Use of Nitrogen Containing Heterocyclic ligand; Phenanthroline to study the kinetics of uncatalysed ligand substitution reaction of hexacyanoferrate (II)

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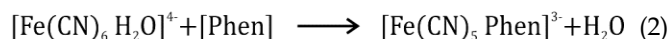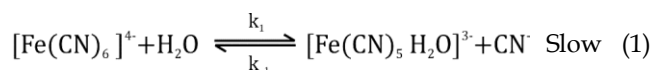
ABSTRACT-The kinetics and mechanism of uncatalysed substitution of co-ordinated cyanide in hexacyanoferrate (II) by a nitrogen donar heterocyclic ligand, phenanthroline at 528nm (λmax of a dark coloured compound [Fe (CN)5Phen]3- as a function of [Fe $(CN)_6]^{4-}$ and [Phen] under the conditions, pH= 3.0±0.02, temperature = 25.0± 0.10oC , Ionic strength (I) = 0.03 $M(KNO_3)$.The reaction is a first order each in [Fe (CN)6]4- and [Phen] at low [Phen] concentration. The rate of the reaction in determined from the slopes of absorbances versus time plots. As [Phen] increases the rate of the reaction increases, passes through a maximum and them falls, suggesting that the course of the reaction is different at low [Phen] and high [Phen]. The effect of temperature and pH on the initial rate have also been explained and studied. The repetitive spectral scans is also provided as an evidence for exchange of cyanide ions by [Phen] in [Fe(CN)6]4-. Activation parameters have also been evaluated and provided in support of the proposed mechanistic scheme. The compositon of the complex was established as 1:1 by the mole ratio method.

Keywords: Nitrogen heterocycle, Phenathroline, hexacyanoferrate (II), ligand substitution, kinetics.

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1 INTRODUCTION

Phenanthroline (Scheme 1) is a heterocyclic organic compound. As a bidentate ligand in co-ordination chemistry, it forms strong complexes with most metal ions. It is used in transition metal chemistry for determination of metals, as an indicator for alkyl lithium reagents. It is used in metallocene industry and co-ordination of organometallic complexes. Complexes of the type [Fe $(CN)_5$ INH_3-] [1] and [Fe $(CN)_5$ $PhNHNH_2$]3- [2] have been obtained either through photochemical aquation of [Fe $(CN)_6]_4$- or by Hg+2 assisted complexes of the type Fe $(CN)_5$ L (L= N_3^- , Ph NO, amines) have been prepared by substitution in pentacyano amino ferrate (II) or mercury catalysed substitution in hexacyanoferrate (II) molecular complexes of Pyrazine (Pz) and [Ru $(CN)_6]4$- having molecular formula [Ru $(CN)5$ Pz]3- [7] and N-methyl Pyrazine and [Fe $(CN)6]4$- [8] have been reported.The thermal decomposition of hexacyanoferrate (II) ion is a slow reversible process according to equation 1. The pentacyanoaquo complex produced has been reported [9] to react with aromatic nitroso compounds giving intensely coloured products. There in limited information on the kinetics and mechanism concerning substitution in hexacyanoferrate (II) [10-13]. Exchange of labelled cyanide between [Fe $(CN)6]4$- and free cyanide is extremely slow, but under U.V. light reversible aquation takes place [14].

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Most of the substituted cyano complexes of lron (II) are metal assisted dissociation of hexacyanoferrate (II) [11, 15] followed by reaction with the incoming ligand. Many complexes of the pentacyano (ligand.) ferrate (II) type have been prepared by substitution in pentacyano (amino) ferrate (II) or by metal catalysed substitution in hexacyanoferrate (II) [2,8,11,12,16-21].
In accordance with our earlier investigation of the reaction of phenyl hydrazine [1] and pyrazine [7] with hexacyanoferrate (II), phenonthroline has also been shown to react with [Fe (CN)6]4- according to Equations [1-3].

$$[Fe(CN)_6]^{4+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5 H_2O]^{3-} + CN^- \quad \text{Slow} \quad (1)$$

$$[Fe(CN)_6 H_2O]^{4+} + [Phen] \longrightarrow [Fe(CN)_5 Phen]^{3-} + H_2O \quad (2)$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad (3)$$

The uncatalysed reaction takes about 24 hours to attain maximum absorbance. The stoichiometry of the complex has been established as 1:1 by the mole ratio [22] and slope method [23].

