



# Kinetics and Mechanism of Substitution Reaction of *Trans*-Dichloro-bis-(Ethylenediammine) Cobalt (III) Chloride with Cysteine, Aspartic acid and Phenylalanine

K. Asemave, S.G. Yiase, S. O. Adejo

Department of Chemistry, Benue State University, P.M.B 102119 Makurdi, Nigeria

## ABSTRACT

Kinetics and mechanistic studies of the substitution reactions of *trans*-dichloro-bis-(ethylenediammine)cobalt(III) chloride (*trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl) by cysteine, aspartic acid, and phenylalanine were carried out in aqueous media at ionic strength of 0.01 mol dm<sup>-3</sup> (NaNO<sub>3</sub>), and at the temperature range of 35°C to 55°C. The amino acids evidently coordinated to the Co(III) complex through the carboxylate group as indicated by the shifts in IR frequencies; 1582.40 – 1625.39 cm<sup>-1</sup>, 1340.33 – 1066.41 cm<sup>-1</sup>; 1645-1641 cm<sup>-1</sup>, 1309-1112 cm<sup>-1</sup>; and 1555.44-1571 cm<sup>-1</sup>, 1301.29 – 1050 cm<sup>-1</sup> for cysteine, aspartic acid and phenylalanine, and their Co(III) complexes respectively. Stoichiometries of the reactions were also determined as 1:1. That is, one mole of *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl requires one mole of amino acid to give a product. Also the molar conductivity of the complex was obtained as 270 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. This showed that *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl can produce a total of three ions per mole. The pseudo- first order plots of ln [A<sub>t</sub>-A<sub>∞</sub>/ A<sub>0</sub>-A<sub>∞</sub>] vs. time for the reaction are linear. The linearity of the plot is a clear indication that the reaction is first order in *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl. Also, plots of log k<sub>1</sub> vs. log [Amino acids] show a linear relationship; with the slope of 1.00, explicitly implying that the reaction is first order in [Amino-acid]. Hence, the reaction is second order overall. Therefore the rate equation for the reaction is; -d[*trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl]/dt = k<sub>2</sub>[*trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl][A]. Rate constants k<sub>2</sub>, of the reactions were obtained as 11.40 × 10<sup>-1</sup> ± 0.0739 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, 4.29 × 10<sup>-1</sup> ± 0.0705 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, and 2.97 × 10<sup>-1</sup> ± 0.0337 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for cysteine, aspartic acid and phenylalanine, respectively. Activation enthalpies and entropies (ΔH\*, and ΔS\*), were evaluated to be 93.32 kJ mol<sup>-1</sup>, 2.94 J mol<sup>-1</sup> K<sup>-1</sup>, 90.74 kJ mol<sup>-1</sup>, 0.14 J mol<sup>-1</sup> K<sup>-1</sup>, and 96.63 kJ mol<sup>-1</sup>, 15.71 J mol<sup>-1</sup> K<sup>-1</sup> for cysteine, aspartic acid, and phenylalanine, respectively. From the values of the activation entropies (ΔS\*), dissociative mechanism is proposed for these substitution reactions. Thus the studies of rate of substitution of *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl by these amino acids provide an insight of complexation of these amino acids and Co(III) centre. The study of substitution reaction between Co(III) complexes with these amino acids give useful information in the development of detoxifying agents using these amino acids especially cysteine.

**Keywords:** kinetics, dissociative mechanism, substitution reaction, cysteine, aspartic acid and phenylalanine

## 1. INTRODUCTION

Amino-acids are the main constituents of proteins and have the ability to coordinate to transition metals through their amino or carboxylic groups. The complexation of transition metal ions with amino-acid and other compounds have been reported quite frequently in the last decades. Many biological reactions are catalyzed by transition metal ions. The interactions between amino-acids and metallic ions are responsible for enzymatic activity and stability of protein structures. Also antibacterial, anticancer and antifungal activities have been linked to amino acid complexes of Co (III). Transition metals are known to have great affinity for –SH groups [1, 2, 3]. Many of Co (III) complexes are known for their anticancer and antibacterial effects [4]. Amino-acids are used in food, pharmaceutical, and personal care industries. In this research work, the substitution reaction of *trans*-[Co(en)<sub>2</sub>(Cl)<sub>2</sub>]Cl with cysteine, aspartic acid and phenylalanine were investigated by spectrophotometric method at constant ionic strength = 0.01M NaNO<sub>3</sub>, in aqueous media.

