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Research Article

KINETICS AND MECHANISM OF THE INTERACTION OF PHENYLALANINE WITH $[(H_2O)(TAP)_2RUORU(TAP)_2(H_2O)]^{2+}$ (TAP ={2-(M-TOLYLAZO)PYRIDINE}) ION AT PHYSIOLOGICAL PH

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ABSTRACT
The interaction of the title complex with selected amino acid such as Phenylalanine(L^1H) has been studied spectrophotometrically in aqueous medium as a function of [substrate complex], [ligand] and temperature. The reaction has been monitored at 600nm where the spectral difference between the reactant and product is maximum. At pH 7.4, the reaction has been found to proceed via two distinct consecutive steps i.e., it shows a non-linear dependence on the concentration of ligands: first process is [ligand] dependent but the second step is [ligand] independent. The rate constants for the processes are: $k_1 \sim 10^{-3}$ s^{-1} and $k_2 \sim 10^{-4}$ s^{-1}.The activation parameters were calculated from Eyring plots. Based on the kinetic and activation parameters an associative interchange mechanism is proposed for the interaction processes. From the temperature dependence of the outer sphere association equilibrium constant, the thermodynamic parameters were also calculated, which gives a negative ΔG^o value for both the steps at all temperatures studied, supporting the spontaneous formation of an outer sphere association complex. The product of the reaction has been characterized, as conductance measurement and IR spectroscopic analysis.

Key Words: *Ligand substitution, Phenylalanine, cis-diaqua-bis-{2-(m-tolylazo)pyridine} ruthenium(II), Kinetics*

INTRODUCTION
The binding of the antitumor drug cisplatin and other platinum group metal complexes, especially ruthenium(II), rhodium(III), iridium(III), platinum(II) and palladium(II) to amino acids, nucleosides, nucleotides and particularly to DNA is still an interesting subject and has given considerable impetus to research in the area of metal ion interactions with nucleic acid constituents [Lippert (1999), Benerjee (1981), Umapathy(1989), Clarke(1980)]. It is reported that ruthenium complexes are an order of magnitude less toxic than cisplatin[Clarke(1980),Yasbin(1980),]. It is now established [Reedjik(1987)] that cis-platin at first hydrolyses in the biological condition and the aqua variety is the active species. Some of the hydrolyzed products are also responsible for toxicity. Thus it is expected that aqua complexes if used directly will be less toxic.
The importance of the work lies in the fact that (a) the reaction has been studied in aqueous medium and (b) the reaction has been studied at pH (7.4), which is a physiological pH of the human body, (c) the aquaamine complex is chosen, (d) Ruthenium(II) than ruthenium(III) is chosen, as ruthenium(III) is a pro-drug which is reduced in the cell to ruthenium(II), (e) the title complex maintains its +2 oxidation state even at pH 7.4,due to the presence of a strong pi-acceptor ligand [Ghosh(1989)] tap (tap ={2-(m-tolylazo)pyridine}) where most other ruthenium(II) complexes are oxidized to ruthenium(III).

MATERIALS AND METHODS
The compound cis-diaqua-bis-{2-(m-tolylazo)pyridine} ruthenium(II) diperchlorate, monohydrate, cis-$[Ru(tap)_2(H_2O)_2](ClO_4)_2.H_2O$ was prepared following the literature method [Goswami(1981), Goswami(1983)] and the reacting complex ion $[(H_2O)\ (tap)_2RuORu(tap)_2(H_2O)]^{2+}$ (***1***) was prepared in situ at pH 7.4.

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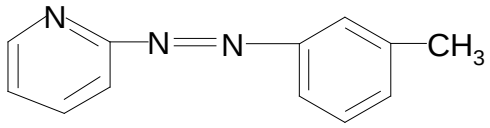


Tap {tap=2-(m-tolylazo) pyridine}.

The product $[(tap)_2Ru(\mu\text{-}O)(\mu\text{-}\ L^1H)Ru(tap)_2]^+$ of the reaction between complex (***1***) and Phenylalanine(L^1H) was prepared by mixing the reactants in 1:1, 1:2, 1:3, 1:5 and 1:10 ratios and thermo stated at 50ºC for 72 h. The spectrum of the product (Fig. 1) shows good complexation between Phenylalanine (L^1H) and (***1***). The composition in the solution was determined by Job's method of continuous variation. The metal: ligand ratio was found to be 2:1 (Fig. 2). This is possible only when a bridged product is formed (vide mechanism and conclusion section).

