Synthesis and Characterization of Different Ion-pairs $[Co(PY)_4Cl_2]^+X^-$ and measurement of association and aquation rate constants.

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To my father Kebede Wudie who was dedicated for the education of his children and could see only flowers, but not lucky enough to see the fruits.

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Abbreviations

en: Ethylendiamine

PY: Pyridine

4-Mepy: 4-Methylpyridine

acac: acetylacetonato

gly: glycine

diars: o-penylene (bisdimethylarsine)

L-AA: L-aminoacid anion

UV: Ultra violete

Vis: Visible

IR: Infrared

eqn: equation

meq: milliequivalent

mmol: millimole

dec: decomposition

M.P: melting point

Abstract

The dichlorotetrapyridineCobalt(111) complexes $[Co(PY)_4Cl_2]X$ ($X = Cl^-$, NO_3^-, ClO_4^-, IO_4^-, SCN^-, N_3^-) were synthesized and characterized by using elemental analysis and spectroscopic techniques. The spectral data for complexes in the UV, Vis (λ_2 , λ_1), and IR (ν (Co-Cl), ν (Co-N)) regions have been determined.

From conductivity measurement equivalent conductivity at infinite dilution (λ_0) and association constants (K_Λ) were estimated in various solvents. Non-linear correlation of the association constant of the medium has been shown. Larger association constants for IO_4^- and SCN^-, whereas lower association constants for NO_3^- and Cl^- salts were found.

Rates of aquation of the complexes were measured in water as a function of Co-solvents (50:50); (v/v); and with the different composition of ethanol; and faster rate of aquations were observed for SCN^- and NO_3^- and slower for IO_4^- counter ions.

The nucleophilic order of the counter ions of the complexes was also established. The increasing order of the nucleophilicity of the counterions was found as follows:

$$SCN^- < NO_3^- < Cl^- < ClO_4^- < IO_4^- < N_3^-$$

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CHAPTER I

1. INTRODUCTION

1.1. Electronic spectra of Transition metal complexes

Both the colours and the magnetic properties of transition metal compounds were noticed very early and are striking in contrast to those of non-metal compounds. Observations of colour and reaction-related colour changes of coordination complexes have been important throughout the history of the coordination compounds.

Any chemical compound is coloured if light of a wave length conjugate to that colour is absorbed; the colour of the complex derives, of course, from the wavelength of transmitted light. The absorption of light occurs because there are accessible higher energy electronic states of the system[1]. In general three types of electronic transitions have been determined in transition metal complexes.

1.1.1. d-d or Ligand field transitions[2]

In the absence of the ligand field the transition metal ion d-orbitals remain degenerate. However, in the presence of electrostatic field of surrounding ligands, the set of five d-orbitals split apart to give two or more sets of energy state.

This effect brings about also the splitting of various Russel-Saunder's states of a d^n configuration into different states labelled as A (non-degenerate), E(two-fold degenerate T(three-fold degenerate

.../2

states), etc. The upper states may have different or identical multiplicities as that of lower states. The transition of the electrons from lower energy state to higher energy state of these d orbitals is known as d-d or ligand field transitions. d-d transitions are forbidden thus it weak and found invisible region.

1.1.2. Charge Transfer (CT) Transition[3]

In charge transfer (CT) spectra, electronic transitions occur between electronic levels of different atoms. Thus the charge distribution is considerably different in the ground and the excited states. In most cases charge transfer processes are of higher energy than d-d transitions, and they usually lie at the extreme blue end of the visible spectrum, or in the ultraviolet region. Also nearly all observed CT transitions are fully allowed and hence the CT bands are strong. The charge-transfer process are either from ligand to empty orbitals of the metal or from metal to ligands in which an electron being ionized from the metal atom to a vacant orbital of the ligand. For example, in an octahedral complex, electrons, may be promoted from a filled orbitals on the metal (e.g., the t_{2g}) to various antibonding orbitals on the ligand (like Π^* orbitals on carbon monoxide).

1.1.3. Intra-ligand transitions[4]

These transitions occur between energy levels that are primarily located on the ligand. For any free ligand containing non-bonding and π - electrons, the transitions will be in the order of decreasing energy:

$$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$$

In the complex, this order is usually violated. For many complexes the corresponding free ligands possess non-bonding electrons(n) that are easily excited. When these ligands coordinate with a metal ion, the n-electrons on the coordinating ligand atoms form a σ-bond with the ion. This lowers the energy of the n-electrons such that they can no longer be excited by lowest energy. The $\pi - \pi^*$ transitions are not greatly affected by complexation, however, and usually lie in the same energy region in the complex as they did in the free ligand.

1.2. Conductivity of Electrolytic solution

When a voltage is applied to electrodes immersed into an electrolyte solution[11], ions of the electrolyte move, and an electric current flows through the electrolyte solution. During the motion in the solution, an electrolyte ion experiences retarding effect both from the solvent molecules and from ionic atmospheres[11,12]. In the absence of ionic atmosphere, the retarding effect of the solvent molecules may be linked to friction forces acting on undeformable ball moving in a continuous viscous medium.

1.2.1. Specific Conductivities of Electrolyte Solutions[13,14,34]

Electrolyte solutions as well as metal conductors exhibit a certain resistance to the passage of an electric current.

The reciprocal of resistivity is called specific conductivity:

$$k = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{\ell}{A}$$

Where ρ is the resistivity

k is the specific conductivity

R- is resistance

l- is the distance between two electrodes

A- is the area of the electrode

Specific conductivity depends[15] on solution concentration. At low concentration, the numbers of ions of the solution is small, thus, the specific conductivity is low.

Specific conductivity depends also on the temperature[16]. As temperature rises the specific conductivity increases due to a decrease in the ionic friction coefficient.

1.2.2. Equivalent Conductivity of Electrolyte Solution

In addition to specific conductivity, equivalent conductivity is widely used. The equivalent conductivity (λ) represents the conducting power of all the ions produced by one gram equivalent of electrolyte in solution.

$$\lambda = \frac{k}{C_{eq}} \qquad (2)$$

$$\lambda = \frac{1}{R} \cdot \frac{1}{A} / C_{eq} \qquad (3)$$

C_{eq} = equivalent concentration.

The equivalent conductivity also depends on the concentration of the electrolyte. As the concentration of the electrolyte solution increases, the equivalent conductivity may decrease.

1.2.3. Equation for Electrolytic Conductance

Debye and Huckel[15] have proposed a theory for the effect of the ionic atmosphere on the mobilities of the ions. According to that theory the decrease in equivalent conductance should be proportional to the square root of the concentration. The empirical relationship was found by Kohlraush[15].

However, Onsager[18] has pointed out that in calculating the first or so called ionic effect, Debye and Huckel neglected to take into account the influence of Brownian movement of the ions, and also used a treatment, which is valid only if the negative and positive ions have equal mobilities. Onsager's treatment also confirmed the square-root relationship between the equivalent conductance and concentration.

Electrical conductance measurements are also applied in non-aqueous solvents for the extraction of some important parameters[25]

The basic quantity of interest is the equivalent conductance of the electrolyte at infinite dilution (λo). The parameter λo, coupled with transference number data procides information on single ion conductance or mobilities, λo^+ and λo^-, for cations and anions respectively.

In general the conductance is influenced by the dielectric constant of the medium[27]. It has been shown that, at sufficiently low concentrations, the equivalent conductance increases with dilution, even in solvents of very low dielectric constant. The decrease in equivalent conductivity is confirmed by increase of concentration of the electrolyte, because of decreasing the viscosity of the solution. On the other hand an increase in the dielectric constant of the medium may increase the conductance of a strong electrolyte in more concentrated solutions.

The other important parameter which can be obtained from electrical conductance measurement is an ion association constant[26]. Determination of the equivalent conductance as a function of concentration of the electrolyte, may give us association constant, K_A.

$$K_A = e^b \qquad (4)$$

where $$e^b = \frac{e^2}{a \varepsilon \kappa T} \qquad (5)$$

Where e = electron charge in eqn. (33)

a = centre-to-centre distance of the ion-pairs.

k = Boltzman constant

ε = dielectric constant

T = absolute temperature

Later on Gilkersen[27] found a relation

$$KA = K_A^o\ e^b \qquad (6)$$

KA^o is a factor which includes the effect of interaction between solvent and solute, and the free volume of the solute.

Later on Kraus and co-workers found that, the association constant is proportional to e^b.

The equivalent conductance of the salt varies with concentration suggests the existence of ion-pair equilibria in the solution[28]. In general when the dielectric constant is low, the expected duration of contact of ion-pairs after collision will be long compared to the duration in media of high dielectric constant.

Generally the conductance of smaller negative ions is markedly greater than that of corresponding positive ions[29]. This is because of strong interaction between the free ion and the solvent molecule as result of which the mobility of the ion is greatly reduced.

Introduction of the anion into the cation results in a marked decrease of conductance. These effects are significant and indicate increased interaction with the solvent molecules as result of the presence of the negative ions or groups in the cation.

Therefore the main factors which contribute to ionic association are ion size, the dielectric constant of the solvent and specific ion-solvent interactions.

Association of ions in non-aqueous solvents may be by contact ion pairs[30] as well as solvent-separated ion-pairs. In general large cations form solvent separated ion-pairs, whereas the smaller ions polarized the solvent molecules that surround them, so that contact pairs are formed.

Arrhenius and Ostwald[31] developed a simplified relation between the association constant K_A and the equivalent conductivity at infinite dilution (λo); that is:

$$\frac{1}{\lambda} = \frac{1}{\lambda o} + \frac{K_A \, C}{\lambda o^2} \qquad (7)$$

Where K_A = association constant

λo = equivalent conductivity of dilution

C = Concentration (in mole/lit)

λ = Equivalent Conductivity at any concentration

1.3. Substitution reaction of octahedral complexes

The kinetics of octahedral substitutions have been studied by a number of research groups, but the whole work has been done in water, in which the molecules have a higher nucleophilic property towards the ions of transition metals than the molecules of any other common solvents. It has been shown that the replacement of halogen in the bromo- or chloropentammine cobalt (III) ion by hydroxyl, through reaction with alkali solution is kinetically second order.[54,59]

The reaction in aqueous solution is solvolytic aquation in which the kinetics of the reaction was followed by replacement of chloro-, bromo-, and nitrate- groups by water from the pentammine cobalt (III) ions as dissociative mechanism.

Many substitution reactions have been studied by methods such as spectrophotometric method and potentiometric titration.

1.3.1. Spectrophotometric Study of the Displacement of Chlorine by the thiocyanate Ion[54]

Spectrophotometric technique is used in kinetic studies, either by measuring the increase or decrease of the absorbance of the reaction. For example, when a solution of lithium thiocyanate is added to one of the dichlorocobalt (III) chloride in methyl alcohol, substitution takes place, and evidenced from the gradual colour change which is followed by visible spectrophotometre. The introduction of thiocyanato group was followed by the increase of the absorption at 540nm.

$$\begin{tikzcd}
{[\mathrm{Co(en)_2Cl_2}]^+} \arrow[r, "\mathrm{NCS^-}"] & {[\mathrm{Co(en)_2\,Cl(NCS)}]^+ + \mathrm{Cl^-}} \arrow[d, "\mathrm{NCS^-}"] \\
& {[\mathrm{Co(en)_2(NCS)_2}]^+ + \mathrm{Cl^-} \quad (1a)}
\end{tikzcd}$$

1.3.2. Potentiometric Titration of the Rate of Displacement of chlorine by the Azide Ion[54]

The reaction between azide ion and the dichlorocobalt(III) cation proceeds through two stages of substitution:

$$\begin{tikzcd}
{[\mathrm{Co(en)_2Cl_2}]^+} \arrow[r, "\mathrm{N_3^-}"] & {[\mathrm{Co(en)_2ClN_3}]^+ + \mathrm{Cl^-}} \arrow[d, "\mathrm{N_3^-}"] \\
& {[\mathrm{Co(en)_2(N_3)_2}]^+ + \mathrm{Cl^-} \qquad (1b)}
\end{tikzcd}$$

The kinetics of the substitution have been followed by potentiometric titration of the librated chloride ion.

CHAPTER II

2. LITERATURE SURVEY

The complex compounds of cobalt (III) are numerous and stable and have played an important role in the development of coordination chemistry.

Virtually all of these have the octahedral structure[47]. They undergo Ligand exchange reactions at conveniently measurable rates and have therefore been extensively studied. Thus, a large amount of kinetic data has been given in the literature on simple substitution reactions under various conditions. In addition spectral data for many complexes are available

In general three types of substitution reactions have been studied[48].

a. Aquation, or replacement by water in neutral or acid solution.

b. Hydrolysis, or replacement by hydroxide ion in basic media and

c. Anation, or substitution of one anion by another.

The rate of substitution in octahedral complexes my be affected by the solvent used for the reaction. For example, the following may influence the rate of aquation of octahedral complexes in non-aqueous solution[49].

a. Ion-pairs cause only a small increase in rate over that of the free ion.

b. A change in solvent causes only modest changes in rate probably because of differing solvation effects of leaving groups.

c. Reactions are remarkably similar to the corresponding reactions in water, except that ion-pairing is more noticable.

Some of the cobalt (III) complexes reported in the literature, are described below.