## 2. EXPERIMENTS

### 2.1. Materials

Co(II) chloride hexahydrate (Hopkins & Williams), NaNO<sub>3</sub> (M & B), the amino acids (Qualikems), ethylenediammine (Qualikems), and concentrated hydrochloric acid (M & B), were received in analytical grade and used without further purification. Distilled water was used for solution preparations. FTIR-100 IR- spectrophotometer was used for the product analysis. The complex *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl was prepared according to the literature [1]. The visible absorption spectrum (λ<sub>max</sub> = 618 nm, ε<sub>max</sub> = 37.60 M<sup>-1</sup> cm<sup>-1</sup>) was in good agreement with the published spectra [5]. The molar conductivity of the complex was obtained as 270 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

### 2.2 Kinetic Studies

Stoichiometry of reactions was determined at λ = 618nm by spectrophotometric titration using mole ratio method, [6]. The rate of the reaction was monitored spectrophotometrically, following the decrease in

concentration of *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl at 618nm. The kinetic measurements were made under pseudo-first order conditions at temperature range of 30°C to 55°C. The rate constant was computed from the plot of  $\ln [A_t - A_\infty / A_0 - A_\infty]$  against time. Plot of  $\log k_1$  vs.  $\log [\text{amino acid}]$  was obtained. Kinetic activation parameters (activation entropy and enthalpy) were obtained from Eyring's plots,  $\ln (k/T)$  vs.  $1/T$ , [1, 7 and 8].

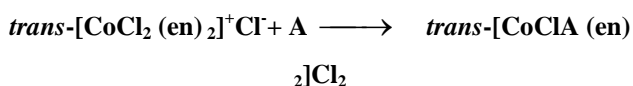
### 3. RESULTS AND DISCUSSION

#### 3.1 Product Analysis

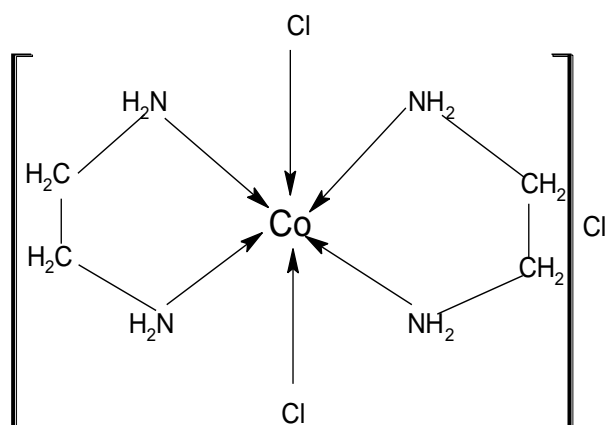
From the IR spectra of the amino acids and the substituted complex the following shifts in the IR frequencies of carboxylate group were observed, 1582.40 – 1625.39cm<sup>-1</sup>, 1340.33 – 1066.41 cm<sup>-1</sup>; 1645-1641cm<sup>-1</sup>, 1309-1112 cm<sup>-1</sup>; and 1555.44-1571cm<sup>-1</sup>, 1301.29 – 1050 cm<sup>-1</sup> for Cysteine, aspartic acid, Phenylalanine; and their substituted products respectively. These indicate that the chloride was substituted by amino acids in the *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl to form *trans*-[Co(en)<sub>2</sub>CIA]Cl<sub>2</sub> products respectively [1, 5, 9-11].