2 RESULTS AND DISCUSSION
Effect of [Fe $(CN)_6]^{4-}$
Effect of [Fe $(CN)_6]^{4-}$ on the initial rate of unanalyzed reaction between[Fe $(CN)_6^{4-}]$ and Phenanthroline was studied taking [Fe $(CN)_6^{4-}]$ = (1.0-8.0) x 10^{-3}M. The reaction was found to exhibit first order behavior in [Fe $(CN)_6^{4-}]$ in the concentration range studied. The plot of initial rate (Vi) versus [Fe $(CN)_6^{4-}]$ in a straight line as shown in Figure 1 ($r^2 \leq 0.995$, sd≤ 0.223).

Effect of [Phen]
The effect of [Phen] on the initial rate for uncatalysed ligand

substitution reaction between [Fe (CN)$_6^{4-}$] and [Phen] was studied by varying Phenanthroline concentration from 0.4x10^{-3}M to 14.0x10^{-3}M. The plot of initial rate versus [Phen] is shown in Figure 2. It is seen that the initial rate increases with increasing the concentration of phenanthroline. It rises till and remains constant between 9x10^{-3}M to 12x10^{-3}M and then starts declining at further increase in [Phen].

Effect of pH on initial rate

The dependence of initial rate on pH in co-ordinated cyanide substitution from [Fe (CN)$_6^{4-}$] by [Phen] was studied in the pH vange 1.5-7.0. The initial rate is represented in Table 1. In the beginning i.e. pH range 1.5-3.0 the rate increases and at still higher pH the rate decreases. This behavior shows the existence of protonated and deprotonated forms of [Fe (CN)$_6$]$^{4-}$ and [Phen], all having different reactivities. From species distribution of [Fe (CN)$_6^{4-}$] shown in Figure 3, it can be seen that in the lower pH range there exist mono, di, tri and tetra protonated species of [Fe (CN)$_6^{4-}$]. The initial increase in the rate between pH 1.5 – 3.0 is due to inter conversions of highly protonated forms of hexacyanoferrate (II) into lower protonated forms. The rate law for the pH range 3.0-7.0 can be expressed according to equation (4) where deprotonated forms of [Fe (CN)$_6^{4-}$] and [Phen], [PhenH]$^+$ or both are prominent reacting species.

$$\text{Rate} = k_f [\text{Fe(CN)}_6^{4-}]_T [\text{Phen}]_T \quad (4)$$

Here subscript 'T' refers to the total concentrations of the reacting species and k_f (k_f= Rate / [Fe (CN)$_6^{4-}$] [Phen]) in the forward bimolecular rate constant. In the above mentioned pH region [Fe (CN)$_6^{4-}$] exists predominantly in deprotonated form and phenanthroline exists as Phen and PhenH$^+$, Therefore equation (4) can be transformed to equation (5).

$$Rate = \{k_{Phen} + k_{PhenH^+} K_{PhenH^+}[H^+]\}[Fe(CN)_6^{4-}]_T [Phen]_f \quad (5)$$

From equation (4) and (5) we get

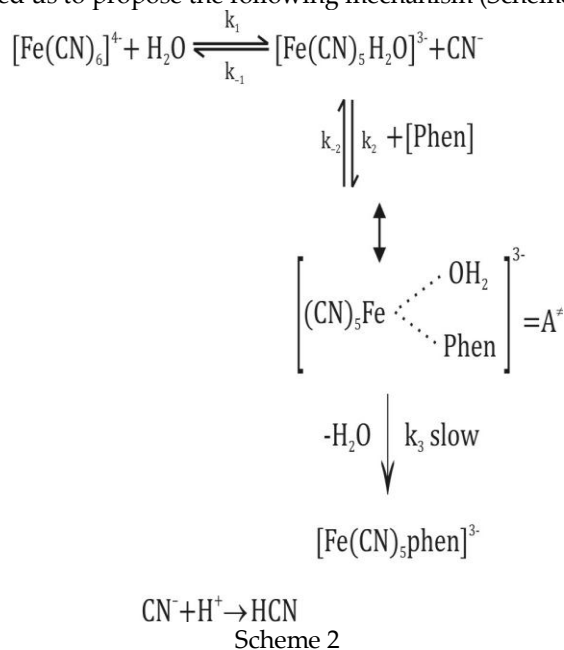$$k_f \frac{[Phen]_T}{[Phen]_f} = k_{PhenH^+} + k_{PhenH^+} K_{PhenH^+}[H^+] \quad (6)$$