2.1. Ammine Cobalt (III) Complexes, $[Co (NH_3)_n X_{6-n}]^{n-3}$ (where $n = 6,5,4$, and $x = Cl^-$, $SCN^- OH^- NO_2^-$, ReO_4^-)

The absorption spectra, ligand field parameter Δo, bond properties of $[Co(NH_3)_5X]^{2+}$ 50,51 and Cis- and trans- $[Co(NH_3)_4X_2]^{+}$[51] were measured (where $X = Cl^-$ SCN^-, OH^- and NO_2^-). The number of transitions in the visible region cobalt (III) complexes depends on the type of ligands that are coordinated to the metal[52]. For example, for low spin complexes like $[Co(NH_3)_6]^{3+}$, two absorption bands were observed, whereas for high spin complexes like $[CoF_6]^{3-}$ one absorption band was found. On the otherhand, the electronic transitions of UV spectra of substituted amine cobalt(III) complexes, $(Co(RNH_2)_5(H_2O)]^{3+}$ were obtained from the acid hydrolysis of $[Co(RNH_2)_5Cl]^{+2}$ complexes[53].

The mechanism of hydrolysis of complex ions such as:

$$[Co(NH_3)_5Cl]^{+2} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^- \quad (2)$$

has been considered by Brown, Ingold and Nyholm to be a direct displacement of halide ion by hydroxide (S_N2 process)[54,59]. This is in agreement with the observed kinetics of such reactions which are first order in hydroxide ion and first order in complex ion. Others have considered the mechanism to involve a prior acid-base equilbrium followed by release of halide ion from the conjugate base of the complex cation (an S_N1 CB process).

$$[Co(NH_3)_5Cl]^{+2} + OH^- \underset{fast}{\rightleftharpoons} [Co(NH_3)_4ClNH_2]^+ + H_2O \qquad (3)$$

$$\begin{array}{ccc} [Co(NH_3)_4NH_2Cl]^+ & \xrightarrow[slow]{H_2O} & [Co(NH_3)_4NH_2(H_2O)]^{+2} \\ & & \downarrow \\ & & [Co(NH_3)_5(OH)]^{+2} \end{array} \qquad (4)$$

The mechanism is in agreement with the observation that complexes containing no acidic protons release their replaceable ligands at a rate independent of the pH of the solution. In such compounds step 3 cannot occur.

The way in which water replaces chloride ion in step 4 is presumably the same as for aquation of the parent ion under acid conditions (acid hydrolysis).

$$[Co(NH_3)_5Cl]^{+2} + H_2O \text{ ---------}\rangle\ [Co(NH_3)_5(H_2O)]^{+3} + Cl^- \qquad (5)$$

Evidence has been presented showing that step 5 probably involves a dissociative mechanism (S_N1) in which a penta coordinated intermediate is formed[61].

$$[Co(NH_3)_5Cl]^{+2} \rightleftharpoons [Co(NH_3)_5]^{+3} + Cl^-$$

$$[Co(NH_3)_5]^{+3} + H_2O \xrightarrow[fast]{} [Co(NH_3)_5(H_2O)]^{+3}$$

The aquation kinetics of ions $[Co(NH_3)_5X]^{+2}$ ($X = Cl^-, Br^-$) in acetone-water have been investigated[151] over a wide range of solvent composition and temperatures. For these complexes logarithms of rate constant versus Grunwald-Winstein Y[81] values showed good linearity for both complexes studied with gradient slopes (m) of 0.175 and 0.187 for the chloro and bromo complexes respectively. The slope was significantly lowered as compared with aquation reactions in other organic solvents. This behavior of acetone - water was observed in similar aquation reactions and was attributed to the fact that some other properties of the solvent, such as its nucleophilicity (N) must be important in determining the aquation rate. The low apparent slope in acetone-water was associated with the low N value of acetone. The proposed mechanism for this reaction was dissociative.

Similarly in the aquation of the complex $[Co(NH_3)_5OReO_3]^{+2}$ a first order rate constant was observed[55]. The hydrolysis of pentamineperrhenatocobalt(III) ion in dilute acid, base, or in neutral conditions is discribed by:

$$[Co(NH_3)_5ReO_4]^{+2} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{+3} + ReO_4^- \qquad (7)$$

The complex $[Co(NH_3)_5OH]^{+2}$ is the only observable product. This observation can be related to the eqn.:

$$[Co(NH_3)_5NO_2]^{+2} + OH^- \longrightarrow [Co(NH_3)_5OH]^{+2} + NO_2^- \qquad (8)$$

A competing reaction was the formation of cobalt(III) hydroxide and free ammonia[56] in eqn. 8.

As has been shown, the direct replacement of one ligand by another is not common in water, because of the formation of aquo compound". In solvents with poorer coordinating properties, it, might be possible to demonstrate a direct substitution and hence find an S_N2 mechanism. Methanol was considered as a suitable solvent in most experimental work, since complexes such as $[Co(NH_3)_5Ch_3OH]^{3+}$ are unstable[57].

The aquation of $[Co(NH_3)_5Cl]^{2+}$ in t-butyl alcohol-water mixture with the view to observing the effect of structural changes in the solvents on aquation rates of this complex was described[58]. The rate of aquation in mixed solvents for complex the $[Co(NH_3)_5Cl]^{2+}$ gave first order rate constant from release of chloride of the complex.

Table 1.

First order rate constant for aquation of chloropentammine cobalt(III) in aqueous-t-butyl alcohol in 0.013M-$HClO_4$, at 35^oc.

% t-BuOH V/V	$Kx10^6(S^{-1})$	% t-BuOH V/V	$Kx10^6(S^{-1})$
0	6.7	16.7	6.5
3.3	6.6	20.0	6.4
6.7	6.4	23.3	6.4
10.0	6.4	26.7	6.4
13.3	6.5	30.0	6.4

2.2. Ethylene Diamine Cobalt(III) Complexes

2.2.1. $[Co(en)_2XY]^+$ (x,y, = Cl^-, OH^-, NCS^-, NCS^-, NO_2^-)

From absorption spectral data, the ligand field parameters Δo for complexes of cobalt of the type cis - and trans-$[Co(en)_2XY]^+$ were calculated.

Similarly the visible absorption spectra were used to study stereochemistry of cobalt(III) complexes $[Co(en)_2H_2OF]^{2+}$. In general the absorption maxima of cis - isomers were at lower wavelengths and had a larger extinction coefficient than those of trans[63]. For this system λ_{max}, for trans-isomers is some 70nm larger than that of the cis - cations, while the corresponding molar extinction coefficient is about 57 l $mol^{-1}cm^{-1}$, smaller. Further, for a given isomeric series λ_{max} is in the order of $F^- < Cl^- < Br^-$, reflecting the relative strength of the ligand fields. The corresponding extinction coefficient also appear to be in the same order.

From kinetic point of view, aquation reactions are considered to be pseudo-first order[64]. The following hydrolysis reactions were reported[64,65]

$$cis\text{-}[Co(en)_2(NH_3)Cl]^{+2} + NaOH \dashrightarrow cis\text{-}[Co(en)_2(NH_3)(OH)]^{+2} \quad (9)$$

$$cis\text{-}[Co(en)_2(NCS)Cl]^{+} + NaOH \dashrightarrow cis\text{-}[Co(en)_2(OH)_2]^{+} \quad (10)$$

$$cis\text{-}[Co(en)_2(NO_2)Cl]^{+} + NaOH \dashrightarrow cis\text{-}[Co(en)_2(NO_2)(OH)]^{+} \quad (11)$$

$$cis\text{-}[Co(en)_2(NH_3)\ (H_2O)]^{+3} + NaNO_2 \dashrightarrow cis\text{-}[Co(en)_2(NH_3)(NO_2)]^{+2}\ 80\% + trans --- 20\% \quad (12)$$

$$\text{cis-}[Co(en)_2(NO_2)(H_2O)]^{+2} + NaNO_2 \text{---}> \text{cis-}[Co(en)_2(NO_2)_2]^{+} \quad (13)$$

The rate of acid hydrolysis (aquation) of the cobalt(III) complex $[Co(en)_2PyCl]^{+2}$ was shown to increase with increasing size of the "inert" ligands[66,73]. The greater rate of aquation of the more sterically hindered complex was cited in support of a dissociation mechanism (S_N1). Thus in a series of complex ions, containing substituted ethylendiamine ions, an alkyl substituent increased the rate of aquation. In addition to steric factors, it is also possible to rationalize the data interms of the inductive effect of the alkyl groups which increase the negative charge on the cobalt atom and hence repel the chloride ion in the complex. The rate of acid and base hydrolysis for this complex were - also given.

$$[Co(en)_2PyCl]^{+2} + H_2O \text{---}> [Co(en)_2Py(H_2O)]^{+3} + Cl^- \quad (14)$$

$$[Co(en)_2PyCl]^{+2} + OH^- \text{----}> [(Co(en)_2Py(OH))]^{+2} + Cl^- \quad (15)$$

Such base hydrolysis takes place due to the greater base strength of the coordinated pyridine, electron density of cobalt(III) and the more labile nature of the Co-Cl bond. This is consistent with the observed increased rates of acid hydrolysis with increased base strength.

Some solvolysis reactions were observed on various complexes like trans-$[Co(en)_2NO_2Cl]^+$ and trans- $[Co(en)_2NO_2Br]^+$ in various solvents[67]. It was concluded that the electron withdrawing nitro group facilitates aquation by facilitating a nucleophilic attack at cobalt (S_N2 mechanism), while the electron donor chloro group facilitates aquation by facilitating dissociation S_N1 mechanism). These two processes should be responsive to the properties of the solvent. Nucleophilic attack should be facilitated by increased solvent nucleophilicity. Dissociation rates should respond to the ability of the solvent to solvate the ions produced.

In both cis and trans- $(Co(en)_2NO_2Cl]^+$ methanolysis is rate determining in the replacement of chlorine by thiocyanate in methanol[68]. Methanolysis is followed by fast replacement of coordinated methanol by thiocyanate.

$$[Co(en)_2(NO_2)Cl]^+ + CH_3OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(en)_2(NO_2)(CH_3OH)]^{+2} + Cl^- \qquad (16)$$

$$[Co(en)_2(NO_2)(CH_3OH)^{+2} + SCN- \xrightarrow{k_2} [Co(en)_2NO_2SCN]^+ CH_3OH$$

This substitution of cobalt(III) complex cation in methanol by S_N1 weakly nucleophilic reagents (Cl^-, SCN^-) follows S_N1 kinetics, whereas for a strongly nucleophilic reagent like azide ion the substitution has an S_N2 mechanism.

The kinetics for the appearance of halide ions from some cis - aquo (halogenalkylamine) bis (ethylenediamine)cobalt(III) cations and their corresponding cis-hydroxocomplexes have been investigated in aqueous solutions under various conditions[69]. In acid solutions the reaction is first order and presumably yields cis-aquo (alkanolamine) bis(ethylenediaminecobalt(III) complexes. The reactivities of the corresponding cis-hydroxocation in basic solution are considerably greater and the corresponding aquation reaction is second order.

$$[Co(en)_2(\text{halogenoakylamine})\ (H_2O)]^{3+} + OH^- \text{------>}$$
$$[Co(en)_2\ (\text{halogenoalkylamine}\ (OH))]^{+2} + H_2O \qquad (18)$$

Because of the acidic properties of the coordinated water in aqueous solutions, hydroxo(halogenoalkylamine)bis (ethylenediamine) cobalt(III) cation is obtained under basic media.

A mechanism for base hydrolysis of Cobalt(III) complexes, e.g. $[Co(en)_2AX]^{n+} + OH^- \text{---->} [Coen_2AOH]^{n+} + X^-$ (19)

is suggested to involve electron transfer from hydroxyl into cobalt(III)[70].

Table 2

Products of base hydrolysis of $(Coen_2AX]^{n+}$[70]

Factor		Product		%cis
A	X	A	X	
trans---NCS	Cl	NCS	OH	76
cis--NCS	Cl	NCS	OH	80
cis--NCS	Br	NCS	OH	81
trans---NCS	N_3	NCS	OH	70
cis--NCS	N_3	NCS	OH	70
trans---Br	OH	OH	OH	90
trans---Cl	OH	OH	OH	94
cis--Cl	OH	OH	OH	97

cis--Br	OH	OH	OH	96
trans--Cl	Br	Cl	OH	5
trans--Cl	Cl	Cl	OH	5
cis--NH_3	Cl	NH_3	OH	84
trans--NH_3	Cl	NH_3	OH	76
cis--NH_3	Br	NH_3	OH	85
cis--NH_3	NO_3	NH_3	OH	86

The reaction of hydroxide ions with the cobalt(III) complexes $[Co(en)_2AX]^{n+}$ differs remarkably from those of analogous chromium(III) and rhodium(III) complexes. The following differences are observed.

a. The rate of base hydrolysis of a given cobalt(III) complex is faster than its acid hydrolysis. For rhodium(III)[72], as well as chromium(III) this is not the case, the rate of hydrolysis in acid and in base being of the same order. In general, hydroxide is not a particularly good nucleophile except for cobalt(III).

b. Stereochemical change occurs very frequently during base hydrolysis of cobalt(III) complexes, but not in the analogous rhodium(III) compounds[77].