#### 3.2 Stoichiometric Studies

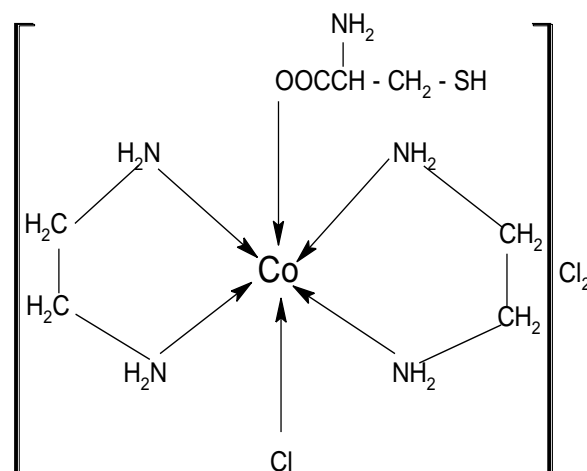
The calculation of the mole ratio at the equivalence point of the spectrophotometric titration gave the stoichiometry of the reaction as 1:1. Similar stoichiometry has been reported for the reaction between the complex *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl and the amino acids alanine and valine [1, 5].



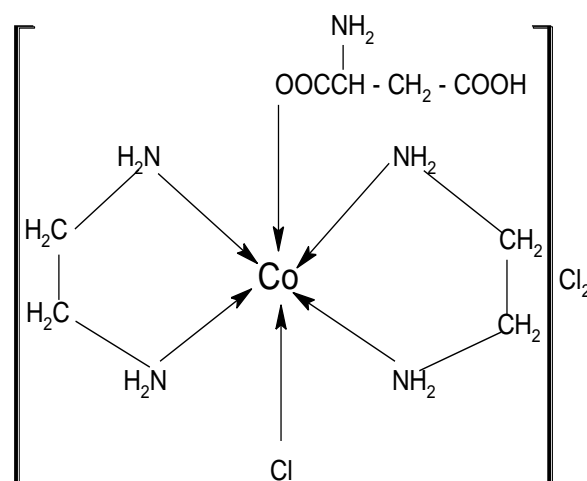
A = amino acid



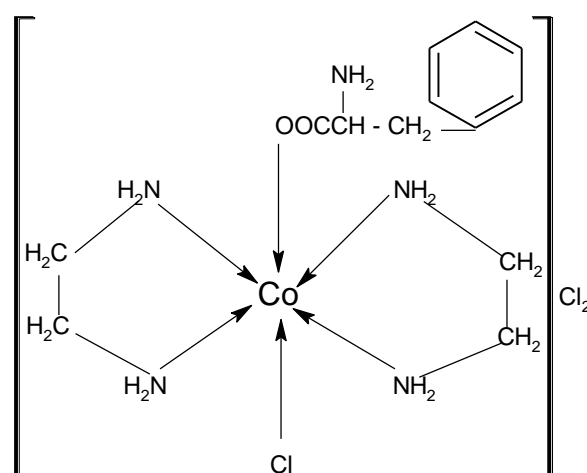
*trans*-dichloro-bis-(ethylenediammine) cobalt(III) chloride  
(*trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl)



Cysteine substituted product of *trans*-[CoCIA(en)<sub>2</sub>]Cl<sub>2</sub>



Aspartic acid substituted product of *trans*-[CoCIA(en)<sub>2</sub>]Cl<sub>2</sub>



Phenylalanine substituted product of *trans*-[CoCIA(en)<sub>2</sub>]Cl<sub>2</sub>

### 3.3 Determination of Order

The pseudo- first order plots of  $\ln [A_t - A_\infty / A_0 - A_\infty]$  vs. time for the reaction is linear as shown in Figure (4, 5 and 6). The linearity of the plot is a clear indication that the reaction is first order in *trans*-[CoCl<sub>2</sub> (en)<sub>2</sub>] Cl. Table 1 summarizes the values of  $k_{obs}$  and  $k_2$  for the amino acids. A plot of  $\log k_1$  vs.  $\log$  [amino acids] in Figure 7 shows also a linear relationship; with the slope of 1.00, explicitly implying that the

reaction is also first order with respect to the amino acids. Hence, the reaction is second order overall [5]. Therefore the rate equation for the reaction is

