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Kinetics and mechanism of the ligand substitution reaction of di-μ-hydroxobis(bipyridyl)dipalladium(II) ion with diethyldithiocarbamate anion in aqueous solution

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Abstract. The kinetics of the interaction between diethyldithiocarbamate (Et_2DTC) and the title complex has been studied spectrophotometrically in aqueous medium as a function of nucleophile concentration, temperature and pH at constant ionic strength. The reaction is a two-step process in which the first step is ligand-dependent, but the second step is ligand-independent and is assigned to ring closure. The rate and activation parameters, conductivity studies and IR data were used to deduce a plausible mechanism.

Keywords. Kinetics; palladium(II); diethyldithiocarbamate; mechanism; activation parameters.

1. Introduction

Cisplatin is one of the most active antitumour agents in clinical use[1] but its clinical use is limited by undesirable side effects, including nephrotoxicity, ototoxicity, neurotoxicity, nausea, vomiting and myelosuppression.[2,3] Pd(II) and Pt(II) complexes have the same structure, with a five orders of magnitude higher reactivity in the case of Pd(II) complexes, but similar thermodynamic parameters. Pd(II) complexes are good models for the analogous Pt(II) complexes in solution.

Much work has been performed on the equilibrium studies of palladium(II) complexes with aliphatic amines[4–7] and it is of interest to extend this work to the reactions of palladium(II) complexes with heterocycles, such as 2,2′-bipyridine. Aromatic heterocycles generally act as σ-donors and also function as fairly effective π-acceptors. In addition, heterocycles can be involved in π–π stacking with purine and pyrimidine bases. This can lead to complex formation with DNA subunits, which is an important target in cancer chemotherapy.[8] Besides this, non-covalent interaction of palladium complexes with nucleic acids is also possible.[9] This type of non-covalent interaction may inhibit the reactivity of the metal complexes.[10]

The sulphur-containing ligands have high affinity for Pd(II) and Pt(II). These ligands will compete with the DNA for the reaction with any antitumour agent. Therefore, it is of biological significance to evaluate the equilibrium constants for the displacement reaction. These equilibrium constants may give a measure of the effectiveness of the antitumour agent.

Diethyldithiocarbamate is an effective chemoprotective agent and is the only chemoprotector effective when administered 1–4 h after cisplatin.[11,12] Moreover the dithiocarbamato derivatives of Pd(II) and Pt(II) complexes, containing 2,2′-bipyridyl and 1,10-phenanthroline as a ligand showed antitumor activity against leukemic cells.[13]

In view of the above, we now describe the interaction of a palladium(II) complex towards Na-diethyldithiocarbamate ($NaEt_2DTC$) which may throw some light on the bioinorganic chemistry of palladium(II).

2. Experimental

2.1 *Materials*

$[Pd(bipy)Cl_2]$ (bipy = 2,2′-bipyridine) was prepared by literature methods.[14,15] The diaqua complex, $[Pd(bipy)(H_2O)_2](ClO_4)_2$, was prepared in solution by the method of Hay and Basak[16] by stirring the chloro complex with two mole equivalents of $AgClO_4$ followed by keeping it overnight (with careful protection

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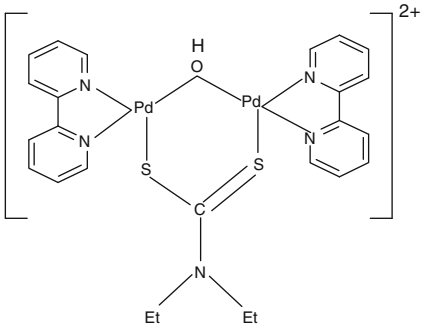
from light). The precipitated AgCl was removed by filtration and the filtrate made up to the requisite volume in a standard flask.

The reactant complex, di-μ-hydroxobis(bipyridyl) dipalladium(II) ion (complex **1**), was obtained *in situ* by adjusting the pH to 7.4 with NaOH/$HClO_4$. The reaction product of diethyldithiocarbamate and complex **1** was prepared by mixing the reactants in different ratios, namely, 1:1, 1:2, 1:3, 1:5, and 1:10, and keeping at 50°C for 24 h. The absorbance spectra of these mixtures (figure 1) all exhibited the same λ_{max} with nearly identical intensities.