2.2.2. $[Co(en)_2X_2]^+$ (X = Cl^-, NO_2^-, ---)

The absorption spectra of trans - $[Co(en)_2Cl_2]Cl$ cis-$[Co(en)_2(NO_2)_2]NO_3$, and trans-$[Co(en)_2(NO_2)_2]Cl$ were observed in methanol - water mixture[74]. The mixtured solvent was found to be necessary because of the rapid rate of aquation of some of these complex ions. Dichlorobis-(ethylenediamine) cobalt(III) chloride, which in water is almost entirely changed to the chloroaquo complex in one hour, 99% remains unchanged in methanol-water for a period of time. The displacement of chloride by thiocyanate was also studied by spectrophotometric techniques results in the formation of $[Co(en)_2(SCN)_2]SCN$[75].

The reaction

$$cis\text{-}[Co(en)_2Cl_2]^+ + X^- \dashrightarrow [Co(en)_2ClX]^+ + Cl^- \qquad (20)$$

depends upon the nature of the entering group[76]. Reagents such as Cl^-, Br^-, SCN^- and NO_3- enter at a common rate that is independent of their concentration, whereas CH_3O^-, N_3^-, and NO_2^- react more repidly at rates that are dependent upon their concentration.

It was shown that, the behavior of N_3^- and NO_2^- was due to the formation of the radical ions from solvolysis of these basic reagents, e.g.,

$$N_3^- + CH_3OH \rightleftharpoons HN_3 + CH_3O^- \qquad (21)$$

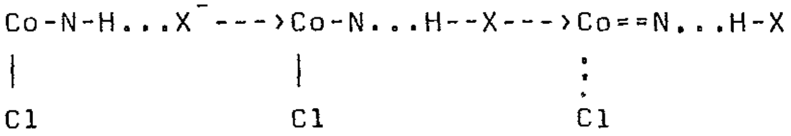
The rates of reaction of cis-$[Co(en)_2Cl_2]^+$ with acetate azide and nitrite ion in methanol are found to be some what greater in non-basic anions[77,78]. For this complex ion-pair formation has been postulated. According to the theory of ion-pairs, the degree of association expected is a function of the size, charge of the ions and the dielectric constant of the medium.

For the ion $[Co(en)_3]^{3+}$ in water, ion-pair formation constants of 21 and 11 have been reported for Br^- and N_3^- respectively. Since the dielectric constant of methanol is less than that of water the expected ion-pair formation for $[Co(en)_2Cl_2]^+$ with azide in methanol will be less than for $[Co(en)_3]^{3+}$ in water.

From the usual method of examination of the shift in ultraviolet absorption spectra produced by the formation of ion-pairs, cis-$[Co(en)_2Cl_2]^+$ does show a substantial shift to longer wavelengths upon addition of Cl^- and Br^-. The approximate ion-pair formation constants of 135 for Cl^- and 35 for Br^- have been calculated for cis-isomers.

Ion-pair formation may increase the rate of reaction but it is not the main cause since the cis-complex forms ion-pairs with chloride and bromide ion, and the rate of reaction is not accelerated by increasing concentrations of these ions under conditions where ion-pair formation is not complete. Nor is the rate different from that with NO_3^- and SCN^-, and from the rate of racemization. Only basic anions increase the rate. Pyridine, which would not form an associated pair with the complex, does not cause an accelerated rate. Since the nucleophilic character of an anion towards the metal complexes is generally expected, it is certainly possible that the ion-pair reacts by an S_N2 - displacement process.

Another possible mechanism would be based on the possibility that there is a strong interaction of the basic anion with the acidic protons of the complex in an ion-pair. Such interaction is expected on electrostatic grounds, and would permit the electron of the N-H bond to behave at least somewhat like the electrons of amido group. That is, they would perhaps be labilized enough to form a partial π - bond to the cobalt atom and help to release chloride ion.



$$\underset{\underset{\displaystyle \mathrm{Cl}}{|}}{\mathrm{Co}}\text{-N-H}\ldots\mathrm{X}^{-}\text{--->}\underset{\underset{\displaystyle \mathrm{Cl}}{|}}{\mathrm{Co}}\text{-N}\ldots\text{H--X--->}\underset{\underset{\displaystyle \mathrm{Cl}}{\vdots}}{\mathrm{Co}}{=}{=}\text{N}\ldots\text{H-X} \qquad (22)$$

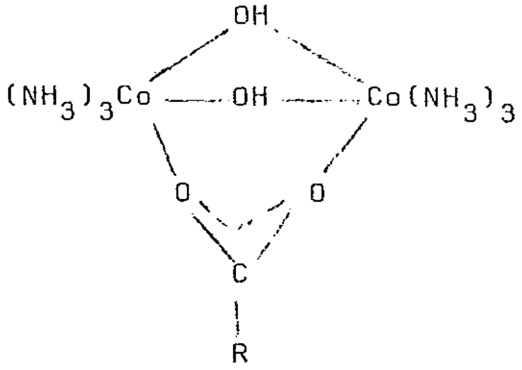
Also the rate of aquation in mixed solvents for complex $[Co(en)_2Cl_2]^+$ gave first order rate constants for release of the first chloride from the complex. The observations indicated that, the results for relatively water rich[79] solvent (greater than around 50% v/v water), corrosponded to a good first order reaction. In organic rich mixtures ion-pairing is likely to have a significant effect on the observed rate constants for doubly charged cations and probably for singly charged species as well.

First order rate constant for aquation of cis-$[Co(en)_2Cl_2]^+$ in water - methanol, acetone, dioxane, formic acid, acetic acid mixture have also been determined[80]. The variation of rate constant with dielectric constant for mixed aqueous solvents has been used as an indication of the dissociative or associative character of the rate determining step. Most of the discussion of the rate constant variation were given interms of Grunwald-Winstein[81] solvent Y-values. These are direct measures of the solvating abilities of pure and mixed solvents, derived from the kinetic data based on solvolysis of t-Butylchloride.

The rate of aquation of cis-$[Co(en)_2Cl_2]^+$ has also been studied in various t-butyl alsohol mixtures[82]. In this case the rate of aquation is a function of solvent composition. In aqueous mixture t-butyl alcohol enhances the structure of water at mole fractions below about 0.04; and at higher mole fractions the structure is progressively disrupted. On going from a t-butyl alsochol mole fraction of 0 to nearly 0.04, the enhancement of water structure makes the cation less sensitive to incoming water. But as the proportion of butyl alsohol rises beyond 0.04 mole fraction, the disruption of the water structure makes water molecules freely available; and thus facilitates the transition state. This behavior would lead initially to a slower reaction then to increasingly rapid reaction as the mole fraction of t-butyl alcohol increases.

2.3. Miscellaneous Cobalt(III) Complexes

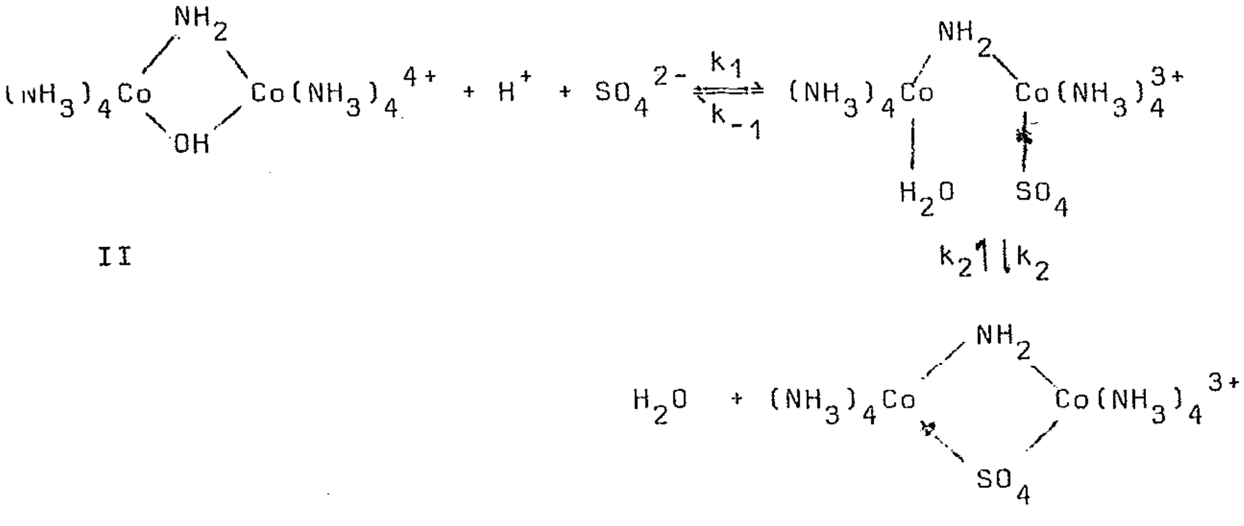
The ultraviolet and visible absorption spectra of di-μ-hydroxo-bis (triammine Cobalt(III) complex with a carboxylatobridging group have been described[84].



(I)

For this complex λ_{max} of 300nm and 524nm with extinction coefficients ε = 2700 and 109 l mol^{-1}cm^{-1} respectively were reported. The presence of two hydroxo-bridges gives rise to an intense charge transfer absorption band at 300nm.

Equilbrium and kinetic studies also have been made on the interconversion of the μ-amido-μ-hydroxo(II) and μ -amido-μ sulfato complexes(III)[85].

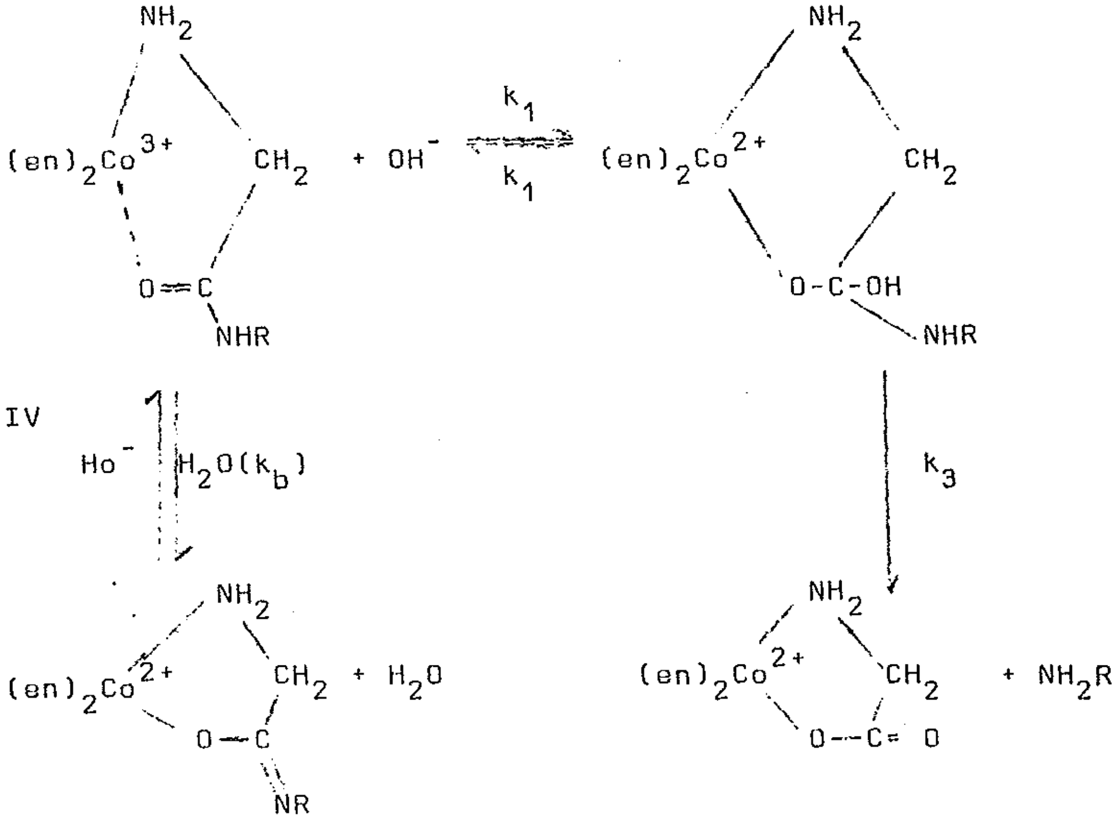


II

III

In the forward reaction, the conversion of the μ-hydroxo into the μ-sulfato complex is the rate determining step.

The glycine amide and dipeptide complexes (IV) used for the kinetic studies are chelated to the cobalt via the thermal nitrogen and carbonyl oxygen atoms[86]. The results establish that hydrolysis in the bis (Ethylenediamine) systems consumes 1 equivalent of base at high pH to produce $[Co(en)_2gly]^{2+}$ and NH_2R (R=H, CH_3, CH_3CO_2-, CH_2CO_2R). The following proposed mechanism is consistent with the observed rate law and stoichiometry is also obeyed in the pH range 9-14.



The kinetics obey the first order rate law and the results are consistent with attack of solvent hydroxide at the carbonyl C of the chelated amide, and require the amide conjugate base to be unreactive.

The kinetics of the reaction between sodium hydroxide and chloropentaminecobalt(III) perchlorate in aqueous solution indicated second order rate law[87] and a pseudo-first-order rate constant was also obtained.

Complexes of the type $[Co(diars)_2X_2]^{n-2}$ [where diars = O-phenylene (bisdimethylarsine) and X = Cl^-, Br^-, or I^-] have also been reported[88]. From the point of characterization of the complexes, Co^{III}-Cl stretching frequencies ν(Co-Cl) for $[Co(diars)_2Cl_2]$ ClO_4, 388, and for $[Co(diars)_2Cl_2]Cl$, 384 cm^{-1} have been obtained.