$$-d [trans-[CoCl_2(en)_2] Cl]/dt = k_2 [trans-[Co(en)_2Cl_2]Cl][A]$$

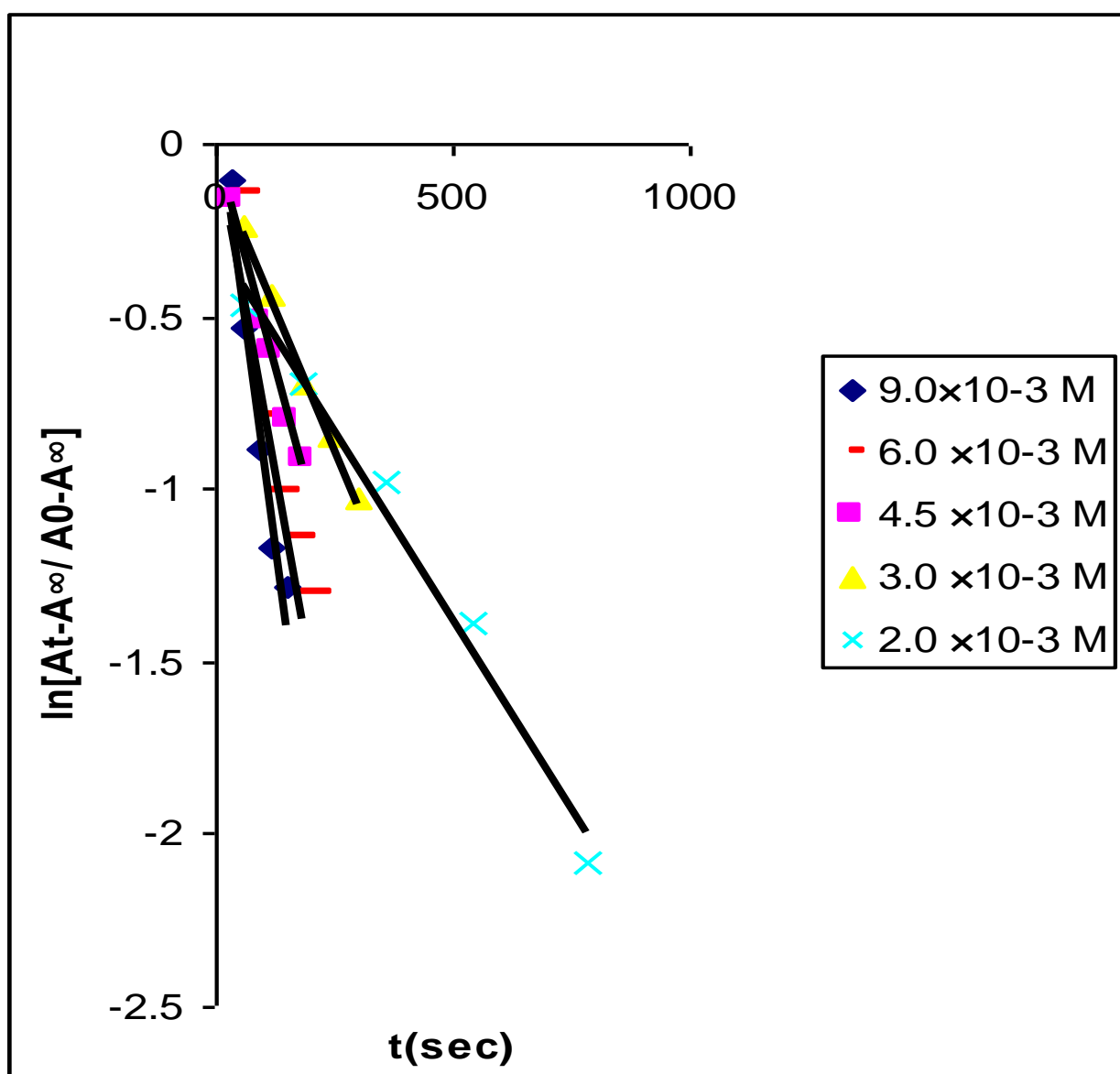


Fig. 1: Pseudo First- Order Plots of  $\ln [A_t - A_\infty / A_0 - A_\infty]$  vs. Time for the Complex with cysteine