Complex (***1***) and Phenylalanine (L^1H) were mixed in 2:1 molar ratio at pH 7.4 and a violet product was obtained. Then the product is characterized by IR and conductance measurements.

The IR spectra of the violet product in the KBr disc show strong band at 3435 cm^{-1} together with medium bands at 1630, 1110 and 626 cm^{-1}. The strong bands at 3435 cm^{-1} indicates that the product is hydrated. The asymmetric COO^- stretching frequency (ν_{asym}) of the amino acids occurs at 1580-1660 cm^{-1} when the group is coordinated to metals, where as a non coordinated COO^- group has the ν_{asym} (COO^-) stretching at lower frequency[Pneumatikakis (1979)]. The band at1630$cm^{-1}$is therefore due to the coordinated COO^- group. As the product is hydrated the stretching frequency for N-H bond in free $–NH_2$ can't be isolated. The sharp peak at 1110 cm^{-1} indicates the counter anion (ClO_4^-).

Conductance measurement also helps us to assign the product formation. As with progress of the reaction there is release of $–H^+$ ion (Fig.9) it is expected that conductance of the reacting solution increase with progress of the reaction and it also found experimentally. Due to release of $–H^+$ ion, pH of the resulting solution found to be decreased.

Physical Measurement

All the spectral scanning and kinetic measurements were done in a Shimadzu UV-VIS spectrophotometer (UV-1601 PC), attached to a thermoelectric cell temperature controller (model TCC-240A with an accuracy of $\pm$ 0.1 ^oC). IR Spectra (KBr disc, 4000 - 300 cm^{-1}) were measured in Perkin-Elmer FTIR model RX1 Infrared spectrophotometer. The pHs of the solutions were adjusted with $HClO_4$/NaOH and measured with a Sartorius pH meter (model PB11) with an accuracy of $\pm$ 0.01.

Kinetics

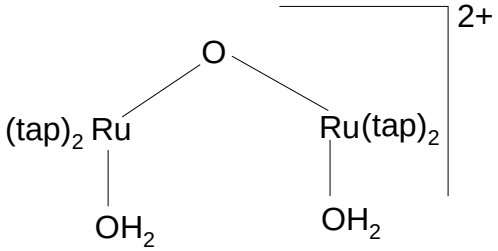
Kinetic measurements were carried out on a Shimadzu UV 1601 spectrophotometer attached to a thermoelectric cell temperature controller (model TCA 240A, accuracy ± 0.1º). The conventional mixing technique was followed and pseudo-first order conditions were employed throughout. The progress of the reaction was followed by measuring the decrease in absorbance at 600 nm, where the spectral difference between the substrate and the product complex is maximum. The $k_{1(obs)}$ and $k_{2(obs)}$ values were calculated graphically (Figs. 5 and 6) using the method of Weyh and Hamm[Weyh(1969)]. We did not use softwares like ORIGIN to calculate k_1 and k_2 as we observed that when the first step is a curved one, Weyh and Hamm method give good results. We took the help of ORIGIN software for other calculations. The rate data represented as an average of duplicate runs are reproducible within ± 4%.

RESULTS AND DISCUSSION

Phenylalanine is the amino acid which contains two separate functional groups; terminal amino group ($-NH_3^+$) and terminal carboxylate group ($-COO^-$). The two dissociation constants are pK_1(-COOH) 1.83 and pK_2 ($-NH_3^+$) 9.13 at 25 ºC. Hence at the experimental pH (7.4), Phenylalanine exists as dipolar ion[Dawson(1959)].

On the other hand, first acid dissociation equilibrium of the complex $[Ru(tap)_2(H_2O)_2]^{2+}$ is 6.6[Mahanti

(1992)] at 25◦C. At pH 7.4, the complex ion exists in dimeric oxo-bridged form, $[(H_2O)(tap)_2RuORu(tap)_2(H_2O)]^{2+}$[Raven(1988), Kutner(1986), Gersten(1982), Ghosh(1984)].