Here, $\frac{[Phen]_T}{[Phen]_f} = 1 + K_{PhenH^+}[H^+]$, subscript 'f' denotes the concentration of Phenanthroline in the unprotonated form, k_{Phen}, k_{PhenH^+} and K_{PhenH^+} refers to the rate constants due to reactions of phen and PhenH+ and protonation constant of Phenanthroline respectively. The plot of the left hand side of equation (6) versus [H$^+$] yields a straight line (Figure 4). $r^2 \leq 0.9952$ and its slope and intercept give the value of k_{PhenH+}=37.8±5.50 mol^{-1}Ls^{-1} and k_{Phen}= 58.9±5.12 mol^{-1} Ls^{-1}. The values resolved rate constants are in fairly good agreement with the experimentally observed values at high and low pH values respectively (Table 1).

Effect of Temperature on Initial rate

The effect of temperature on the initial rate of the unanalyzed reaction between hexacyanoferrate (II) and Phenanthroline was studied at different temperatures ranging from 25-45^{0}C and the activation parameters were calculated by Arrhenius and Erying equations. The value of Ea, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are 55.7±4.8KJmol $^{-1}$, 53.6±3.6KJmol^{-1} and–147.2±5.1JKmol^{-1} respectively. Higher temperatures were avoided due to decomposition of the complex [Fe (CN)$_5$ Phen]$^{3-}$. The evaluated activation parameters show the dissociation type mechanism. The high value of Ea shows the rupture of metal ligand bond, which supports the proposed mechanism.

Effect of Ionic strength

The effect of ionic strength on the rate of the uncatalysed reaction between [Fe (CN)$_6^{4-}$] and [Phen] was studied in the range 0.01-0.3 M using KNO$_3$. The initial rate of the reaction was found to decrease with increase in ionic strength of the medium that indicates a negative salt effect. The observed rate dependence on the reactants, temperature, pH and Ionic strength allowed us to propose the following mechanism (Scheme 2).

$$[Fe(CN)_6]^{4-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5H_2O]^{3-} + CN^-$$

$$k_{-2} \Updownarrow k_2 + [Phen]$$

$$\left[(CN)_5Fe \overset{\cdots OH_2}{\underset{\cdots Phen}{\cdots}} \right]^{3-} = A^{\neq}$$

$$-H_2O \downarrow k_3 \text{ slow}$$

$$[Fe(CN)_5phen]^{3-}$$

$$CN^- + H^+ \rightarrow HCN$$
Scheme 2

The rate law based on the above scheme can be expressed by equation (7)

$$d[Fe(CN)_5 Phen]^{3-} / dt = k_3[A^{\neq}] \quad (7)$$

If $k_{-2} \gg k_3$, the formation of [A]$^{\neq}$ is due to a fast equilibrium and for the condition where, [Fe (CN)$_5$H$_2$O]$^{3-}$ < [Phen], the equilibrium concentration of activated complex [A$^{\neq}$] (or ion pair) is evaluated by using the following algebraic manipulation and finally given by equation (8).

$$[A^{\neq}] = [Fe(CN)_5H_2O^{3-}] - [Fe(CN)_5H_2O^{3-}]_f$$

Or

$$[A^{\neq}] = [Fe(CN)_5H_2O^{3-}] - \frac{[A^{\neq}]}{K_2[Phen]}$$

Where

$$K_2 = \frac{[A^{\neq}]}{[Fe(CN)_5 H_2 O^{3-}]_{/}[Phen]}$$

And 'f' refer to the free concentration of $[Fe(CN)_5 H_2 O]^{3-}$,

Or

$$[A^{\neq}] = \left(1 + \frac{1}{K_2[Phen]}\right) = [Fe(CN)_5 H_2 O^{3-}]$$

Or

$$[A^{\neq}](1 + K_2[Phen]) = K_2[Fe(CN)_5 H_2 O^{3-}][Phen]$$

Or

$$[A^{\neq}] = \frac{K_2[Fe(CN)_5 H_2 O^{3-}][Phen]}{1 + K_2[Phen]} \tag{8}$$

Applying steady state approximation to the intermediate $[Fe(CN)_5 H_2 O]^{3-}$, one gets