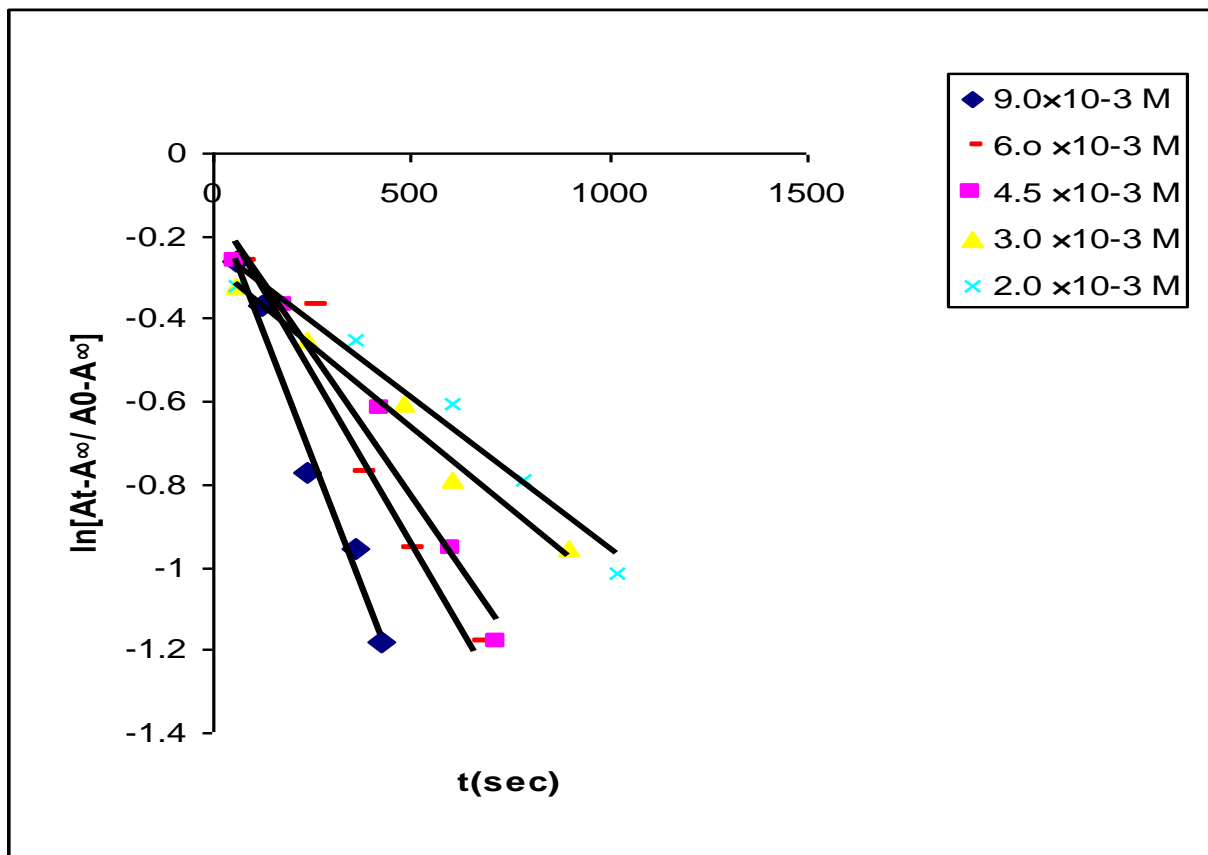


Fig. 2: Pseudo First- Order Plots of  $\ln [A_t - A_\infty / A_0 - A_\infty]$  vs. Time for the Complex with phenylalanine