Various pentacyanocobaltate(III) complexes, $[Co(III)(CN)_5X]$ (X = OH_2, OH^-, Cl^-, Br^-, N_3^- and SCN^-) were found to react with CN^-, in the presence of $Co(CN)_5^{3-}$ to form $Co(CN)_6^{3-}$ [89]. Kinetic results were interpreted in terms of an indirect substitution mechanism involving an inner sphere electron transfer between $Co(CN)_5^{3-}$ and $CO^{III}(CN)_5$ X through a bridging cyanide ligand.

$$Co^{III}(CN)_5X + Co(CN)_5^{3-} \dashrightarrow [X(NC)_4\underbrace{Co^{III}\text{--}CN\text{-}Co^{II}}_{e^-}(CN)_5] \dashrightarrow$$

$Co^{II}(CN)_4X + Co(CN)_5(NC)^{3-}$ (rate determining) (23)

$Co(CN)_5(NC)^{3-} \text{-----}\rangle Co(CN)_6^{3}$ (24)

$Co^{II}(CN)_4X + CN^- \text{----}\rangle Co(CN)_5^{3-} + X$ (25)

$Co^{III}(CN)_5X + CN^- \text{----}\rangle Co(CN)_6^{3-} + X$ (26)

Some complexes of (L-aminoacid) triethylenetetraaminocobalt(III) iodides of the type:

$[Co(trien)(L\text{-}AA)]I_2, H_2O$ (in which L-AA refers to an L-amino acid anion) have been reported[90]. The complexes $[Co(C_6H_{18}N_4)(C_5H_{10}NO_2)]I_2,H_2O$ (L-valinato) and (27)

$[Co(C_6H_{18}N_4)(C_6H_{12}NO_2)]I_2H_2O$ (L-leucinato), (28)

and several others have been investigated by their characteristic ultraviolet and visible absorption frequencies. There are two symmetrical bands at 482-484m (ε = 135-136) and 345-347nm ($\varepsilon \approx$ 150-230 l $mol^{-1}cm^{-1}$). The positions, intensities and shapes of these two bands are similar to those of many octahedral complexes.

The solvolysis of trans-$[Co(4\text{-}MePy)_4Cl_2]^+$ in water and water-propan-2-ol is always first order in the complex[23]. The logarthm of rate constant shows a non-linear correlation with the reciprocal of dielectric constant of the medium. The linearity shows that changes in solvent structure; with composition are[94,95] important in determining the variation of rate constant with entropy of activation and enthalpy of activation in the region where the physical properties of the mixture indicate a maximum in the structure formation.

The solvolysis of trans-$[Co(4\text{-}MePy)_4Cl_2]^+$ in water-acetonitrile, and water-dioxane[150] has also been reported. Quantitative measurements have shown that, the solvent basicity of water-acetonitrile was greater than that of water-dioxane mixtures. The intermolecular hydrogen bonding between water and acetonitrile gives rise to an increased basicity of the hydroxyl oxygen of water in contrast, dioxan has a minor effect on the basicity of water. The solvation of the cation under investigation in the ground state was probably favoured by two factors;

(i) The high activity of water molecules as a result of its presence in a non-associated state.

(ii) The para-methyl group in the pyridine rings which increased the solvation of the cation.

This solvation by a more basic solvent may reduce the activation energy of the reaction.

Solvolysis of trans-$[Co(Py)_4Cl_2]^+$ in isopropyl alsohol-water obeys an S_N1 mechanism[93]. Similarly the kinetics of solvolysis of this complex were reported in water and water-methanol and have been shown first order solvolysis[96] and a non-linear dependence of log (rate constant) with the reciprocal of the dielectric constant suggesting that the effects of solvent structures are important; and this is confirmed by the comparison of the variation with the solvent composition of a range of physical properties of the solvent mixture. A free-energy cycle relating the intial state of the process to the transition state in water and to that in water-methanol mixture shows that changes in solvation of the transition state have a dominant effect on the rate.

The kinetics of solvolysis of the trans-dichlorotetrapyridine cobalt(III) ion in water-t-butyl alcohol was also reported[152]. The effect of t-butyl alcohol on the solvent structure and the non-linear correlation of the rate constant with the reciprocal of the dielectric constant of the medium have been reported.

2.4. The quantitative measure of ionizing power of the solvent

Grunwald and Winstein[81] found quantitative measure of ionizing power (Y) of the ethanol-water mixture for the solvolysis of t-butyl chloride. They defined Y by eqn. (8):

$$Y = \mathrm{Log}k^{BuCl} - \mathrm{Log}k_o^{BuCl} \qquad (8)$$

where k^{Bucl} and k_o^{Bucl} are the rate constants of the t-butyl chloride at 25°c in the given solvent and in 80% ethanol respectively. By definition Y is zero in 80% ethanol. Although 25°c is chosen as reference temperature for computing values of Y, it has also been observed that, any other reference temperature would give an almost identical set of Y values.

Y values for all solvents except the acetone-water mixtures were calculated from the available data of t-butyl chloride at 25^{o}c.

The nucleophilic character N of the medium can be derived from the ionizing power Y and the rate constant of the solvolysis[8] as shown by eqn. (9)

$$d\log k = \left(\frac{\partial \log k}{\partial Y}\right)_N dY + \left(\frac{\partial \log k}{\partial N}\right)_Y dN \qquad (9)$$

CHAPTER III

3. Objective of the Research

The objective of the research project consists of the following points.

(i) Synthesis and characterization of the $[Co(Py)_4Cl_2]^+X^-$ ($X = Cl^-, NO_3^-, ClO_4^-, IO_4^-, SCN^-, N_3^-$)

(ii) Measurement of the association constant K_A of the complexes.

(iii) Determination of the aquation rate constants of the complexes.

(iv) Determination of the nucleophilic order of the counterions.

CHAPTER IV

4. Experimental

4.1. General

Ultraviolet and visible spectra were measured over the range 700-200 nm on a Beckman model 24 spectrometer,

IR spectra were measured over the range 4000-200 cm^{-1} on a PYE UNICAM PU9512 Infrared spectrophotometer.

Melting points were determined with a BOCKMONOSCOP <M> electrically heated microscope.

Conductivities were measured by Teraohmmeter GUARD instrument. The resistance of the solution was measured within 5-10 minutes after preparation of the solution at room temperature for concentrations between 10^{-4} and 10^{-6}M.

The rates of aquation were followed by a spectronic 1001 spilt-Beam spectrophotometer at room temperature for the concentrations of the order, 10^{-6}M. Release of chloride was counterchecked by a chloride sensitive electrode[131].

Synthesized complexes were decomposed by 5ml of 5N sodium hydroxide[109] for analysis.

Cobalt was analyzed following standard method,[111,112] and chloride was determined following reported procedure[110].

*Cobalt was determined by 1-nitroso-2-naphthol from extruct of chloroform at 425 nm.

4.2. Starting Material

4.2.1. Preparation of dichlorotetrapyridine Cobalt(III) chloride: $[Co(Py)_4Cl_2]Cl^{96}$

$$CoCl_2.6H_2O+Py+Cl_2 \dashrightarrow [Co(Py)_4Cl_2]Cl. \qquad (29)$$

Pyridine (30 g, 0.38 mol) was added to a solution containing cobalt(III) chloride (20g 0.1mol) dissolved in water (40g 2.2mol). The precipitate which formed was redissolved by heating at 35^{o}C. Chlorine gas was passed through the solution, and it was then cooled in ice and allowed to stand for 6-8 hrs. The precipitate was then filtered off and washed successively with 5-10ml of ice-water, then ethanol and diethyl ether, The solid obtained was recrystallized from concentrated HCl several times to give an analytically pure green product (yield 28.2 g, 69%), m.p. 160^{o}c (dec.); (Found: Co,11.7; Cl, 21.5; Calcd; Co, 12.25; Cl, 22.1%).

i.r. (kBr disc): ν(Co-Cl), 385 cm^{-1}, Lit.^{88,117} 384cm^{-1};
ν(Co-N), 345 cm^{-1}

UV(Ethanol): λ_{max}: 298nm; Lit^{96}, 295nm, ε_{max}: 10680 ℓmol^{-1}cm^{-1}.
Vis (Ethanol): λ_2: 632nm: ε_2 = 32.9 l.mol^{-1}.cm^{-1}.
λ_1: 505nm, ε_1: 23.8 l.mol^{-1}cm^{-1}

*Chloride was obtained gravimetrically from 0.01M silvernitrate.

4.3. Synthesis of $[Co(Py)_4Cl_2]$ X (X = NO_3^-, ClO_4^-, IO_4^-, SCN^-, N_3^-

4.3.1 $[Co(Py)_4Cl_2]NO_3$

$$[Co(PY)_4Cl_2]Cl + HNO_3 \text{---›} [Co(Py)_4Cl_2NO_3 + Cl^- + H^+ \qquad (30)$$

The dichlorotetrapyridine cobalt(III) chloride (5.723 g, 0.012mol) was dissolved in distilled water 5 ml) at 45°c, and concentrated nitric acid (0.7 g, 0.012 mol) was added drop by drop for about 10 minutes. The solid obtained was purified by recrystallization from concentrated nitric acid followed by repeated washing as described for the chloride complex. After drying a green analytically pure product was obtained (yield 4.83 g, 80); m.p.,146 - 150°c; (Found: Co, 11.20; Cl, 13.4; NO_3^{113}, 12.79; Calcd; Co, 11.60; Cl, 13.95; NO_3, 12.2%)

i.r. (KBr disc): ν(Co-Cl), 385; ν(Co-N), 345cm^{-1}; for NO_3 found: 825,785,1630cm^{-1}, Lit.[120,123,128] 828,716, 1630cm^{-1} respectively).

UV(ethanol): λ_{max} 299nm, Lit[96], 295nm; ε_{max}: 8300ℓ.mol^{-1}cm^{-1}.

Vis(ethanol): λ_2 630nm, ε_2: 37.4 l.mol^{-1}cm^{-1}

λ_1 502nm ε_1 28.2 l.mol^{-1}cm^{-1}

*Nitrate was determined by concentrated perchloric acid at 300 nm.

4.3.2. Preparation of dichlorotetrapyridine cobalt(III) perchlorate $[Co(Py)_4Cl_2]ClO_4$

$[Co(Py)_4Cl_2]Cl + HClO_4$ ----> $[Co(Py)_4Cl_2]ClO_4 + Cl^- + H^+$ (31)

The dichlorotetrapyridine cobalt(III) chloride (4.321g, 8.98 mol) was dissolved in distilled water (50 ml) at 45°c, and concentrated perchloric acid (0.89 g, 8.94 mmol) was added drop by drop for about 10 minutes. The solid obtained was purified by recrystallization from concentrated perchloric acid followed by repeated washings as described for the chloride complex. After drying, a dark-green analytically pure product was obtained (yield: 4,89 g, 83%; m.p. 171°c (dec,); (Found: Co, 9.9, Cl. 11.47; ClO_4[114], 18.77; Calcd; Co, 10.6; Cl, 12.12; ClO_4, 18.22%.

i.r. (KBr disc): ν(Co-Cl), 390; Lit[88] 388; ν(Co-N), 346cm^{-1}; (for ClO_4 found: 625, 928, 1119; Lit.[120,122] 625,865, 1100 cm^{-1} respectively).

UV(ethanol): λ_{max}: 297nm, ε_{max}: 11720 l.mol^{-1}cm^{-1}.

Vis(ethanol): λ_2: 627nm: ε_2 : 32.8 l.mol^{-1}cm^{-1}.

λ_1: 512nm : ε_1 : 26.0 l.mol^{-1}cm^{-1}

*Perchlorate was obtained by 1.6% methylene blue solution from extruct of chloroform at 638nm.

4.3.3. Preparation of dichlorotetrapyridine Cobalt(III) per iodate $[Co(Py)_4Cl_2]IO_4$

$[Co(Py)_4Cl_2]Cl + HIO_4$ -----> $[Co(Py)_4Cl_2]IO_4 + Cl^- + H^+$ (32)

The dichlorotetrapyridine cobalt(III) chloride (6.757 g, 14.0mmol) was dissolved in distilled water (50ml) at 45^{o}c and concentrated periodic acid (3.2 g, 14.0 m mol) was added drop by drop for about 10 minutes. The solid obtained was purified by recrystallization from concentrated periodic acid followed by repeated washings as described for the chloride complex. After drying a dark green analytically pure product was obtained (yield: 5.56 g, 82%); m.p. 185^{o}c (dec); (Found: Co, 10.14; Cl,11.12; IO$_4$[114], 31.17; Calcd. Co, 9.27; Cl, 11.14; IO$_4$, 30.78%).

i.r.(KBrdisc): ν(Co-Cl), 390; ν(Co-N), 346cm^{-1}; (for IO$_4$, found: 853,320;Lit[122],850,325cm^{-1} respectively).

UV (ethanol): λ_{max}: 298nm; ε_{max}, 11940 l.mol^{-1} cm^{-1}

Vis (ethanol) λ_2 627nm ε_2 : 42.61.mol^{-1} cm^{-1}
λ_1 512nm ε_1 : 30.4 l.mol^{-1}.cm^{-1}

* Periodate was obtained by 1.6% methylene blue solution from extruct of chloroform at 638nm.