The starting complex does not react well with azide, cytidine or with thymidine, but easily reacts with sulphur-containing molecules such as cysteine, thiosemicarbazide, methionine etc. So we may say that the sulphur atom of the ligand is involved in bonding with Pd(II) due to soft nature of both atoms.

From the above discussion, the possible structure of the product complex can be represented as in scheme 1.



Scheme 1. Possible structure of the product complex.

2.2 *Product analysis*

The composition of the product was determined by Job's method of continuous variation, which indicated a 2: 1 metal–ligand ratio (figure 2).

The IR spectrum of the product in KBr disc indicates the presence of a coordinated hydroxide group is confirmed[17,18] by the OH stretching absorption at *ca.* 3400 cm^{-1}. Absorption peak at *ca.* 1030 cm^{-1} assigned as the bending mode and peak at *ca.* 575 cm^{-1} assigned as the Pd–O stretching vibration for a bridging hydroxide group.[19] From this, we may conclude that there is a bridged OH group in the resultant product complex. For this complex the δ(OH) mode is obscured by the intense anion absorption. The bands in the region of *ca.* 940–1010 cm^{-1} were attributed to the stretching mode of the C–S bond. The position of this band has been used as a criterion for symmetric or asymmetric coordination of the dithiocarbamato group. The singlet in the IR spectrum confirms the equivalence of the S atom, but the doublet at *ca.* 987 cm^{-1} in the IR spectrum indicates non-equivalence of the S atoms in the compound. Presence of doublet at 940–1010 cm^{-1} indicates non-equivalence of two sulphur atoms. So we can say that both S atoms of the ligand involved in bonding. The presence of γ(Pd–S) band in the 300–400 cm^{-1} region confirms the coordination of the ligand to Pd(II) via sulphur atom.[20] Broad and strong bands at *ca.* 1089 and at *ca.* 627 cm^{-1} are assigned to the perchlorate salt of the complex (figure 3).

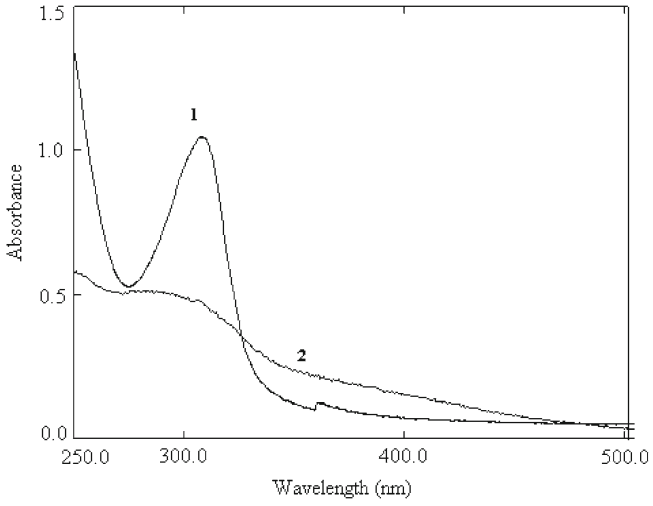


Figure 1. Spectra of the starting [complex **1**] (1), and the diethyldithiocarbamate substituted complex (2); [complex **1**] = 2.85 × 10^{-4} mol dm^{-3}, [Et_2DTC] = 5.7 × 10^{-3} mol dm^{-3}, pH = 7.4, cell used = 1 cm quartz.

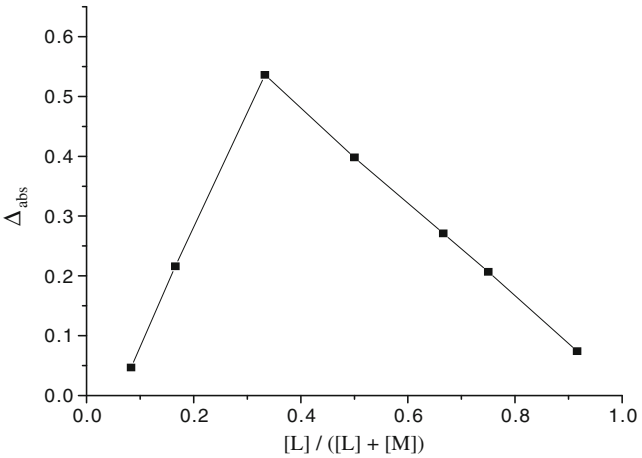


Figure 2. Job's plot for the reaction of complex **1** with Et_2DTC.