At pH 7.4, the mononuclear species exists in the hydroxoaqua form. Two such species assemble to form the dinuclear oxo-bridged diaqua complex due to thermodynamic force mainly arising from pi-bonding [Cotton(1999)] (O^{2-} donor, Ru^{II} acceptor) which is favorable for 4*d* ion, Ru^{II}. Now, such strong covalency reduces the acidity of the coordinated water. The oxobridge formation is solely dependent on pH. Electrochemical studies show that there is pH potential domain, where the μ- oxo structures stay intact. Variable temperature study does not show any effect, which is in line with the fact that oxobridge formation is solely pH-dependent [Gilbert(1985),Gilbert(1986)].

The plot of ln $(A_t - A_\infty)$ versus time indicates that the reaction is not a single step process,
a two step consecutive process may be assumed, the first step being dependent and the final step is independent on the concentration of ligand.

The rate constant for such a process can be evaluated by assuming Scheme 1.

A is the oxo-bridged diaqua complex, B is the intermediate with ligand and C is the final chelated product complex $[(tap)_2Ru(\mu\text{-}O)(\mu\text{-}L^1H)Ru(tap)_2]^+$.

Scheme 1

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Calculation of k_1 value

The rate constant for this path was calculated from the absorbance data using the Weyh and Hamm equation.

$$(A_t - A_\infty) = a_1 \exp(-k_{1(obs)} t) + a_2 \exp(-k_{2(obs)} t) \quad (1)$$

Where a_1 and a_2 are constants that depend upon the rate constants and extinction coefficients.

Values of $a_2 \exp(-k_{2(obs)} t)$ at different times (when t is small) were obtained from the linear portion of the curve (Fig.3) extended to t equals zero, i.e.

$a_2 \exp(-k_{2(obs)} t) = (A_t - A_\infty)_{limiting}$

Therefore values of $(A_t - A_\infty) - a_2 \exp(-k_{2(obs)} t)$ were calculated from X and Y values (Fig.3) at different t;

$\Delta = a_1 \exp(-k_{1(obs)} t)$

or, $\ln \Delta = \text{constant} - k_{1(obs)} t \quad (2)$

$k_{1(obs)}$ was then derived from the slope of lnΔ *versus* time, for small values of t (Fig.4).

A similar procedure was applied for each Phenylalanine concentration in the 1.0×10^{-3} mol dm^{-3} to 5.0×10^{-3} mol dm^{-3} range using the experimental conditions specified in Table 1. The $k_{1(obs)}$ values are collected in Table 1.

The rate increases with increase in $[L^1H]$ and reaches a limiting value (Fig. 5). The limiting rate is probably due to the completion of outer sphere association complex formation. Since the metal ion reacts with its immediate environment, further change in $[L^1H]$ beyond the saturation point will not affect the

reaction rate. The outer sphere association complex may be stabilized through H-bonding. Based on the experimental findings, the following Scheme 2 may be proposed for the path **(1)** → **(2)** (k_1 path)**;**

$$\mathbf{(1)} + (L^1H) \xrightarrow{K_E} \mathbf{(1)} \cdot (L^1H)$$

Outer sphere association complex

$$\mathbf{(1)} \cdot (L^1H) \xrightarrow{k_1} \mathbf{(2)}$$

Scheme 2

Based on the above scheme a rate expression can be derived.

$$d[\mathbf{2}]/dt = k_1K_E[(H_2O)\,(tap)_2RuORu(tap)_2(H_2O)]^{2+}[\,L^1H] \quad (3)$$

$$\text{or, } d[\mathbf{2}]/dt = k_{1(obs)}\,[(H_2O)\,(tap)_2RuORu(tap)_2(H_2O)]^{2+}{}_T \quad (4)$$

Where T stands for total concentration of Ru(II).We can then write,

$$k_{1(obs)} = k_1K_E\,[L^1H]/(1+K_E[L^1H]\,) \quad (5)$$

Where k_1 is the rate constant for the k_1 path, i.e., the rate constant for the interchange of outer sphere complex to the inner sphere complex; K_E is the outer sphere association equilibrium constant.

The equation can be represented as:

$$1/k_{1(obs)} = 1/k_1 + 1/k_1K_E[L^1H] \quad (6)$$

The plot of $1/k_{1(obs)}$ against $1/[\,L^1H]$ should be linear with an intercept of $1/k_1$ and slope $1/k_1K_E$. This was found to be the case at all temperatures studied. The k_1 and K_E values were calculated from the intercept and slope (Fig.6) and are collected in Table 2.