$$[Fe(CN)_5 H_2 O^{3-}] = \frac{k_1(1 + K_2[Phen])[Fe(CN)_6^{4-}][H_2 O]}{k_1(1 + K_2[Phen])[CN^-] + k_2 K_2[Phen]^2} \tag{9}$$

Substituting equation (9) in equation (8) we get

$$A^{\neq} = \frac{k_1 K_2[Phen][Fe(CN)_6^{4-}][H_2 O]}{k_{-1}[CN^-](1 + K_2[Phen]) + k_2 K_2[Phen]^2} \tag{10}$$

Considering equations (9) and (10), the rate law given is expressed as equation (11)

$$d[\{Fe(CN)_5 Phen\}^{3-}]/dt = \frac{k_3 k_1 K_2[Phen][Fe(CN)_6^{4-}][H_2 O]}{k_{-1}[CN^-]K_2 k_{-1}[Phen][CN^-] + k_2 K_2[Phen]^2} \tag{11}$$

If in Equation (11) k_2 and k_1 are comparable (both are fast), the following two conditions may exist. (i) At low [Phen], k_{-1} [CN$^-$] > k_2 [Phen]. The second term of denominator in equation (11) is greater than the third term and second term comprises multiple and small concentration terms. Thus, both can be neglected in comparsion to k_{-1} [CN$^-$]. Therefore, Equation (11) is reduced to equation (12).

$$d[\{Fe(CN)_5 Phen\}^{3-}]/dt = \frac{K_2 k_3 k_1[Phen][Fe(CN)_6^{4-}][H_2 O]}{k_{-1}[CN^-]} \tag{12}$$

Equation (12) shows an increase in rate with increase in [Phen]; (ii) At high [Phen], k_2 [Phen] >> k_{-1} [CN$^-$]. This implies that the third term in the denominator in Equation (11) is greater than the first and second terms and consequently the rate law can be expressed by equation (13)

$$d[\{Fe(CN)_5 Phen\}^{3-}]/dt = \frac{k_3 k_1[Fe(CN)_6^{4-}][H_2 O]}{k_2[Phen]} \tag{13}$$

In terms of equation (13), we expect a decrease in the rate of formation of product with increase in [Phen], which was ob-

served experimentally (Figure 2). Finally, the repetitive spectral scan (Figure 5) of the unanalyzed substitution reaction between [Fe (CN)64-] and [Phen] have been recorded at definite times in the wavelength range 450 to 650 nm under the specified reaction conditions in order to understand the nature of the product formed during the course of the reaction and provide better understanding of the proposed mechanism. The repetitive spectral scan (Figure5) shows that a peak continuously grows with time at 528 nm. This is attributed to the formation of the final product, [Fe (CN)5Phen]3- during the course of the reaction. The mole ratio studies performed by us show the formation of a 1:1 complex, [Fe (CN)5Phen]3- as the final product of the reaction, as shown by other researchers [25].

3 EXPERIMENTAL

3.1 Reagents
Double distilled water was used throughout to prepare all solutions. All the chemicals used in this study were of analytical reagent grade. The solution of K4[Fe(CN)6]. 3H2O (AR,E. Merck, Germany) was prepared by weighing a desired amount and kept in dark in coloured bottles to prevent photochemical dissociation. The fresh solutions of Phenanthroline (S.D. Fine Chemicals) were prepared in double distilled water everyday before starting the kinetic run. due to its. (A.R. Glaxo) was used to maintain ionic strength in reaction medium. The pH of the reaction mixture was adjusted to a desired value using buffer solutions prepared by adding KCl to HCl or potassium hydrogen phthalate (A.R. Qualigens Fine chemicals) and hydrochloric acid /NaOH as reported in the literature [24].