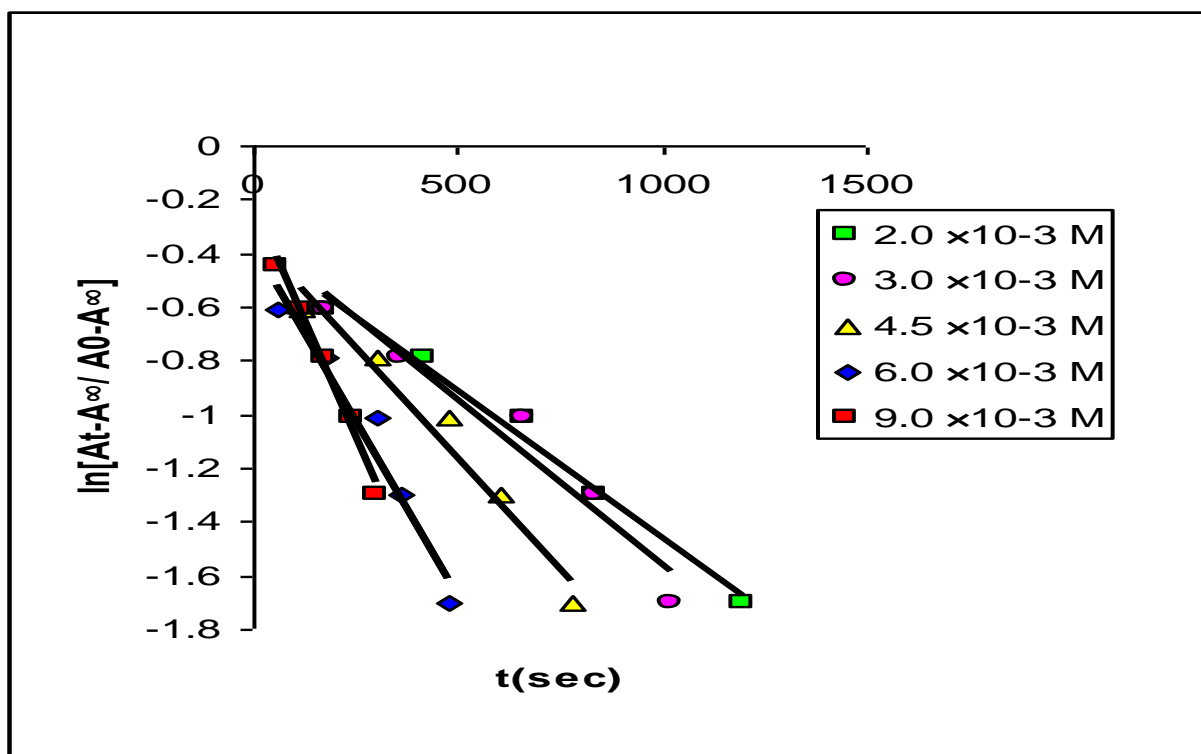
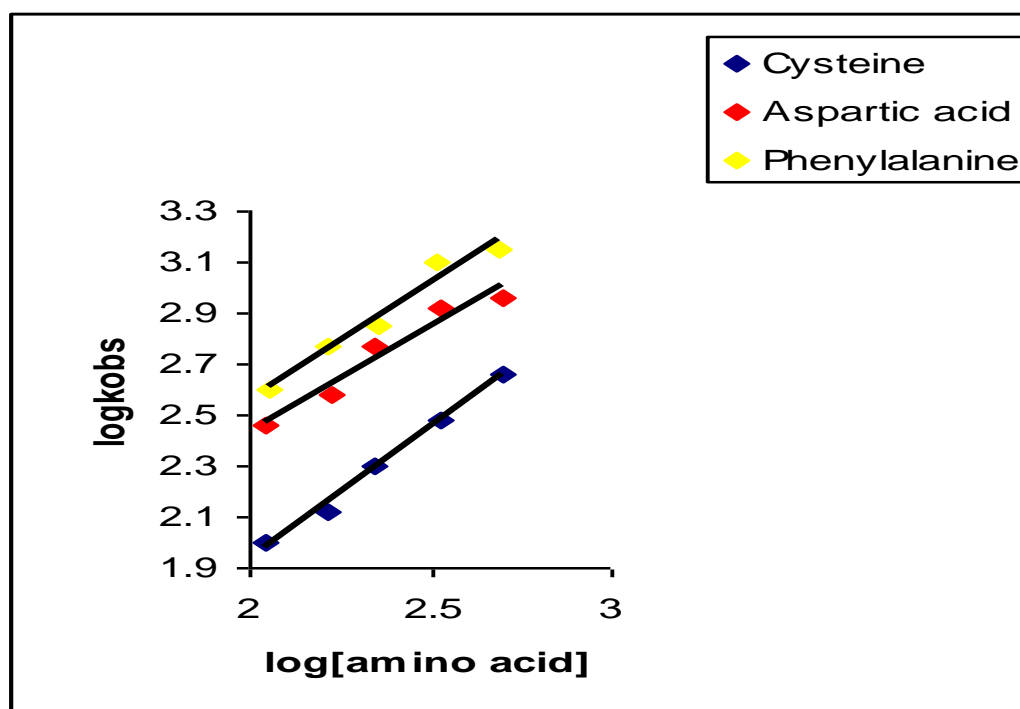