Calculation of k_2 for B→C

The B → C step is intramolecular ring closure and is independent of ligand concentration.

At a particular temperature the slopes of $\ln(A_t - A_\infty)$ versus time plots at different ligand concentrations were found to be constant in the region where the plot is linear (Fig. 3). For different temperatures, the k_2 values are obtained directly from the limiting slopes and are collected in Table 2.

Based on the experimental findings, a two step interchange associative mechanism is proposed for the substitution process. In the first path, an outersphere association complex is formed between the ligand and the two ruthenium (II) centers, which is stabilized by the H-bonding between the incoming Phenylalanine and the coordinated aqua molecules. Now the interchange of the ligand from the outersphere to the innersphere occurs.

Effect of temperature

Four different temperatures were chosen for study and the results are listed in Table 3.The activation parameters for the step A→B and B→C were evaluated from the linear Eyring plots (Figs.7 and 8) and is collected in Table 3.

The low $\Delta H^{\neq}$ values are in support of the ligand participation in the transition state for both the steps. The energy required to break the Metal-departing ligand bond is partly compensated due to the formation of Metal-incoming ligand bond and a lower value of $\Delta H^{\neq}$ is observed. The high negative $\Delta S^{\neq}$ values suggest a more compact transition state, where both the incoming and departing ligands are attached in the transition state, and this is also in support of the assumption of a ligand participated transition state. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values have a good agreement with the previously studied systems[Chattopadhyay(2004),Chattopadhyay(2004),Chattopadhyay(2005),Chattopadhyay(2006),Ghosh (2006)]that also substantiate our study.

Table 1. 10^3 $k_{1(obs)}$ values for different ligand concentrations at different temperatures. [Complex 1] = 1.0 × 10^{-4} mol dm^{-3}, pH = 7.4, ionic strength = 0.1 mol dm^{-3} $NaClO_4$

Ligand	Temperature(^{0}C)	10^3 [ligand]				
		1.00	2.00	3.00	4.00	5.00
HL^1	35	1.52	2.20	2.73	3.00	3.33
	40	1.84	2.50	3.02	3.47	3.75
	45	2.09	2.87	3.40	3.75	4.00
	50	2.38	3.05	3.75	4.15	4.44

Table 2. The k_1, k_2, K_E values for the substitution reaction between ligands and Complex (***1***)

Ligands	Temp.(ºC)	$10^3k_1(s^{-1})$	$K_E(dm^3mol^{-1})$	$10^4k_2(s^{-1})$
L^1H	35	7.96	75	12.68
	40	8.00	103	15.00
	45	8.10	124	17.29
	50	10.60	151	19.00

Table 3. Activation parameters for [complex **1**] by ligands in aqueous medium, pH = 7.4

Ligands	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (kJ mol^{-1})	$\Delta H_2^{\neq}$ (kJ mol^{-1})	$\Delta S_2^{\neq}$ (kJ mol^{-1})
L^1H	15.4 ± 1.6	-233 ± 5	20.2 ± 0.7	-235 ± 2

