	1.45	0.6	1.95
0.7	1.40	0.7	2.04
0.8	1.39	0.8	2.15
1.0	1.47	1.0	2.25
1.2	1.44	1.2	2.45
1.5	1.42	1.5	2.72

a) $[cis\text{-}\beta\text{-}Co(trien)(H_2O)_2]^{3+}=5\times10^{-3}$ M, [HL]=[H-gly]=2.0×10^{-1} M, pH=3.0, T=50 °C.

Table 3. Comparison of Activation Parameters of the Anation Reaction of *cis*-β-$[Co(trien)(H_2O)_2]^{3+}$ and *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ with Different Amino Acid Ligands

System	$\Delta H^{\neq}$ kcal mol^{-1}[a]	$\Delta S^{\neq}$ eu	System	$\Delta H^{\neq}$ kcal mol^{-1}[a]	$\Delta S^{\neq}$ eu
cis-β-$[Co(trien)(H_2O)_2]^{3+}$ -glycine substitution	30.8	21.9	*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ -glycine substitution	30.6	21.0
cis-β-$[Co(trien)(H_2O)_2]^{3+}$ -DL-alanine substitution	31.9	24.7	*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ -DL-alanine substitution	29.4	17.1
cis-β-$[Co(trien)(H_2O)_2]^{3+}$ -L-proline substitution	31.2	22.8	*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ -L-proline substitution	29.8	17.6
cis-β-$[Co(trien)(H_2O)_2]^{3+}$ -DL-valine substitution	31.7	24.0	*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ -DL-valine substitution	29.1	16.7
cis-β-$[Co(trien)(H_2O)_2]^{3+}$ -L-serine substitution	30.7	21.2	*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ -L-serine substitution	30.7	20.7
cis-β-$[Co(trien)(H_2O)_2]^{3+}$ -H_2O^{18} exchange	—	—	*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ -H_2O^{18} exchange	28.8	16.7

a) 1 cal=4.184 J.

times excess) and the results are recorded in Table 2. Increase in NO_3^- concentration leads to an increase in reaction rate, whereas change in ClO_4^- ion concentration did not make any significant change in k_{obs} values (Table 2). Identical "nitrate effect" on anation of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ with amino acids were observed in earlier works.[1-3] This typical "nitrate effect" was first observed by Harris et al.[10]

The substitution reaction was studied at four different temperatures (45—60 °C) and the activation parameters calculated with the help of Eyring equation are presented in Table 3. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are quite comparable to those reported earlier for the amino acid anations of *cis*-diaquabis(ethylenediamine)cobalt(III) complex. Both set of activation parameters are close to one another and also close to those for water exchanger (Table 3) process in *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ complex ion.[11] These observations can be taken as evidences for a dissociative interchange mechanism as concluded previously.[1-3] The values of ion-pair constant (K_E) is almost temperature independent which is in accord with similar findings discussed in details elsewhere.[12]

In conclusion, it can now be stated that the species *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ and *cis*-β-$[Co(trien)(H_2O)_2]^{3+}$ do exhibit very similar kinetic behavior during anation by amino acids. But they differ with respect to the isomerization during product formation. In case of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ there is only one possible isomeric product. However in case of *cis*-β-$[Co(trien)(H_2O)_2]^{3+}$ there are three possibilities of isomeric product. On the basis of IR data of the products it is supposed that the reaction between *cis*-β-$[Co(trien)(H_2O)_2]^{3+}$ with amino acid ligands L is stereo-retentive. However, different geometrical isomers of the product (three possibilities) are possible due to different mode of attachment of N,O donor atoms of the amino acid. From the mechanistic point of view it can be suggested that during substitution the carboxylate oxygen of zwitterionic amino acid first replaces aquo-molecule in the square plane rather than appended one, because entry of substituting ligand from outersphere complex (as formed by ion-pairing) and bonding through carboxylate oxygen is sterically more favorable than through appended position in the octahedral site. In subsequent rapid chelation step amino nitrogen donor atom occupies the appended position.

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