4.3.4. Preparation o dichlorotetrapyridinecobalt(III) thiocyanate [Co(Py)$_4$Cl$_2$]SCN

$$[Co(Py)_4Cl_2]Cl \xrightarrow[\text{acidified}]{\text{KSCN}} [Co(Py)_4Cl_2]SCN + Cl^- + K^+ \qquad (33)$$

The dichlorotetrapyridinecobalt(III) chloride (3.5g, 7.27 m mol) was dissolved in distilled water (50ml) at 45^{o}c and potassium thiocyanate (0.7064 g, 7.27 mmol) in 10 ml of acidified aqueous solution with dil. HCl was added drop by drop for about 15 minutes. The solid obtained was purified by recrystallization from acidified potassium thiocyanate solution followed by repeated washings as described for the chloride complexes. After drying, a light green analytically pure product was obtained (yield: 2.721 g, 74.26%); m.p. 142°C (dec.); (Found: Co, 12.58; Cl,13.69; SCN[115], 22.0; Calcd;, Co, 11.71;Cl,14.09;SCN,22.6).

i.r. (KBr disc): ν(CO-Cl), 380; ν(Co-N),345cm^{-1}; (for SCN, found:2060,748; Lit[125]. 2055, 754 cm^{-1} respectively).

UV(ethanol): λ_{max}: 298, ε_{max}: 6760 l.mol^{-1}cm^{-1}
Vis(ethanol) λ_2: 632nm, ε_2 : 30.3 l.mol^{-1}cm^{-1}
λ_1: 512nm, ε_1 : 24.1 l.mol^{-1}cm^{-1}

*Thiocyanate was obtained by 10% copper sulfate from extruct of chloroform at 410nm.

4.3.5. Preparation of dichlorotetrapyridine cobalt(III) azide $[Co(Py)_4Cl_2]N_3$

$$[Co(Py)_4Cl_2]Cl \xrightarrow[\text{acidified}]{NaN_3} [Co(Py)_4Cl_2]N_3 + Cl^- + Na^+ \qquad (34)$$

The dichlorotetrapyridine cobalt(III) chloride (3.5g, 7.27 mmol) was dissolved in distilled water (50ml) at 45°c and sodium azide (0.4725 g, 2.27 mmol) in 10ml of acidified aqueous solution was added drop by drop for about 15 minutes. The obtained azide complex was purified by recrystallization from acidified sodium azide solution followed by repeated washings as described for the chloride complex. After drying a light green analytically pure product was obtained (yield: 2.62g, 73.86%); m.p. 144^{o}c (dec.), Found: Co,11.33; Cl,14.53; N_3[116], 10.3; Calcd., Co, 12.08; Cl, 14.55; N_3,9.6).

i.r. (KBr disc): ν(Co-Cl), 385; ν(Co-N),344cm^{-1}; (for N_3 found: 2100, 1238, Lit[124,126] 2080,1240cm^{-1} respectively).
UV(ethanol): λ_{max}: 298nm, ε_{max}, 11980 l.mol^{-1}.cm^{-1},
Vis(ethanol): λ_2: 622nm, ε_2 , 35.5 l.mol^{-2}.cm^{-1}
λ_1: 500nm, ε ,25.3 l.mol^{-1}.cm^{-1}

*Azide was determined by 0.11M ferric perchlorate solution at 454nm.

4.4. Association constant determination for $[Co(Py)_4Cl_2]X$ ($X = Cl^-, NO_3^-, ClO_4^-, IO_4^- SCN^-, N_3^-$)

Association econstants (K_A) for complexes were determined in various solvents such as dichloromethane, 2-butanol, ethanol, methanol, dimethylformamide, and 1:1 (v/v) methanol-water mixture. The conductivity was measured and converted to equivalent conductance by the standard method. Association constants for each complex was evaluated by the Arrhenius-Ostwald's equation (Fig. 4), for concentrations from 10^{-4} to 10^{-6} M.

4.5. Aquation rate Constant Determination for $[Co(Py)_4Cl_2]X$ $(X = Cl^-, NO_3^-, ClO_4^-, IO_4^-, SCN^-, N_3^-)$

The reaction rate coefficient was evaluated by the Kezdy-Swin bourne method[132] as follows:

For a complexes having concentration of the order, $10^{-6}M$, absorbance readings A_1, A_2---A_n were made at times t_1, t_2---t_n, and a second series A'_1, A'_2,---A'_n were made at corresponding times $t_1 + \tau$, $t_2 + \tau$,--- $t_n + \tau$ (where τ is constant; 30 minutes)at room temperature then, for first order reaction:

$$\frac{A_t - A_\infty}{A_o - A_\infty} = \exp(-kt) \qquad (10)$$

and

$$\frac{A'_t - A_\infty}{A_o - A_\infty} = \frac{A_{t+\tau} - A_\infty}{A_o - A_\infty} = \exp(-k(t + \tau)) \qquad (11)$$

Dividing eqn. (10) by eqn. (11) and rearranging

$$A_t = A_\infty (1 - \exp k\tau) + A'_t \exp(k\tau) \qquad (12)$$

By plotting the graph A_t against A'_t, a straight line was obtained (appendix 2) and an estimate of the reaction rate coefficient was evaluated from the logarithm of the slope of the line.

CHAPTER V

5. Results and Discussions

All experimental results of the complexes [Co(Py)$_4$Cl$_2$] X ((X = Cl$^-$, NO$_3$-, ClO$_4$-, IO$_4$-, SCN$^-$ and N$_3$-) are given in tables and figures.

5.1. Spectral Analysis

5.1.1. UV-Vis

In cobalt(III) complexes [Co(Py)$_4$Cl$_2$] X (X = Cl$^-$, NO$_3$- ClO$_4$-, IO$_4$, SCN$^-$ and N$_3$-) two absorption bands in visible and on intense band in the uv regions were observed. The two absorption bands (Low intensity ε = 5-100 l.mole^{-1}cm^{-1}) in the visible region probably correspond to the spin allowed transitions from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ states. These transitions are usually observed in the case of low spin complexes[52]. The charge transfer transition is fully allowed, in contrast to d-d transitions with the extinction coefficients of 10^3 - 10^5 l mol^{-1} cm^{-1}. The intense absorption band observed in UV region is assigned to charge transfer transitions with extinction coefficient of 6 x 10^3 - 1.2 x 10^4 l. mole^{-1} cm^{-1}.

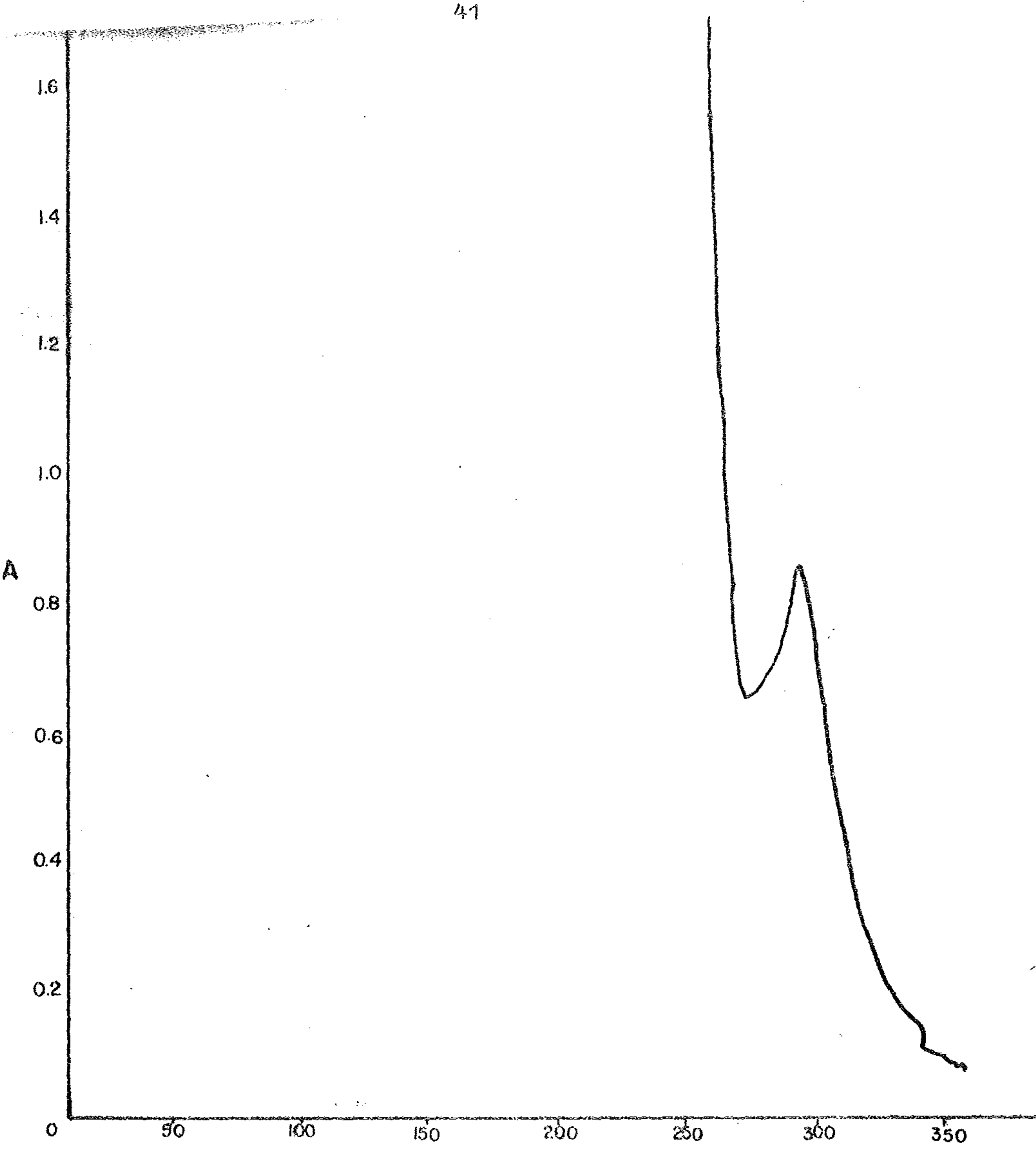


Fig. I. UV. Spectra of $[Co(Py)_4Cl_2]Cl$ (5×10^{-5}M in Ethanol)

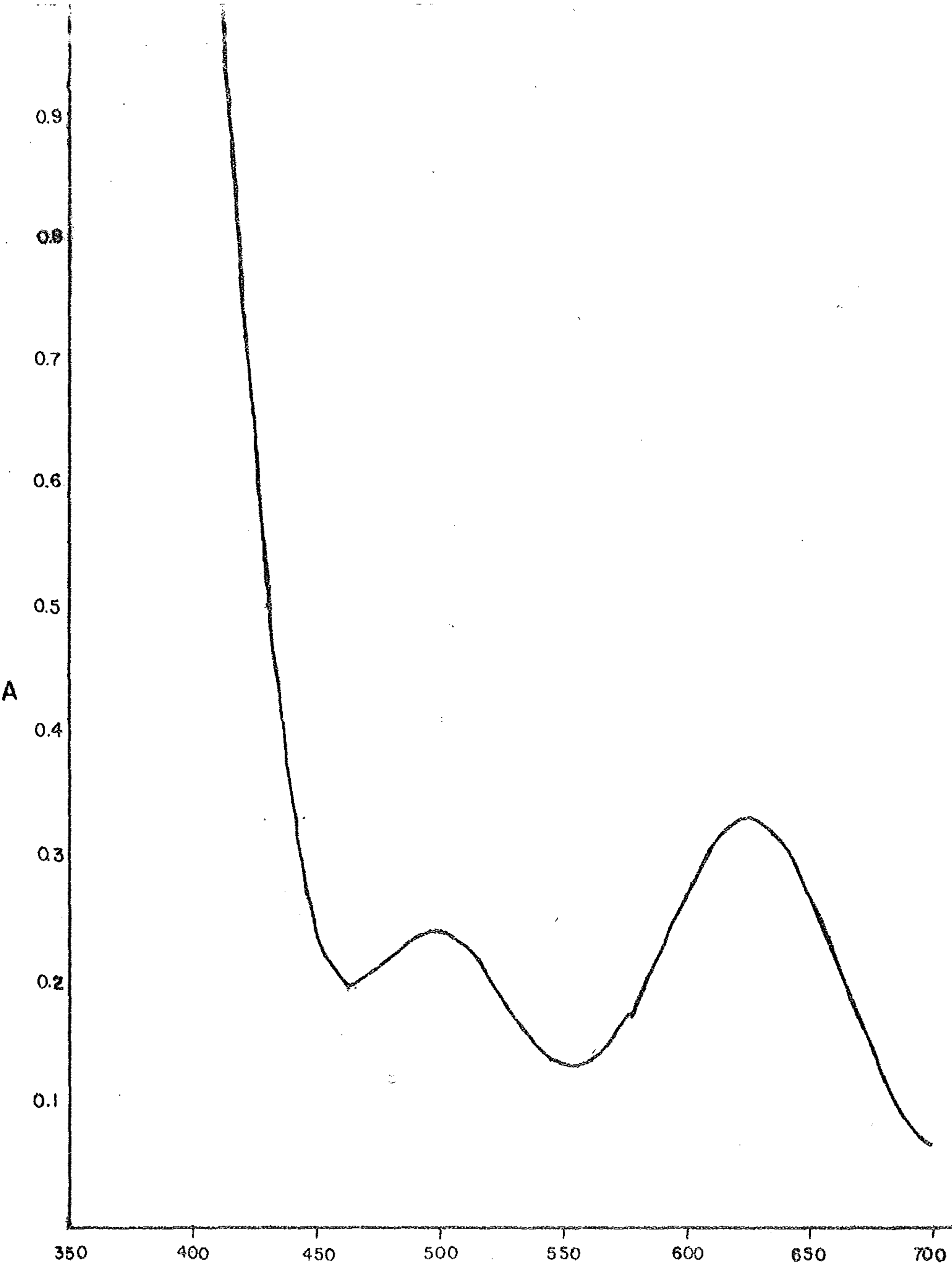


Fig. 2. Visible Spectra of $[Co(Py)_4Cl_2]Cl$ (0.01M in Ethanol)

The splitting Energy (Δo) for complexes $[Co(Py)_6]^{3+}$ is about 275 KJ mol^{-1} [135]. Lower value of Δo for $[Co(Py)_4Cl_2]^+$ compared with that of hexapyridinecobalt(III) complex is expected from theoretical consideration. The dichlorotetrapyridinecobalt(III) complex has the additional weak ligand, chloride, which is directly coordinated with cobalt(III) and which will probably decrease the d-d energy splitting Δo through π - interaction.