3.2 Procedure
All the reactant solutions were equilibrated at 25°C by keeping them inside environmental chamber in order to maintain the desired temperature within the accuracy of ± 0.1°C Genesis model No. 10UV was used to record the spectra of the reaction. The pH measurements were made on a digital pH meter of Sio-global pH meter. After equilibrating the reactants, 2 ml of each reactant was mixed in the sequence, Phenanthroline and buffer. The reaction was finally started by adding 2 ml of hexacyanoferrate (II) to the above mixture. This reaction mixture was shaken thoroughly and quickly transferred to a 10 mm cuvette in the temperature controlled cell compartment of the spectrophotometer. The progress of the reaction was subsequently followed by monitoring the increase in absorbance at 528 n.m. due to formation of the product [Fe(CN)4Phen]3- (Figure 5).

4 FIGURES AND SCHEME

Figure 1 Plot of initial rate of the uncatalysed ligand exchange reaction versus $[Fe(CN)_6]^{4-}$ at [Phen] = 2.5×10^{-3} M, pH = 3.0 ± 0.02, Temp. = 25 ± 0.1^0C, I = 0.03M (KNO_3).
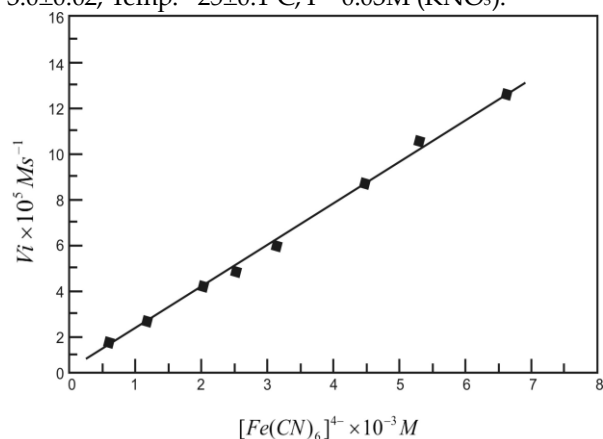
Figure 2 Varying effect of [Phen] on initial rate of unanalyzed ligand exchange Reaction between $[Fe(CN)_6]^{4-}$ and [Phen] at $[Fe(CN)_6]^{4-} = 5.0 \times 10^{-3}$ M, pH = 3.0 ± 0.02, temp. = 25 ± 0.1^0C, I = 0.03 M (KNO_3).
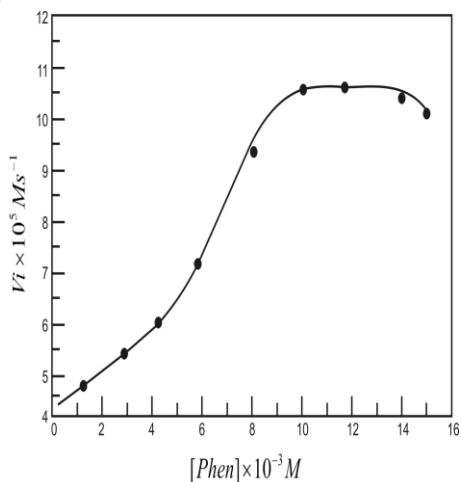
Figure 3 Species distribution of $[Fe(CN)_6]^{4-}$ as a function of pH, A= $[Fe(CN)_6]^{4-}$ B=H $[Fe(CN)_6]^{3-}$, C= H_2 $[Fe(CN)_6]^{2-}$, D= H_3 $[Fe(CN)_6]^{-}$ and E = H_4 $[Fe(CN)_6]$.
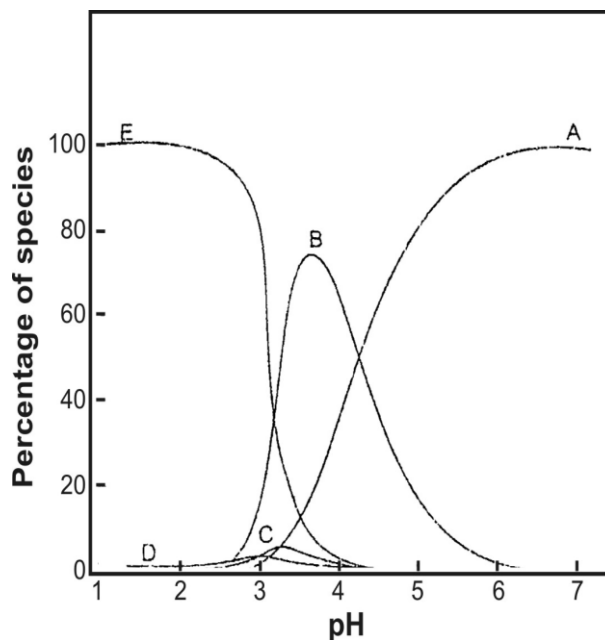
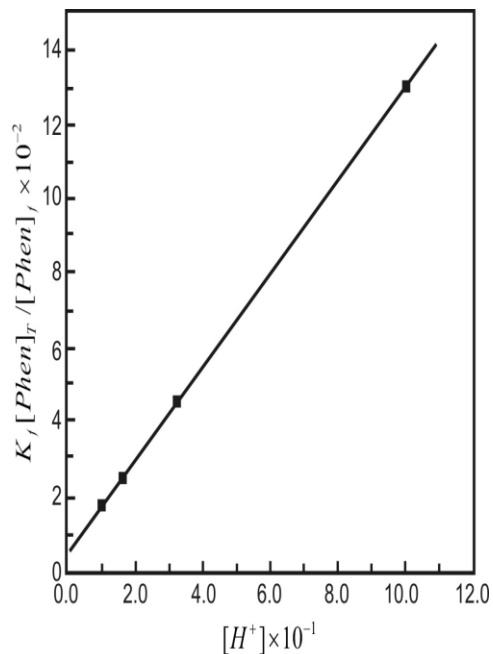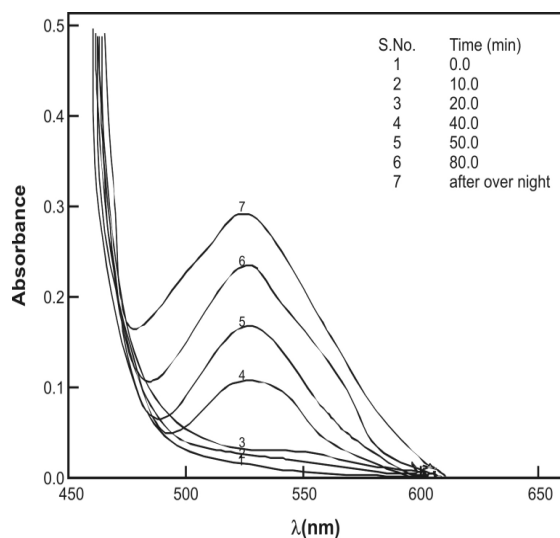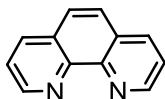**Figure 4** Resolution of rate constants for the reaction of [Phen] and [Phen H]$^+$ with $[Fe(CN)_6]^{4-}$