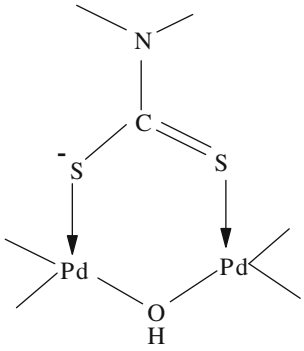


Figure 3. Coordination modes of the ligand.

Conductance measurements also help us to identify the product. During the course of the reaction, there is release of OH^- ion, as shown by increase in conductance and pH. This is consistent with substitution of OH^- by Et_2DTC.

2.3 *Measurements*

The pH of the solution was adjusted by adding $NaOH/HClO_4$, and the pH measurements were made with a Sartorius digital pH meter (model PB11) with an accuracy of ± 0.01 units. Doubly distilled water was used to prepare all the solutions. All other chemicals used were of AR grade. The reactions were carried out at constant ionic strength (0.1 mol dm $^{-3}$ $NaClO_4$).

Spectroscopic measurements were made with a Shimadzu UV-VIS Spectrophotometer (UV-2101). IR Spectra (KBr disc, 4000–300 cm^{-1}) were measured on a Perkin-Elmer FTIR RX1 Spectrophotometer. Conductance measurements were made with a Systronics conductivity meter (model 308), where the cell constant was calibrated with 0.01 M KCl solution and water used as solvent.

The kinetic studies were done on a Shimadzu UV 2101 PC Spectrophotometer attached to a thermoelectric cell temperature controller (Model Shimadzu TB 85 thermobath, accuracy ± 0.1°C). The development of a characteristic peak of the product complex (complex **2**) at 310 nm was monitored with time at different fixed temperatures. The conventional mixing technique was followed and pseudo first order conditions were employed throughout.

The plots of $\ln(A_t - A_\infty)$, where A_t and A_∞ are absorbances at time t and after the completion of the reaction, against time were found to be nonlinear, being curved at the initial stage and subsequently of constant slope (figure 4).

The method of Weyh and Hamm[21] was adopted to calculate rate constants for two consecutive steps.

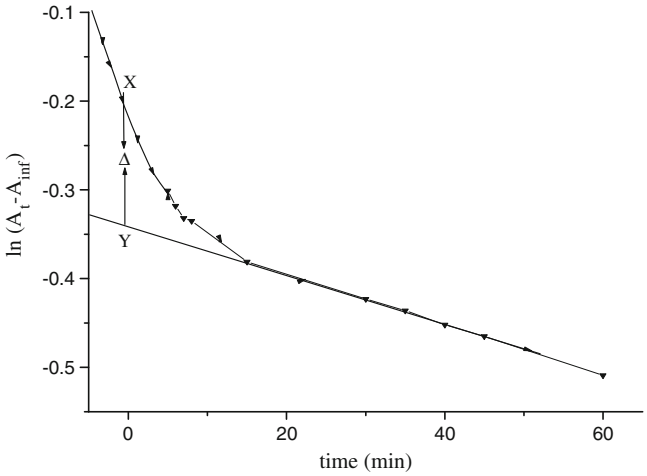


Figure 4. A typical plot of $\ln(A_t - A_\infty)$ versus time. [complex **1**] = 2.85×10^{-4} mol dm^{-3}. [Et_2DTC] = 5.7×10^{-3} mol dm^{-3}, pH = 7.4, temp = 35°C.

From the linear second portion, k_2 values were obtained. The $k_{1(obs)}$ values were obtained from the plot of ln Δ versus t. A typical plot is shown in figure 5. Rate data represented as an average of duplicate runs are reproducible within ± 4%.