This is shown in the following energy level diagram

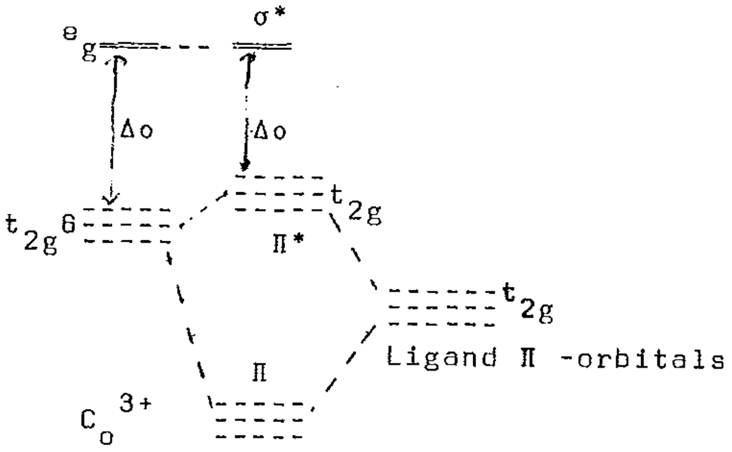


Fig. 3. Energy level diagram for π-interaction

Since the 3p probitals on chloride are filled, these electrons may fill the resultant molecular t_{2g} π-orbitals. The electrons from 3d<t_{2g} orbitals of the cobalt may be in π* orbitals at a higher energy that of π-bonding orbitals. As chloride is a weak ligand, the expected interaction is through p-orbital rather than empty d-orbital of the chloride[140]. This π-inter-

Table 3 Equivalent Conductivity of $[Co(py)_4Cl_2]^+ X^-$ Vs concentration in different solvents

λ $l.Mol^{-1}$ Cm^{-1} Ω^{-1}

CONC.(M)	$X = Cl^-$	$X = NO_3^-$	$X = ClO_4^-$	$X = IO_4^-$	$X = SCN^-$	$X = N_3^-$
	CH_2Cl_2					
10^{-3}	2.2	4.4	6.0	3.6	3.6	3.6
10^{-4}	5.5	7.3	6.6	5.0	6.0	5.2
5.10^{-5}	6.2	9.2	6.9	5.8	6.2	5.8
10^{-5}	8.4	10.4	7.0	6.6	6.6	7.3
5.10^{-6}	8.9	10.8	7.3	8.1	7.0	7.6
10^{-6}	9.1	12.3	7.8	10.1	7.3	7.7
			2- Butanol			
10^{-3}	1.2	1.3	2.7	1.4	2.4	1.0
10^{-4}	2.6	2.7	23.2	21.8	177.0	3.6
5.10^{-5}	22.7	25.9	30.8	26.8	19.6	31.1
10^{-5}	53.2	50.4	46.8	35.0	33.6	39.2
5.10^{-6}	68.0	67.2	50.4	39.2	39.2	44.8
10^{-6}	86.8	84.0	51.0	39.8	42.0	47.6
			Ethanol			
10^{-3}	7.3	11.5	10.9	11.0	9.9	9.0
10^{-4}	34.7	47.0	47.0	31.4	11.0	10.4
5.10^{-5}	45.6	52.9	50.7	37.0	14.0	14.5
10^{-5}	78.4	78.4	54.6	41.2	28.8	31.3
5.10^{-6}	89.6	89.6	58.8	42.3	39.2	43.7
10^{-6}	98.0	106.4	59.0	43.1	42.0	47.6

Table 3 Contd.

Methanol						
M	X = Cl^-	X = NO_3^-	X = ClO_4^-	X = IO_4^-	X = SCN^-	X = N_3^-
10^{-3}	3.8	3.9	5.6	11.0	11.0	4.5
10^{-4}	36.4	31.9	19.8	15.6	16.8	16.7
6.10^{-5}	52.9	51.8	22.7	19.1	20.2	21.4
10^{-5}	90.7	99.1	40.3	33.6	36.4	37.0
6.10^{-6}	100.1	120.4	46.5	34.7	45.4	46.5
10^{-6}	102.0	122.2	62.0	48.2	58.6	61.2
Dimethylformamide						
10^{-3}	4.4	4.2	6.7	13.6	11.0	5.6
10^{-4}	37.5	38.9	30.8	21.8	27.4	21.8
6.10^{-5}	55.2	56.0	39.2	22.7	33.0	30.2
10^{-5}	108.9	121.0	56.0	37.5	39.7	46.7
6.10^{-6}	134.0	139.4	70.0	46.7	46.8	51.2
10^{-6}	173.0	198.8	78.4	51.8	47.6	56.0
Water: Methanol (1:1) (V/V)						
10^{-3}	12	9.2	7.7	6.1	6.1	5.2
5.10^{-4}	18.4	16.8	28.6	10.4	9.8	9.8
10^{-4}	40.0	52.0	49.0	43.0	43.0	46.0
$5,10^{-5}$	92.0	82.0	74.0	64.0	66.0	72.0
10^{-5}	130	85.0	79.0	73.0	69.0	79.0
5.10^{-6}	135	92.0	82	75.0	74.0	81.0

Table: 4 Associat
IO_4^-, SCN^-,

Complex	K_A
$[Co(PY)_4Cl_2]Cl$	1
$[Co(PY)_4Cl_2]NO_3$	1
$[Co(PY)_4Cl_2]ClO_4$	1
$[Co(PY)_4Cl_2]IO_4$	1
$[Co(PY)_4Cl_2]SCN$	1
$[Co(PY)_4Cl_2]N_3$	1

Table:5

Complex
$[Co(PY)_4Cl_2]Cl$ $8.3 \times 10^{-6}M$
$[Co(PY)_4Cl_2]NO_3$ $7.9 \times 10^{-6}m$
$[Co(PY)_4Cl_2]ClO$ $7.33 \times 10^{-6}M$
$[Co(PY)_4Cl_2]IO_4$ $6.28 \times 10^{-6}M$
$[Co(PY)_4Cl_2]SCN$ $7.94 \times 10^{-5}M$
$[Co(PY)_3Cl_2]N_3$ 8.2×10^{-6}

Complex
[Co(Py)$_4$C
[Co(Py)$_4$C
[Co(Py)$_4$C
[Co(Py)$_4$Cl$_2$
[Co(Py)$_4$Cl$_2$

action between chloride and cobalt might also be a cause for the existence of the intense absorption band in ultraviolete region.

The variation of the absorption bands in the visible region might be accounted from the point of solvent separated and contact ion-pairs.

Solvent separated ion-pairs cause a longer wave length while contact ion-pair exhibit shorter wave lengths[136]. The shift in the absorption with counterion has been interpreted in terms of the perturbation of the molecular energy levels by the counterion. In general the formation of solvent separated ion-pairs results an increase in charge delocalization on the anion. The electronic spectra of many large negative ions are particularly solvent sensitive, which has been explained on the basis of extensive delocalization. The association of the cation with the anion perturbs the charge distribution in the latter such that the net dipole is minimized[138]. The shorter wavelength observed in complex salt of azide indicated the association of azide ion in ethanol, solution with the cation. In the ultraviolet region there is no change in position of the absorption bands, but intensity is changed for complexes of various counter-ions. Intensity changes follows the order $SCN^- < NO_3^- < Cl^- < ClO_4^- \cong IO_4^- < N_3^-$, As shown in the table 6. The intensity is larg for azide salt and small for the thiocyanate salt of the complex.

Complex
$[Co(PY)_4Cl_2]Cl$
$[Co(PY)_4Cl_2]NO_3$
$[Co(PY)_4Cl_2]ClO_4$
$[Co(PY)_4Cl_2]IO_4$
$[Co(PY)_4Cl_2]SCN$
$[Co(PY)_4Cl_2]N_3$

The intensity of absorption is dependent upon the differences in the electronic dipolmoments of the ground and excited states[149]. This difference in electronic dipole moment arises because of a different electron distribution in the two states and can be thought of as representing charge migration during the transition. Therefore, the intensity change for complexes of different counterions might be because of changes in the electronic dipole moment of the counterions.

5.1.2. Infra-red

The cobalt(III) pyridine and cobalt(III)-chloride vibrational frequencies are in the range of 344-346 and 380-390 cm^{-1} respectively for the ion-pairs. The νCo-N) stretching vibrational frequency of pyridine is not affected by the presence of counterions. Suggesting that there is no the specific interaction between the ligand pyridine and the counterions. This is supported by the reported[118] data for the complex $[Co(NH_3)_6X_3(X) = ClO_4^-$, NO_3^-, I^-, Br^-, Cl^-). Because of the absence of hydrogen bonding between perchlorate and N-H; observed Shift of N-H stretching frequencies of the perchlorate salt compared with those of free ammonia must be due to the effect of coordination. The other complex salts give lower N-H stretching frequencies than the perchlorate, showing the presence of the effect of hydrogen bonding.

In other reports[119]; metal-pyridine vibrations have been located at lower frequencies than metal-halogen vibrations; ν(m-N) vibrations are strongly dependent on the ligand to which the nitrogen atom is attached, and their frequencies fall of in the order metal-ammonia (420-500cm^{-1}), metal-hydrazine (306----440cm^{-1}), metal-pyridine (200-287 cm^{-1}) for divalent cations, i.e. among other factors, they are influenced by the mass of the ligand. The observed vibrational frequency of cobalt(III)-pyridine in $[Co(Py)_4Cl_2]X$ complex is in the range of 344-346cm^{-1} for various counterions. This shift to higher frequency is due to the higher oxidation number of cobalt.

The vibrational spectra of pyridine ring vibrations are observed at 405 cm^{-1} (out-of plane ring deformation) and at 604cm^{-1} (in-plane-ring deformation). Both absorption bands suffer significant shifts toward higher frequencies on coordination with metals. Thus value of 604--->640cm^{-1} and 405 ----> 465cm^{-1} have been obtained in the complexes of $[Co(Py)_4Cl_2]X$. These results are in close agreement with reported ones.

ν(Co-Cl) vibrational frequencies are different for the different ion-pairs.

For the salts of Cl^-, NO_3^-, N_3^-, ν(Co-Cl) = 385cm^{-1}, while for ClO_4^-, IO_4^-, ν(Co-Cl) = 390cm^{-1} and the salt of SCN^- has shown a stretching frequency of 380cm^{-1}.

These slight variations in ν(Co-Cl) frequency is may be due to ion pairing.

For complexes of trans-dichloro-(o-phnylene bisdimethylarisine)cobalt(III) perchlorate and chloride[88], ν(Co-Cl) is 388 and 384 cm^{-1} respectively. This supports our observation of ν(Co-Cl), stretching frequencies.

Table 8. Infra-red characteristics of the ion-pairs in the complex (cm^{-1}).