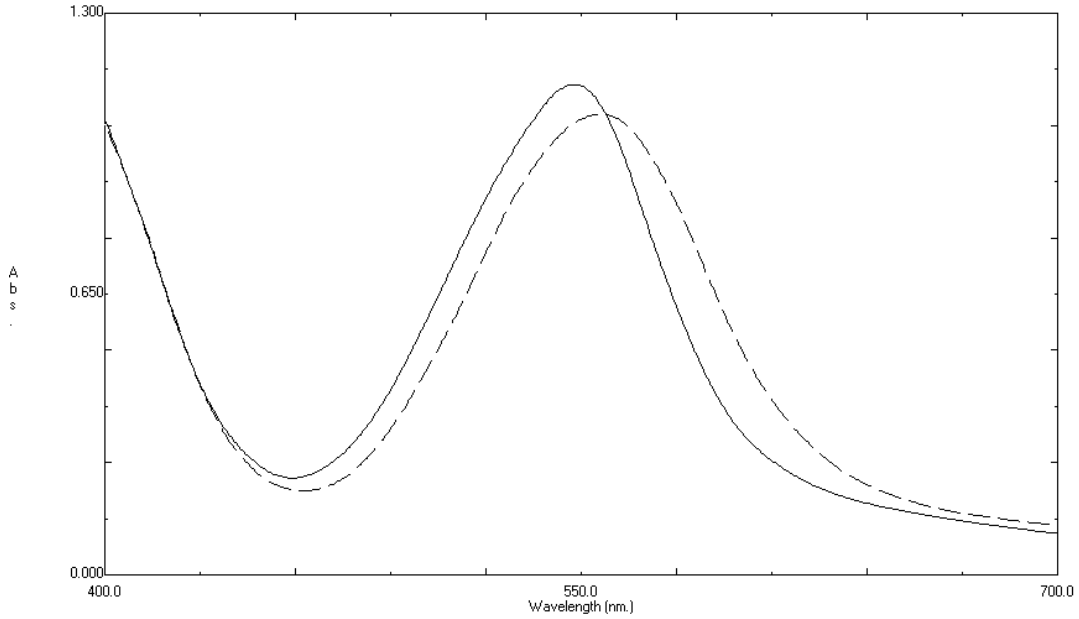


Figure 1. Spectral difference between substrate complex and products.
(------) $[(H_2O)(tap)_2RuORu(tap)_2(H_2O)^{2+}] = 1.0\times10^{-4}$ mol dm^{-3};
(——)$[(H_2O)\ (tap)_2RuORu(tap)_2(H_2O)^{2+}] = 1.0\times10^{-4}$ mol dm^{-3}, [Phenylalanine] = 3.0×10^{-3} mol dm^{-3}, pH = 7.4

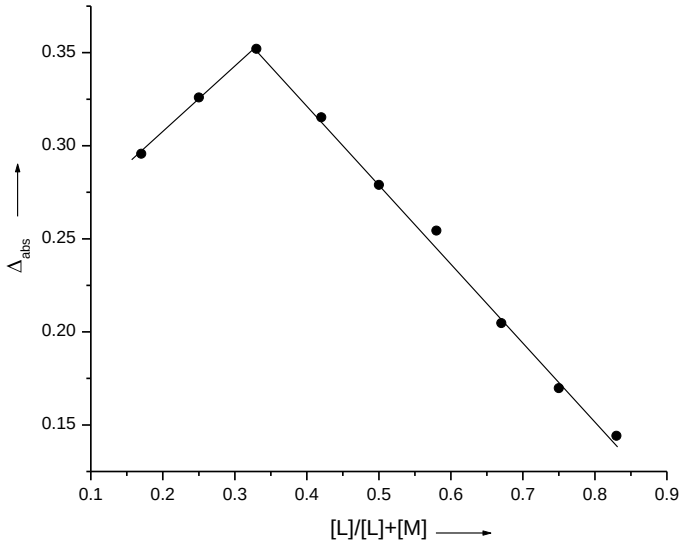


Figure 2. Job's plot for reaction of complex (*1*) with Phenylalanine

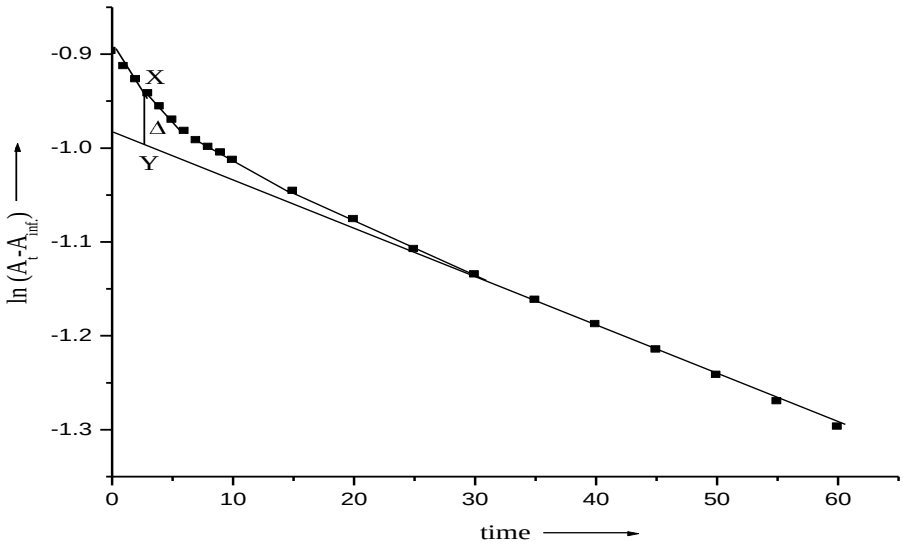


Figure 3. A typical plot of ln (A_t-A_∞) versus time t. [complex] = 1.0×10^{-4} mol dm^{-3}, [Phenylalanine] = 3.0×10^{-3} mol dm^{-3}; pH = 7.4, Temp. = 50°C.