3. Results and discussion

The pKa value of the ligand Et_2DTC is 3.37 at 25°C,[22] so that at pH 7.4, the major species involved in the kinetic process is the anionic form of the ligand which is Et_2DTC^-. The pKa_1 and pKa_2 values for $[Pd(bipy)(H_2O)_2]^{2+}$ as reported in the literature are 4.5 and 9.6 at 25°C respectively[23] and 3.91 and 8.39 at 25°C respectively.[5]

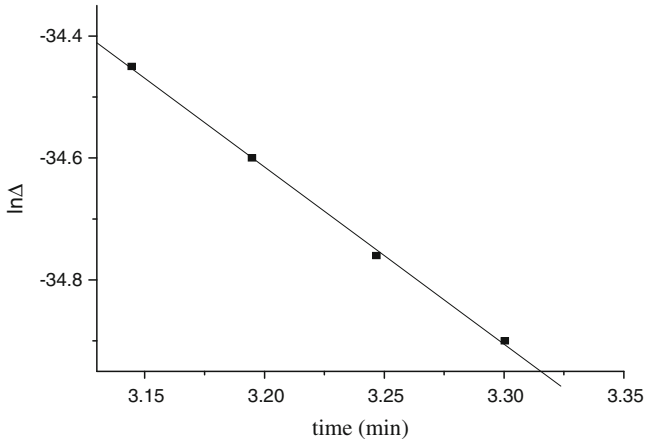
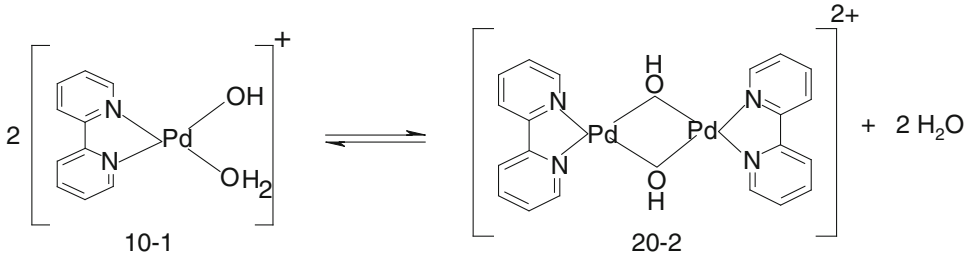


Figure 5. A typical plot of lnΔ versus time. [complex **1**] = 2.85×10^{-4} mol dm^{-3}. [Et_2DTC] = 5.7×10^{-3} mol dm^{-3}. pH = 7.4, temp = 35°C.

We can consider the following equilibria to be in operation:

$$\underset{100}{\left[\mathrm{Pd\,(bipy)\,(H_2O)_2}\right]^{2+}} \overset{\mathrm{pK_{a1}}}{\rightleftharpoons} \underset{10-1}{\left[\mathrm{Pd\,(bipy)\,(H_2O)\,(OH)}\right]^{+}} + \mathrm{H^+} \quad (1)$$

$$\underset{10-1}{\left[\mathrm{Pd\,(bipy)\,(H_2O)\,(OH)}\right]^{+}} \overset{\mathrm{pK_{a2}}}{\rightleftharpoons} \underset{10-2}{\left[\mathrm{Pd\,(bipy)\,(OH)_2}\right]} + \mathrm{H^+} \quad (2)$$



(3)

The equilibrium constant[5] for the dimerization step (3), log K_{dimer} = 3.12. At pH 7.4, the protonation state of the Pd complex will be primarily the hydroxoaqua (10–1). From the pK_a values and from the dimerization constant, it can be shown that at pH 7.4 the percentage of the dimer present in the solution is ~85%. This is supported widely in the literature.[24–26]

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 independent of the concentration of dithiocarbamate.

The rate constant for such a process can be evaluated by assuming the following scheme 2.

where A is the hydroxo-bridged dimer, B is as intermediate with diethyldithiocarbamate and C is the final product complex $[Pd_2(bipy)_2(OH)(L)]$.