NO_3^-		ClO_4^-		IO_4^-	
Found	Lit[123] (KNO_3)	Found	Lit[122] ($NaClO_4$)	Found	Lit[122] ($NaIO_4$)
825	828	625	625	853	791
785	716	928	865	320	325
1630	1630	1119	1100		

SCN^-		N_3^-	
Found	Lit[125] (KSCN)	Found	Lit[124] (NaN_3)
2060	2055	2100	2080
748	754	1230	1240

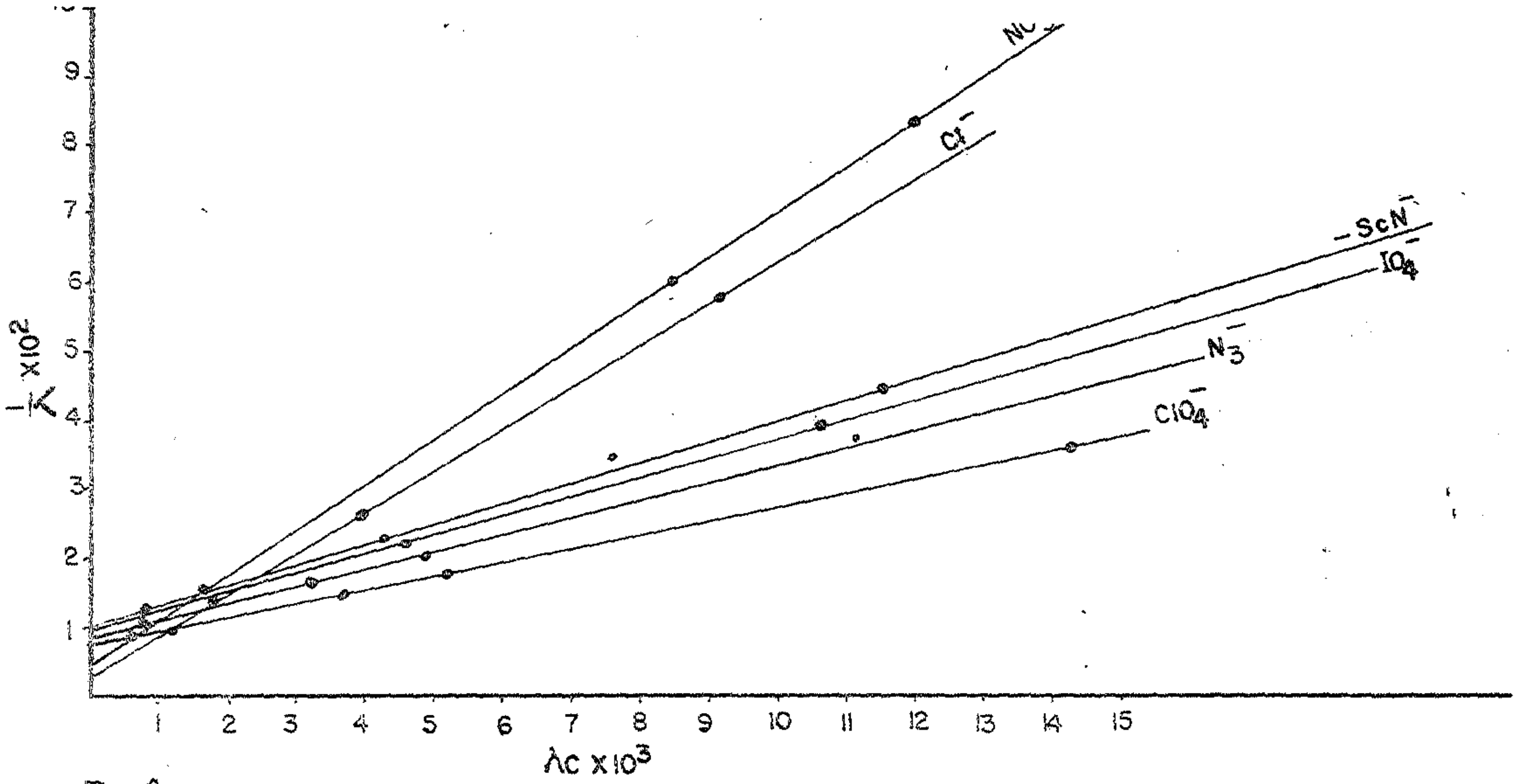


Fig. 4

$\frac{1}{\lambda}$ Vs λc for Determination of λ_0 and K_A in H_2O - Methanol (1:1) (V/V)

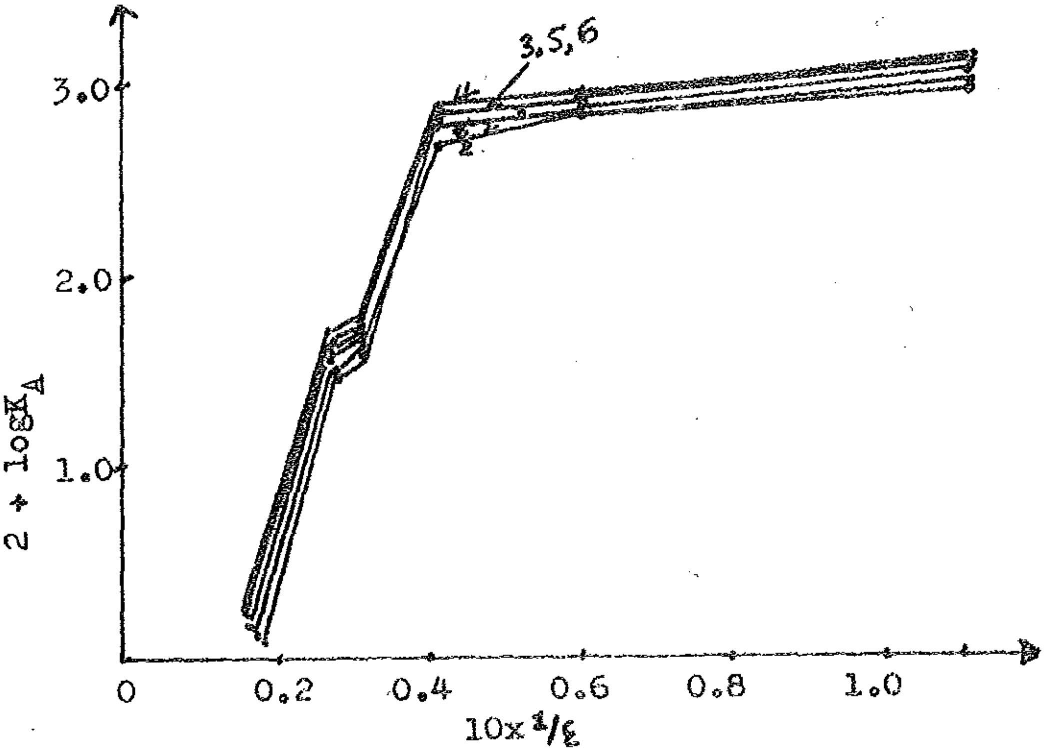


Fig. 5 . The effect of the dielectric constant of the solvent (dichloromethane, 2-buthanol, ethanol, methanol, dimethylformamide, 1:1(v/v) methanol-water mixture) on association constant of the comple $[Co(py)_4Cl_2]X$ (for x: 1=Cl^-, 2=NO_3^-, 3=ClO_4^-, 4=IO_4^-, 5=SCN^-, 6=N_3^-).

The shift in the characteristic frequencies of the ions such as NO_3^-, ClO_4^- and IO_4^- have been observed (Table 8). This result is in good agreement with the observed conductance data particularly for salts of ClO_4^- and IO_4^- complexes as shown in Table 4.

5.2. Conductance and Association in Non-Aqueous Solutions

Generally the conductivity of non-aqueous solutions is lower than that of the corrosponding aqueous solutions. It is quite clear that the greater electrostatic interaction between ions, lowers the degree of dissociation. The factors which contribute to ionic dissociation or association are ionic size, dielectric constant of the medium and specific ion-solvent interaction.

In the complex $[Co(Py)_4Cl_2]X$, the association constants (K_A) and equivalent conductivity at infinite dilution (λo) determined in different solvents are given in Table:4 and 7. As shown in tables 4 and 7, association constants and equivalent conductivities at infinite dilution (λo) vary systematically with the dielectric constant of the solvent. The K_A values of the complexes have the following order with respect to solvent.
dichloromethane › 2-buthanol › ethanol › methanol › dimethylformamide › 1:1 (v/v) (water-methanol) mixture. This is increasing order of dielectric constant of the solvent; the value of λovary in the order of dielectric constant. This shows that, at lower dielectric constants

the electrostatic interaction between cations and anions increases. But for complexes of different counterions, we obtained different K_A and $\lambda_\circ$ values. This may not be explained simply interms of dielectric constant of the medium. The ion association is not merely dependent on the dielectric constant of the medium.

As shown in Fig. 5 there is no linear relationship between logarithm of K_A and the reciprocal of the dielectric constant of the medium, since complexes differed from each other by counterions which have different tendencies towards the solvent. So, the variation of K_A can be accounted interms of size of anion, specific interaction of cation-anion with the solvent, besides the dielectric constant of the medium. The observed dissociation constants are in good agreement with the following explanations. Solvation is enhanced by alcohols due to the strong interaction with the bond pairs of the hydroxyl group. The higher association values for the larger anion, periodate is due to its high polarizability by the cation. The result observed for periodate counterions in 1:1 (methanol:H_2O) (v/v) mixture is interesting, because the K_A value is lowered than that of other counterions when compared in pure organic solvents. This might be due to hydrogen bonding between IO_4^- and H_2O of the solvent as shown in Fig. 9. This may form solvent separated ion-pairs which is the cause for greater dissociation as compared with other organic solvents.

On the other hand, water-methanol mixed solvents have different dielectric constants from that of pure water and methanol, which may introduce[134] variations in:

a. the free volume ion solvent interaction.
b. the nature of the solvent molecules surrounding the ions and ion-pairs, and also,
c. the preferential solvation by the solvent having greater dipole fields.

Therefore all these factors may be encountered in methanol-water mixtures. Thus the solvation by water is higher than that of methanol.

The greater dissociation in organic solvents for Cl^- and NO_3^- counterions in protic solvents such as 2-buthanol, ethanol, methanol and dimethylformamide are suggested as solvent-ion separation frpm hydrogen bonding between anion and solvent[118], while in the case of perchlorate salt hydrogen bonding between ClO_4^- and solvents is weak.

5.3. Rates of equation of complexes $[Co(Py)_4Cl_2]$ X (X = Cl^-, NO_3^-, ClO_4^-, IO_4^-, SCN^-, N_3^-)

The reaction in aqueous solution, even in the presence of some anions, is usually solvolytic aquation. The kinetics of this aquation reaction is reported as first order in the complex

$$[Co(NH_3)_5X]^{+2} + H_2O \dashrightarrow [Co(NH_3)_5(H_2O)]^{+3} + X\ (Cl^-,\ Br^-,\ NO_3^-)^{143} \qquad (35)$$

The exchange of the chloride ion with chlorine in $[Co(en)_2Cl_2]^+$ takes place too slowly to compete with aquation[143,144].

In the reaction:

$$[Co(en)_2(x\text{-}Py)Cl]^{+2} + H_2O \dashrightarrow [Co(en)_2(x\text{-}Py)(H_2O)]^{+3} + Cl^-$$

the expected bond between metal and anion would be broken more readily if electron density were increased on the metal[66,145]. Electron donating ligands should therefore assist the replacement of the ligand. It is found that the basicity of the substituted pyridine does increase the rate of the reaction since it increases the electron density on the metal. Increasing the total negative charge on the complex facilitate the reaction, since departure of the leaving group is facilitated. If the reaction is associative, increasing the negative charge would be expected to repel the incoming ligand.

In general the rate of reactions in which ionic charges increase or decrease into a smaller space during passage through the transition state increase the polarity of medium surrounding the reactants and the activated complex. Reactions in which ionic charges are formed or disappear during passage through the transition state are strongly influenced by the solvent[106].

The acceleration or retardation of the aquation reaction is because of the difference in the stabilization of the starting materials and the activated complex by solvation if the:

a) activated complex is solvated in a given solvent, the enthalpy of activation is reduced, which may accelerate the rate of reaction;

b) starting materials are solvated, the enthalpy of activation is increased which may retard the rate of reaction.

Therefore, the rate of reaction is determined by the differences between the two ethalpies of solvation.

It is known that, solvation can increase the order of the molecular species which may decrease in the entropy; this can reduce the free motion of both reactants and solvent molecules, Molecules of the polar solvents exhibit a high degree of orientation even in the absence of dissolved polar substances, owing to strong interaction between the molecules. Those of non-polar solvents are ordered to a small extent. Therefore, the greater values of entropy of activation may retard the reaction.

Rates of aquation of $[Co(Py)_4Cl_2]$ X were followed by UV at their corresponding wavelength λ_{max} at room temperature, without adjusting the ionic strength (ionic strength has no effect on the rate of aquation[96]).

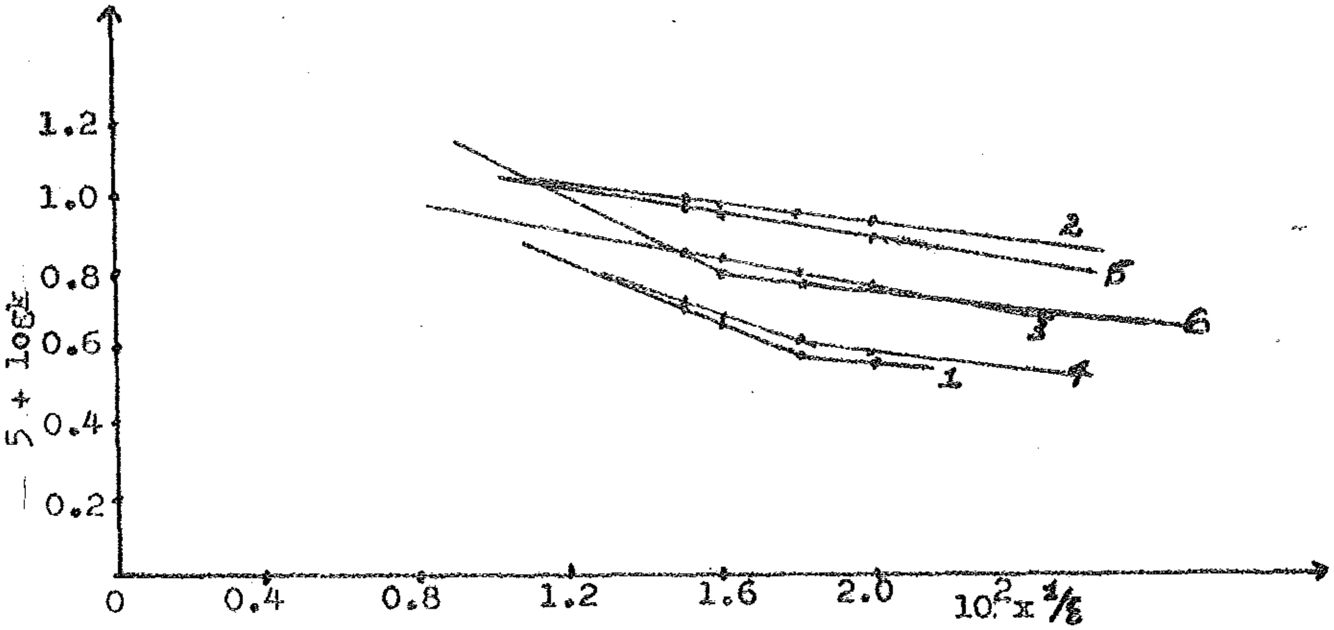


Fig. 6. The effect of dielectric constant of the ethanol-water mixture
rate of aquation of the complex $[Co(py)_4Cl_2]X$ (for x: 1=Cl^-, 2=NO_3^-, 3=ClO_4^-, 4=IO_4^-, 5=SCN^-, 6=N_3^-).