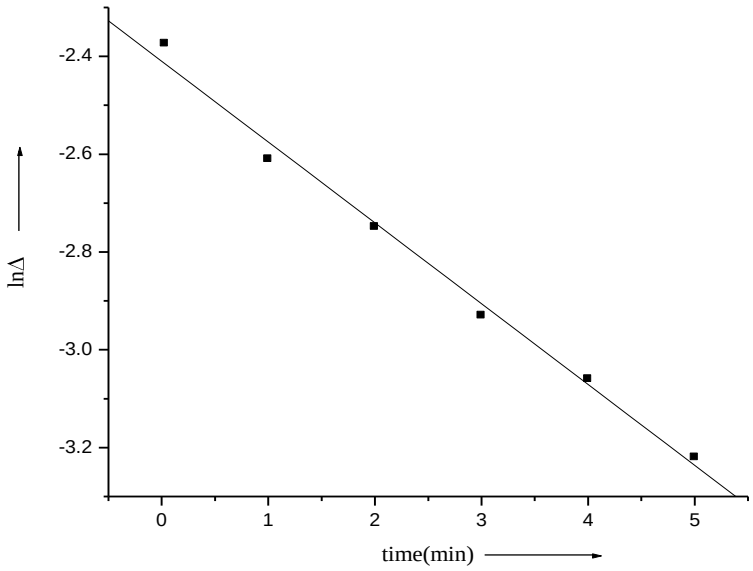


Figure 4. A typical plot of lnΔ versus time t. [complex] = 1.0×10^{-4} mol dm^{-3}, [Phenylalanine] = 3.0×10^{-3} mol dm^{-3}; pH = 7.4, Temp. = 50°C.

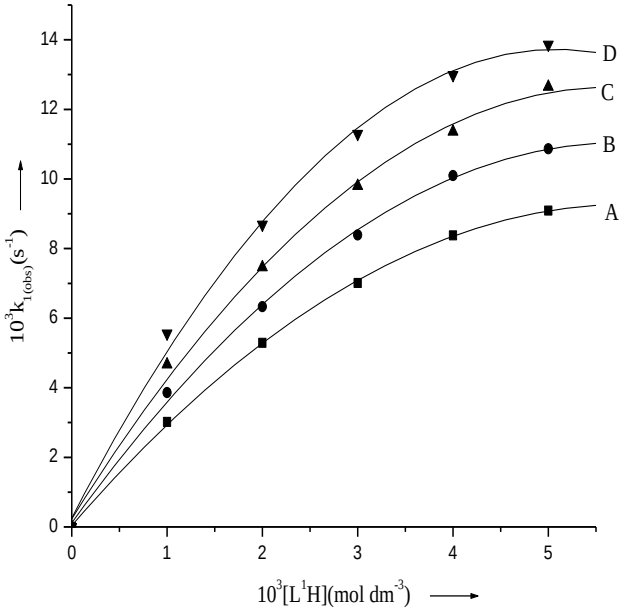


Figure 5. Plot of $k_{1\,(obs)}$ *versus* Phenylalanine [L^1H] at different temperature, A = 35, B = 40, C = 45 and D = 50 ºC

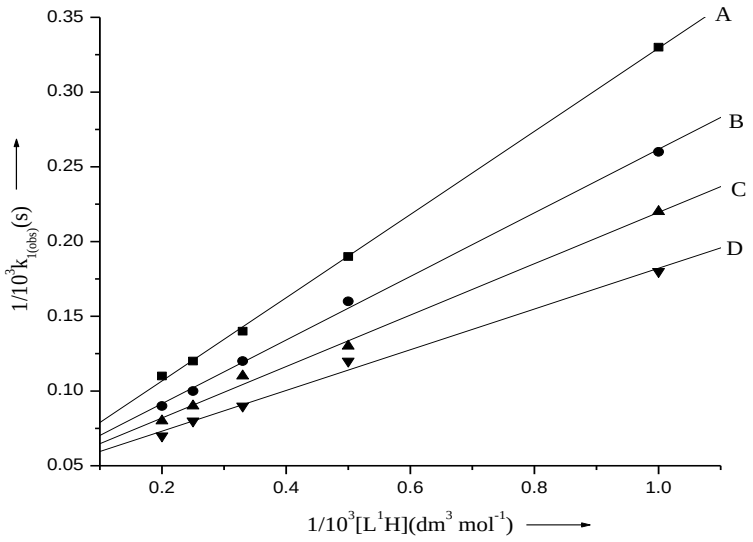


Figure 6. Plot of $1/k_{1(obs)}$ against 1/[L^1H], A = 35, B = 40, C = 45 and D = 50 ºC.