Figure 5 A repetitive spectral scan of the reaction mixture during a typical kinetic run at $[Fe(CN)_6]^{4-}$ = 4.5×10^{-3} M, [Phen]= 2.0×10^{-4} M, pH = 3.0 ± 0.02, temperature = 25 ± 0.1^0C, I = 0.03 M (KNO_3).

Scheme 1

5 TABLE

Table 1 Dependence of initial rate on pH under conditions [Fe $(CN)_6^{4-}$] = 3×10^{-3}M, [Phen] = 2.5×10^{-3}M, temp. = 25 ± 0.1^0C, I = 0.03M (KNO_3)

$_pH$	$Vi \times 10^5$ M sec^{-1}
1.5	2.45±0.01
2.0	6.20±0.03
2.8	6.43±0.04
2.8	7.20±0.03
3.0	7.50±0.04
3.5	6.03±0.03
4.0	5.67±0.02
5.0	4.02±0.03
6.0	3.45±0.02
7.0	2.08±0.02

6 Conclusions

This kinectic study of hexacyanoferrate (II) was not investigated ever before it with N-containing heterocyclic ligand i.e. phenanthroline. All the datas indicate that the reaction is a first order type and substitution was taken place by phenanthroline ligand which relaces cyano ligand by following first order kinetics.

7 Acknowledgements

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