The rate constant $k_{1(obs)}$ for the A → B step can be evaluated by the method of Weyh and Hamm using the usual consecutive rate law:

$$(At - A_\infty) - a_2 \exp(-k_2 t) = a_1 \exp\left(-k_{1(obs)} t\right), \quad (4)$$

where a_1 and a_2 are constants dependent on the rate constants and extinction coefficient.

Values of $[(A_t - A_\infty) - a_2 \exp(-k_2 t)]$ were obtained from X − Y at different times (figure 3). Then,

$$\ln \Delta = \text{constant} - k_{1(obst)} t. \quad (5)$$

The value of $k_{1(obs)}$ was derived from the slope of a plot of lnΔ versus t (where t is small) (figure 5). A similar procedure was applied for each Et_2DTC concentration in the 2.85×10^{-3} to 8.55×10^{-3} mol dm^{-3} range, at constant [**1**] (2.85×10^{-4} mol dm^{-3}) at pH = 7.4, μ = 0.1 mol dm^{-3} $NaClO_4$ and at different temperatures namely 30, 35, 40 and 45°C. The $k_{1(obs)}$ values are presented in table 1.

The rate increases with increase in $[Et_2DTC]$ before reaching a limiting value (figure 6), which is probably due to the completion of the outer sphere association complex formation. At this stage, the interchange of the ligands from the outer sphere to the inner sphere occurs, i.e., dithiocarbamato attacks one of the Pd(II) atoms of the dihydroxo- bridged dimer to give intermediate complex.

From the experimental findings, scheme 3 may be given for the A → B step.

Based on scheme 3, a rate expression can be derived for the A → B step.

$$d[B]/dt = k_1 K_E [B]\left[Et_2DTC^-\right] / \left(1 + K_E\left[Et_2DTC^-\right]\right)$$

$$d[B]/dt = k_{1(obs)} [B]_T,$$

where T stands for total concentration of Pd(II).Thus, it can be written as

$$k_{1(obs)} = k_1 K_E\left[Et_2DTC^-\right] / \left(1 + K_E\left[Et_2DTC^-\right]\right),$$

where k_1 is the rate constant for the formation of intermediate (B) from dihydroxy dimer (A), K_E is the outer sphere association equilibrium constant.

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

Scheme 2.

Table 1. $10^3\ k_{1(obs)}\ (s^{-1})$ values for different Et_2DTC concentrations at different temperatures. [complex **1**] = 2.85×10^{-4} mol dm^{-3}, pH = 7.4, ionic strength = 0.1 mol dm^{-3} $NaClO_4$.

$10^3[Et_2DTC]$ (mol dm^{-3})	Temperature (°C)			
	30	35	40	45
2.85	2.00	2.12	2.87	3.10
4.27	2.37	2.85	3.20	3.90
5.70	2.59	3.14	3.70	4.18
7.12	2.75	3.25	3.80	4.70
8.55	2.98	3.33	4.12	5.16

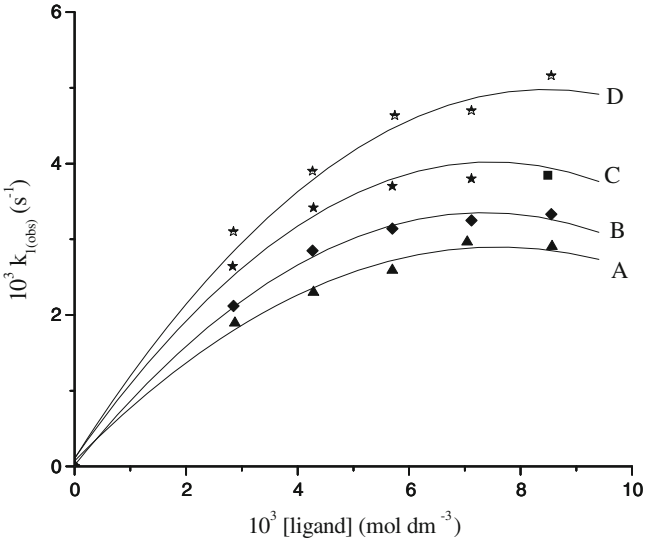


Figure 6. Plot of $k_{1(obs)}$ versus $[Et_2DTC]$ at different temperatures. A = 30, B = 35, C = 40 and D = 45°C.

$$A + Et_2DTC^- \underset{}{\overset{K_E}{\rightleftharpoons}} A.Et_2DTC^-$$

Outer sphere association complex.

$$A\,Et_2DTC^- \xrightarrow{k_1} B$$

Scheme 3. Formation of intermediate complex.