Fig. 3: Pseudo First- Order Plots of  $\ln [A_t - A_\infty / A_0 - A_\infty]$  vs. Time for the Complex with Aspartic acid

**Table 1: Pseudo-First Order and Second Order Rate Constant Data for the Reaction at 26 (±0.1°C)**

[NaNO <sub>3</sub> ]/10 <sup>-3</sup> moldm <sup>-3</sup>	[cysteine]/10 <sup>-3</sup> moldm <sup>-3</sup>	k <sub>obs</sub> /(10 <sup>-3</sup> s <sup>-1</sup> )	k <sub>2</sub> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	[phenyl alanine]/10 <sup>-3</sup> moldm <sup>-3</sup>	k <sub>obs</sub> /(10 <sup>-3</sup> s <sup>-1</sup> )	K <sub>2</sub> /10 <sup>-3</sup> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	[Aspartic acid]/10 <sup>-3</sup> moldm <sup>-3</sup>	k <sub>obs</sub> /(10 <sup>-3</sup> s <sup>-1</sup> )	k <sub>2</sub> /10 <sup>-3</sup> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
0.50	9.00	10.00	1.11	9.00	2.50	2.77	9.00	3.50	3.88
3.50	6.00	7.60	1.27	6.00	1.70	2.83	6.00	2.60	4.33
5.00	4.50	5.00	1.11	4.50	1.40	3.11	4.50	1.70	3.77
6.50	3.00	3.30	1.10	3.00	0.80	2.66	3.00	1.20	4.00
7.50	2.00	2.20	1.10	2.00	0.70	3.50	2.00	1.10	5.50

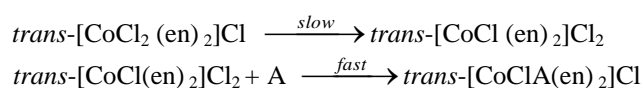
**Fig. 4: Plot log k<sub>obs</sub> vs log [amino acid]**

### 3.4 Temperature Dependence Rates of Reaction

The reaction was investigated at the temperature range 35°C and 55°C (±0.1°C). It was found that k<sub>obs</sub> increases with increase in temperature as presented in Table 2. Values of ΔH\* and ΔS\* were evaluated by the use of Eyring's equation as presented in Figure 8. They are 93.32 kJmol<sup>-1</sup>, 2.94 Jmol<sup>-1</sup> K<sup>-1</sup>, 90.74 kJmol<sup>-1</sup>, 0.14 Jmol<sup>-1</sup> K<sup>-1</sup>, and 96.63 kJmol<sup>-1</sup>, 15.71 Jmol<sup>-1</sup> K<sup>-1</sup> for the reaction with cysteine aspartic acid and phenylalanine respectively. The positive value of activation entropy (ΔS\*) implies