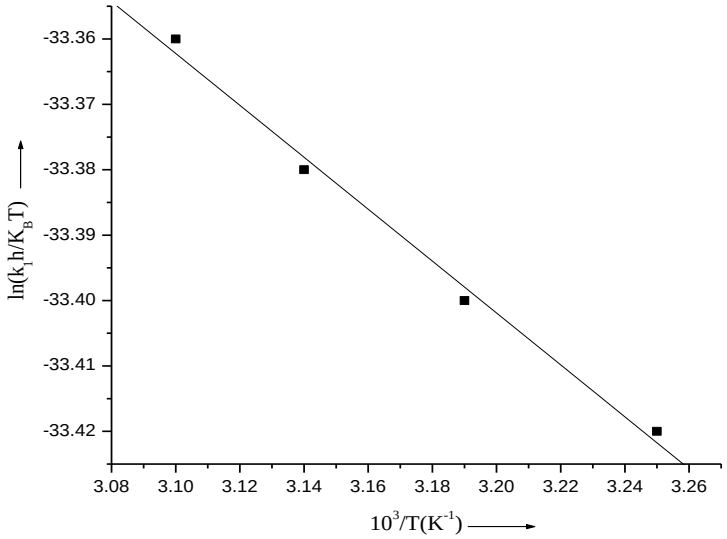


Figure 7. Eyring plot for $k_1(L^1H)$

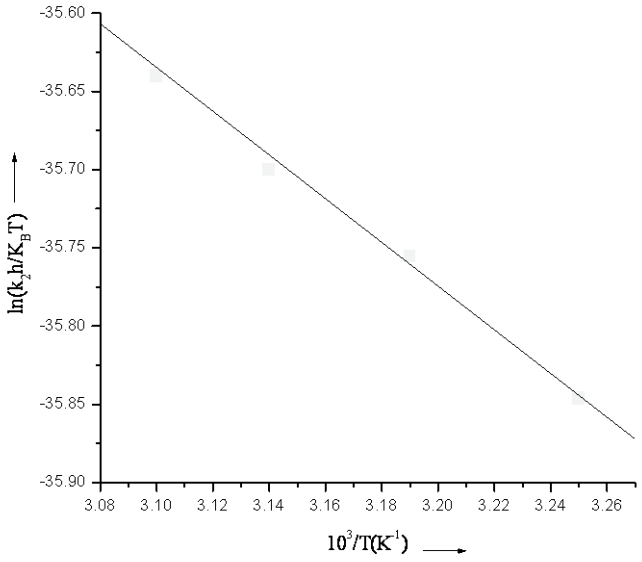


Figure 8. Eyring plot for k_2 (L^1H)