The equation can be written as

$$1/k_{1(obs)} = 1/k_1 + 1/k_1K_E\left[Et_2DTC^-\right].$$

The plot of $1/\ k_{1(obs)}$ versus $1/\ [Et_2DTC^-]$ should be linear (figure 7) with an intercept of $1/\ k_1$ and slope $1/\ k_1K_E$.

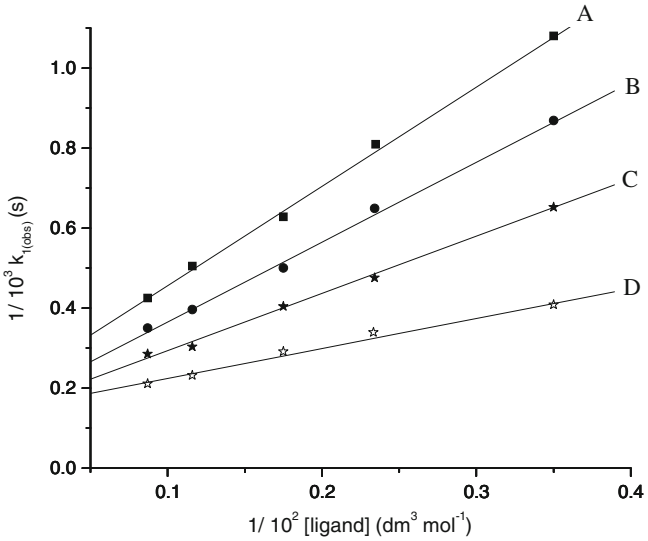


Figure 7. Plot of $1/\ k_{1(obs)}$ versus $1/\ [Et_2DTC]$ at different temperatures, A = 30, B = 35, C = 40 and D = 45°C.

Table 2. $10^3\ k_1\ (s^{-1})$ and K_E ($dm^3\ mol^{-1}$) values for different ligands at different temperatures. [complex **1**] = 2.85×10^{-4} mol dm^{-3}, pH = 7.4, ionic strength = 0.1 mol dm^{-3} $NaClO_4$.

Temperature (°C)	$10^3\ k_1(s^{-1})$	$K_E(dm^3\ mol^{-1})$
30	5.25	110
35	5.85	130
40	6.52	165
45	7.26	199

Table 3. $10^5\ k_2\ (s^{-1})$ values for different Et_2DTC concentrations at different temperatures. [complex **1**] = 2.85×10^{-4} mol dm^{-3}, pH = 7.4, ionic strength = 0.1 mol dm^{-3} $NaClO_4$.

$10^3[Et_2DTC]$ (mol dm^{-3})	Temperature (°C)			
	30	35	40	45
2.85	8.91	9.85	10.59	11.47
4.27	8.93	9.86	10.60	11.47
5.70	8.94	9.86	10.61	11.49
7.12	8.93	9.86	10.59	11.49
8.55	8.94	9.87	10.61	11.48

This was found to be at different temperatures studied.

The k_1 and K_E values obtained from the intercept and slope to intercept ratios are given in table 2.

The B → C step is intramolecular ring closure and is independent of Et_2DTC concentration. At a particular

Table 4. Activation and thermodynamic parameters of [complex **1**] by various ligands in aqueous medium, pH = 7.4.