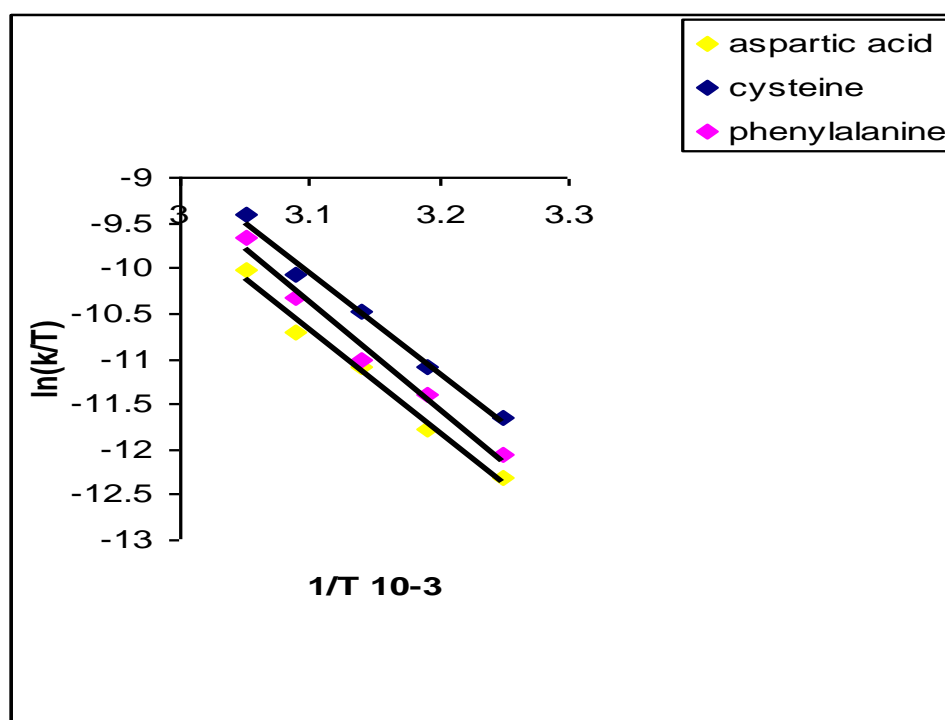
dissociative mechanism for this substitution reaction, [5, 12 - 15]. Therefore the following mechanism has been proposed for the reaction.

### 3.5 Mechanistic Path Way



**Table 2: Temperature Dependent Pseudo First-Order Rate Constant Data for the Reactions**

Tempt.(°C)	$K_{\text{obs}}/10^{-3} \text{ s}^{-1}$ Cysteine	$K_{\text{obs}}/10^{-3} \text{ s}^{-1}$ Aspartic acid	$K_{\text{obs}}/10^{-3} \text{ s}^{-1}$ Phenylalanine
55	27.00	14.60	21.00
50	13.10		
45	9.00	7.30	10.50
40	4.50		
35	2.70	4.90	5.20
		2.40	3.50
		1.40	1.80
$\Delta H^*$ , $\text{kJmol}^{-1}$ ,	93.32	90.74	96.63
$\Delta S^*$ , $\text{Jmol}^{-1} \text{ K}^{-1}$	2.94	0.14	15.71

**Fig.5: Plot of  $\ln(k/T)$  vs.  $1/T$** 

#### 4. CONCLUSION

Kinetic and mechanistic studies of the substitution reaction of *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl with cysteine, aspartic acid, and phenylalanine were carried at the temperature range of 35°C to 55°C. The amino acids evidently coordinated to the Co(III) complex through the carboxylate group. The reaction is second order overall, which is in agreement with other works. The second order

rate constant,  $k_2$  of cysteine is about three times that of aspartic acid, and four times that phenylalanine. Activation Enthalpies and Entropies of ( $\Delta H^*$ ,  $\Delta S^*$ ), were evaluated for cysteine, aspartic acid, and phenylalanine to be 93.32  $\text{kJmol}^{-1}$ , 2.94  $\text{Jmol}^{-1} \text{ K}^{-1}$ , 90.74  $\text{kJmol}^{-1}$ , 0.14  $\text{Jmol}^{-1} \text{ K}^{-1}$ , and 96.63  $\text{kJmol}^{-1}$ , 15.71  $\text{Jmol}^{-1} \text{ K}^{-1}$  respectively. From values of the activation entropies ( $\Delta S^*$ ), the mechanism of the substitution reactions can be said to be dissociative mechanism.



## 5. RECOMMENDATIONS

These Amino acids could be used as detoxifying agent towards metals, especially towards soft acid metal atoms. Also the catalytic activities of Co(III) carboxylate of the cysteine complex could be tested in organic synthesis, such as manufacturing of cyclohexanone and polymerization of butadiene rubber. pH dependent and primary salt effect studies of these substitution reactions should be investigated.

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