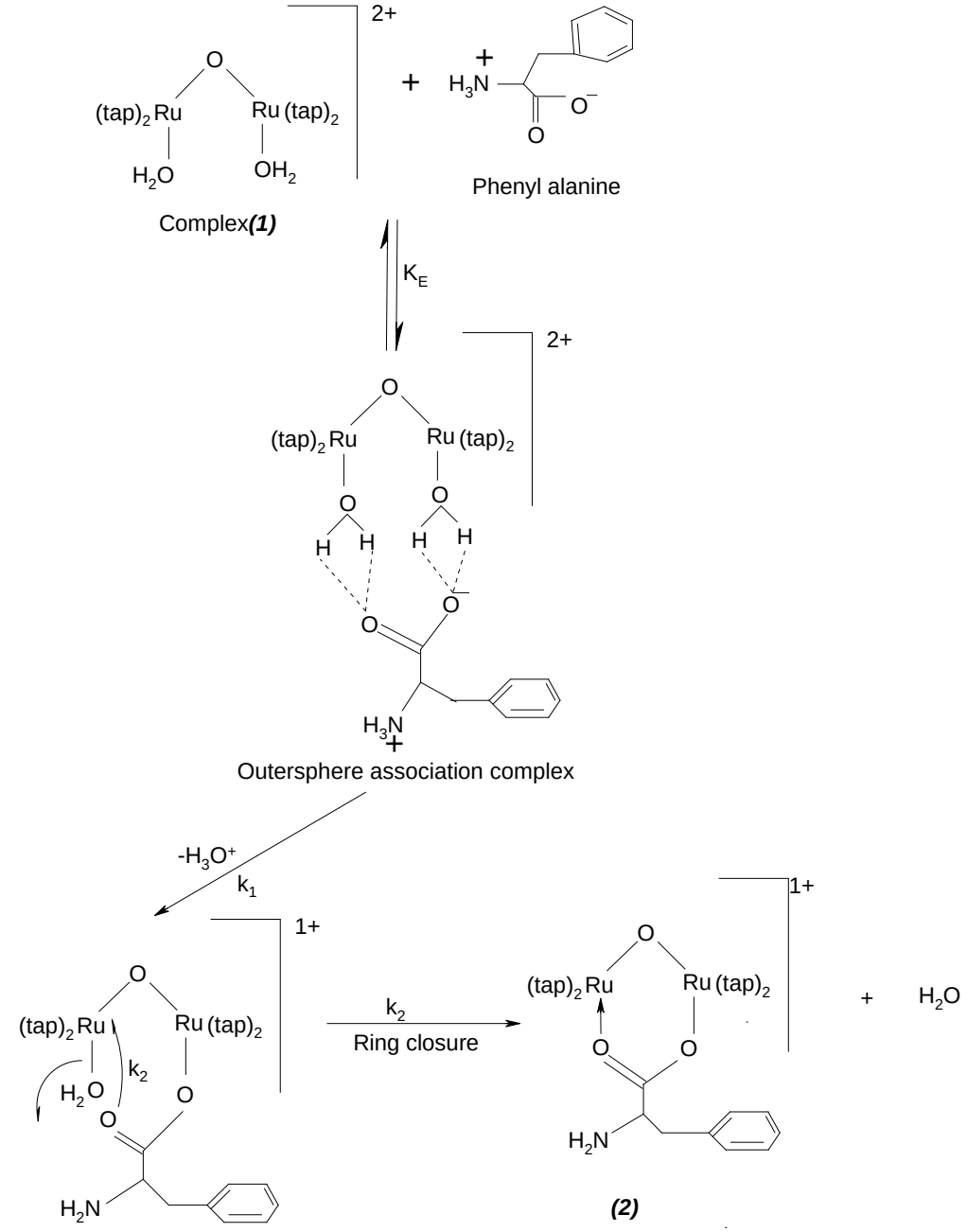


Figure 9. Plausible mechanism for the substitution of aqua ligands from $[(H_2O)(tap)_2RuORu(tap)_2(H_2O)]^{2+}$ by studied ligand.

Conclusion

The interaction of Phenylalanine with the title ruthenium complex proceeds via two distinct consecutive steps ($k_1 \sim 10^{-3}$ s^{-1} and $k_2 \sim 10^{-4}$ s^{-1}). First path proceeds via an associative interchange activation and the second step is the ring closure. At the outset of first path outer sphere association complex results, this is stabilized through H-bonding and is followed by an interchange from the outer sphere to the inner sphere complex. The outer sphere association equilibrium constants, a measure of the extent of H-bonding for

each path at different temperatures are evaluated (Table 2&3). From the temperature dependence of the K_E the thermodynamic parameters are calculated $\Delta H_1^0 = 35.4 \pm 1.9$ kJ mol^{-1}, $\Delta S_1^0 = 94 \pm 6$ J K^{-1} mol^{-} ΔG^0 values, calculated for both steps at all temperature studied, have a negative magnitude which is once again in favour of the spontaneous formation of an outersphere association complex.

MECHANISM

There occurs the formation of stable six membered structure of the product by the coordination of two O atoms of carboxylate group with the two Ru (II) centers. Now O^- of carboxylate group first attacks one of the ruthenium(II) centre by the removal of one water molecule i.e., follow the k_1 path and then after proton release another O atom of the carboxylate group finishes the ring closing process.

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