Ligand	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})	$\Delta H_2^{\neq}$ (kJmol^{-1})	$\Delta S_2^{\neq}$ (J K^{-1} mol^{-1})	Refs.
DL-methionine	46.0 ± 1.5	-101 ± 5	a	a	27
Thiosemicarbazide	50.4 ± 1.9	-105 ± 6	a	a	28
L-cysteine	33.6 ± 1.5	-134 ± 5	a	a	29
Thiourea	24.2 ± 1.6	-210 ± 5	7.5 ± 1.0	-306 ± 6	30
Dithiocarbamate[b]	15 ± 1.2	-239 ± 5	10.4 ± 1.5	-288 ± 4	This work

[a]Previous studies indicated a single step reaction, but we have found a two-step reaction for the present system
[b]$\Delta H_1^{\circ} = 31.4 \pm 1.3$ kJ mol^{-1}, $\Delta S_1^{\circ} = 142 \pm 5$ J K^{-1} mol^{-1}

temperature, the slope of $\ln(A_t - A_\infty)$ versus time plots at different Et_2DTC concentrations were found to be constant in the region where the plots are linear (figure 4). For different temperatures, the k_2 values were obtained directly from the limiting slopes and are presented in table 3 and the average 10^5 k_2 values were 8.93, 9.86, 10.60 and 11.48 s^{-1} at 30, 35, 40 and 45°C respectively.

3.1 *Effect of change in pH on the reaction rate*

The reaction was studied at five different pH values. At a fixed 2.85×10^{-4} mol dm^{-3} [complex **1**], 5.7×10^{-3} mol dm^{-3} [Et_2DTC] and 0.1 mol dm^{-3} $NaClO_4$ ionic strength, the 10^3 $k_{1(obs)}$ values were 2.75, 2.68, 2.65, 2.60 and 2.59 s^{-1} and 10^5 k_2 values were 8.93, 8.92, 8.94, 8.90, and 8.94 s^{-1} at pH 5.5, 6.0, 6.5, 7.0 and 7.4 respectively at 30°C. The change in rate may be explained based on two acid dissociation equilibria of Et_2DTC and the complex, as follows.

Firstly, the Et_2DTC ($pK_a = 3.37$ at 25°C) remains in the anionic form within our studied pH range. The effect of pH on rate is therefore due to the change in reactive forms of the reacting complex. Above pH 5.5, > 90% of the diaqua complex will be in the hydroxoaqua form. As the log K_{dimer} value is 3.12, it is expected that at pH > 5.0, the hydroxo-bridged dimer will be the predominant species (∼85%) and the effect of change in pH will be small, as observed experimentally. On the other hand, the $k_{2(obs)}$ values are dependent only on the nature of the ligand during bridge formation. Hence, the $k_{2(obs)}$ values are independent of pH. Nevertheless, the present kinetic runs were followed at a constant pH of 7.4 to avoid complications caused by adding an additional parameter of $[H^+]$ to the rate equation.

3.2 *Effect of temperature on the reaction rate*

Four different temperatures were chosen for study and the results are listed in table 4. The activation parameters for the steps A→B and B→C were evaluated from the linear Eyring plots and the results are compared with analogous systems in table 4.

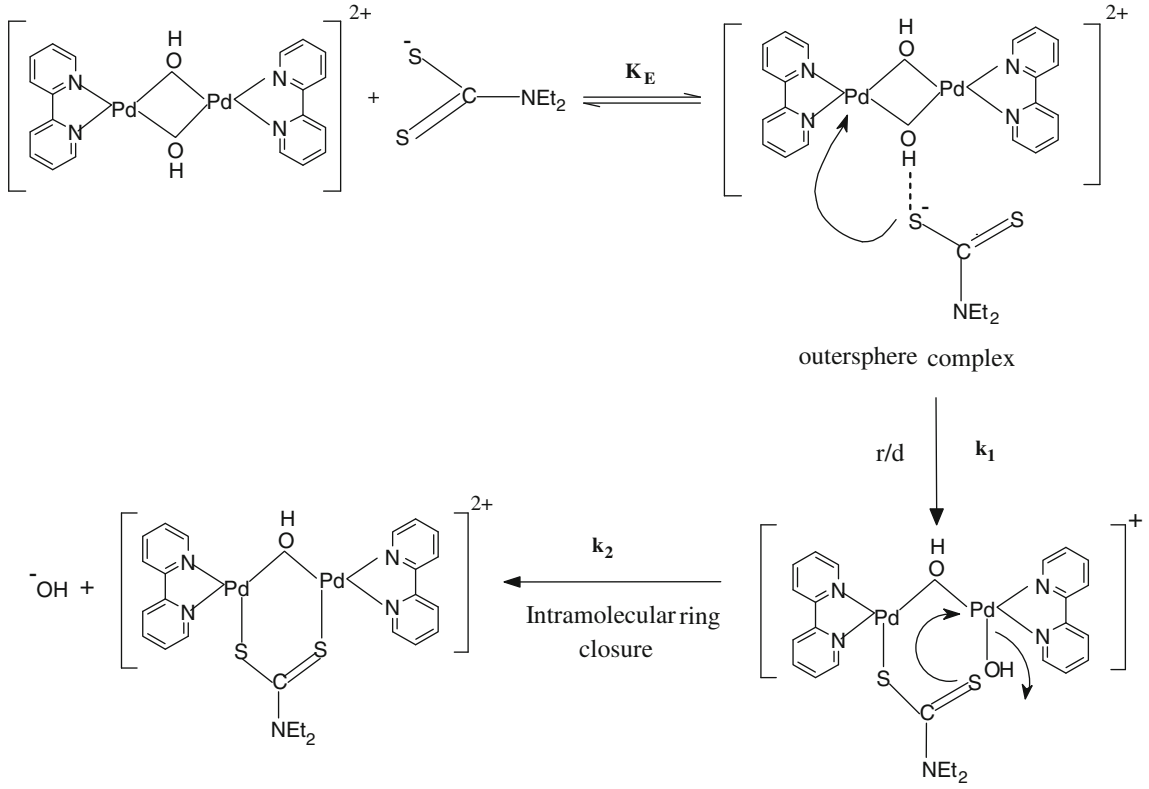
4. Mechanism and conclusion

The Et_2DTC exists as anionic form in the studied pH range. There are two sulphur atoms in the ligand both of them can coordinate to the metal atom. From the IR data it is clear that both the sulphur atoms of the ligand are involved in bonding with two Pd atoms of the complex **1**. This is due to soft nature of both Pd and S atom.

Et_2DTC has been reported to form complexes with soft metal ions like Ir^+,[31] Ag^+,[32] Cu^+,[33] Pt^{2+}[34] using both of its S-donor centers and chelating the metal ion. It is expected that Et_2DTC would show the same type of bonding mode with the complex in the present reaction condition.

In first stage a rapid equilibrium is established, results an outer sphere association complex between complex **1** and ligand. This proposition is supported by the following facts. First, with an increase in ligand concentration saturation in rate is observed. This is possible only when an outer sphere association complex is formed. Secondly, the low enthalpy of activation and large negative value of entropy of activation strongly suggested the ligand participation in the transition state.

The activation parameters ($\Delta H_1^{\neq} = 15 \pm 1.2$ kJ mol^{-1}, $\Delta S_1^{\neq} = -239 \pm 5$ J K^{-1} mol^{-1} for the first and the second steps $\Delta H_2^{\neq} = 10.4 \pm 1.5$ kJ mol^{-1}, $\Delta S_2^{\neq} = -288 \pm 4$ J K^{-1} mol^{-1}) suggest an associative mode



Scheme 4. Proposed mechanism for the interaction of Et_2DTC with complex **1**.

of activation for the substitution processes. The low $\Delta H_1^{\neq}$ and $\Delta H_2^{\neq}$ values imply a good degree of ligand participation in the transition state. The second step is the intramolecular ring closure which is independent on the incoming ligand concentration supported by the value of rate constant (k_2) for this step was found to be actually independent on ligand concentration.

As the same metal atoms (Pd and S) are involved in the bond formation in both the steps, the enthalpies make a slight favourable contribution, but the main source of the chelate effect is still to be found in the entropies. The more negative entropy of activation for the second step implies more ordering, indicates more associative nature of the second step. Due to the higher bond dissociation energy of Pd–OH (non-bridged) than the Pd–OH (bridged) makes the second step more associative.

Previous studies of ligand substitution reactions on this system by different groups proposed a single-step reaction but we have found a two-step process in this case.

Based on the experimental results described above, we propose the reaction mechanism shown in scheme 4.

It was also found that after completion of the reaction, both the pH and conductance of the resulting solution had increased, which might be due to loss of one of the bridging OH groups.

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