The results are given in table 5.

The rate of aquation of these complexes are first order and obeys the S_N1 reaction mechanism.

$$[Co(Py)_4Cl_2]^+ \underset{\text{slow}}{=\!=\!=} [Co(Py)_4Cl]^{+2} + Cl^- \qquad (36)$$

$$[Co(Py)_4Cl]^{+2} + H_2O \text{----}\rangle [Co(Py)_4(H_2O)Cl]^{+2} \qquad (37)$$

In this reaction the release of chloride is estimated by a chloride sensitive electrode using standard method known as Grans plot[131]. Plots of $(V_x + V_s)_{10}E/S$ versus Vs (where: E = change of potentials after addition of standard solution, V_s = volume of standard, V_x = volume of sample, S = Nernest slope) gives a straight line which intercepts the abscisaa for a value of Vs called Vs where CxVx = CsVs. Thus Cx can be evaluated since Vs, Vx and Cs are known. (Table 9).

5.3.1. Effect of dielectric constant of the medium

The plots of logarithms of rate constant versus the reciprocal of the dielectric constant in ethanol-water mixed solvents give some linear curves (Fig. 6). This suggests that there is a change in rate of aquation with respect to dielectric constant of the medium. The solvolysis rate is higher in media of higher dielectric constant indicating that the rate-determining step of the reaction depends to some extent on the ionizing power of the medium.

Table;9 Chloride Sensitive Electrode Potential reading of $[Co\ (Py)_4Cl_2]^+\ X^-$ Vs time (minutes)

Potential (mV)

Time(min)	$X = IO_4^-$	ClO_4^-	N_3^-
0	301	313	290
30	289	306	260
60	280	304	250
90	270	289	245
120	268	280	241
150	264	263	240
180	262	260	237
210	260	259	235
240	259	256	234
270	258	254	234
300	258	253	234
330	257	253	234
360	256	253	234
390	256	253	234
420	256	253	234

Hydrogen bonding may exist between water and ethanol which may give rise to an increased basicity of the hydroxyl oxygen of the water. Therefore the solvation by water-ethanol mixed solvent may reduce the activation energy of the reactions. Thus the positive charge on the metal ion would diminish as a result of the interaction with the solvent which would facilitate the extension of the metal-chlorine bond. This extension is expected to be enhanced as the basicity and the dielectric constant of the medium are increased[150].

But in 1:1 (v/v) (organic to aqueous) mixed solvents containing t-butanol, iso-propanol,, ethanol,and methanol the plot of logarithms of rate constant versus the reciprocal of the dielectric constant do not show any liner relationship (Fig. 8). This result was expected, because the change of the solvent may cause change in the structure of the water, and hence change in solvation of the ground and transition states due to the difference in magnitude of the charge on both states[146].

The variation of rate constant with the dielectric constant for mixed aqueous solvents has been used as an indication of the dissociative or associative character of the rate determining step. We used the approach of Grunwald-Winstein[81] solvent Y values to discuss the rate variation with solvent. The correlation of rate constants

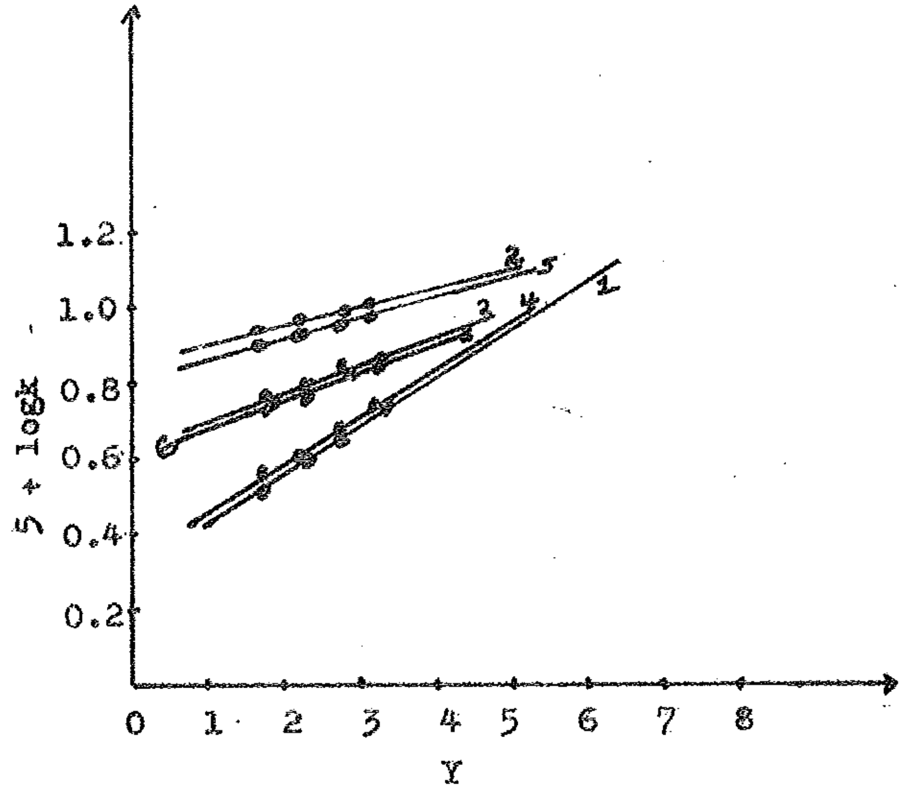


Fig. 7 . Correlation of the first order rate constant (k) for aquation of the complex $[Co(py)_4Cl_2]X$ (for x: 1=Cl^-, 2=NO_3^-, 3=ClO_4^-, 4=IO_4^-, 5=SCN^-, 6=N_3^-), in aqueous-ethanol mixed solvent with Y values.

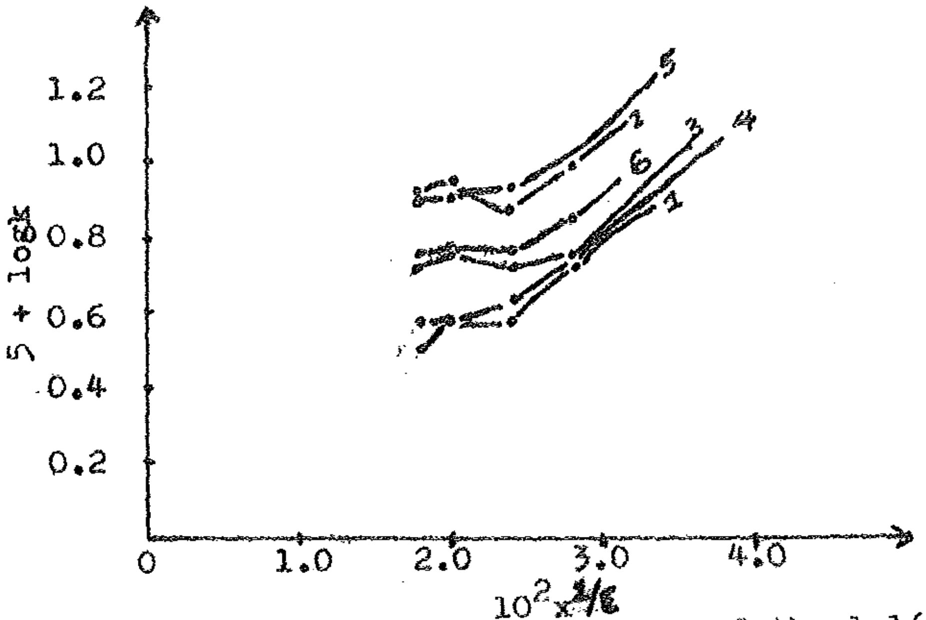


Fig.8. The effect of dielectric constant of the 1:1(v/v) organic solvents (methanol, ethanol, isopropanol, t-buthanol)-water mixture on the rate of aquation of the complex $[Co(py)_4Cl_2]X$(for x:1=Cl^-, 2=NO_3^-, 3=ClO_4^-, 4= IO_4^-, 5=SCN^-, 6=N_3^-).

of metal-water bonds in the transition state; and hence incoming water molecule to metal bond would be enhanced in weaker polar organic solvents. The extent of approach of water to metal in different polar organic solvents is different. This is because of differences in polarity and structure of the organic solvents; thus a linear correlation with respect to dielectric constant of the mixed medium is not also expected.

Anions are preferentially solvated by solvents if hydrogen bonding is possible between them. The low rate of aquation of $[Co(Py)_4Cl_2]IO_4$, may be due to hydrogen bonding between IO_4^- and H_2O, as shown in the reaction scheme shown[139] in Fig. 9.

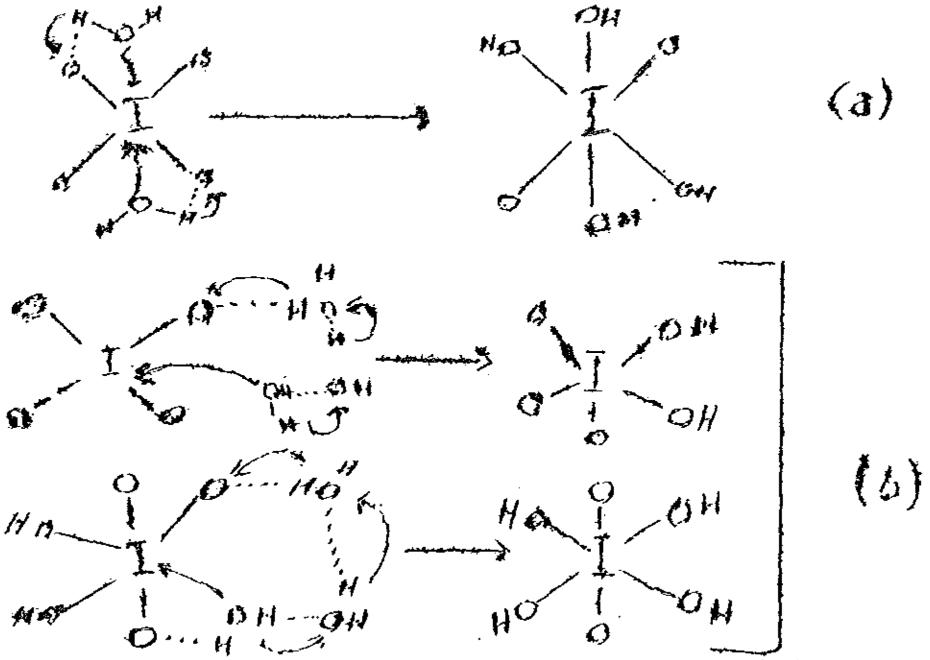


Fig. 9. Schematic representation of (a) the one-step and (b) the two-steps mechanism for aquation of IO_4^- to $IO_2(OH)_4^-$, Dotted lines represent hydrogen bonding.

The different steps of the reaction between IO_4^- and H_2O may retard the rate of the aquation reaction.

Similarly because of greater solvation of chloride by water the rate if aquation for the chloride salt is comparable with that of the periodate. The rest of complex salts, are accounted interms of electrochemical series. Thus SCN^- and NO_3^- with greater rate of aquation since, they are weak ligands, while ClO_4^- and N_3^- are with low rate of aquation.

5.3.2. Ion-pair rate coefficient

The ion-pair rate coefficient (kip) was derived according to the equation[148].

$$K_{obs} \cdot C = k_1(c-[CPXL]) + K_{ip}\ [CPXL] \qquad (13)$$

c = constant from quadratic eqn. which is approximated to zero.

where k_{obs} is the observed pseudo - first order rate constant.

k_1 is the rate constant of the aquation of the starting complex in aqueous solution.

C is the stoichiometric concentration of complex salt and CPXL is initial concentration of the ion pair (CPXL). CPXL was estimated from the approximate dissociation constants which were obtained from conductivity measurements. Since the conductivity measurement was strongly dependent on factors like ionic size, dielectric constnat of the medium, specific interaction between solute and solvent, etc, the value of k_{ip} can be assumed to be only approximate.

The various values of k_{obs}, k_{ip} were obtained from measurement in a 1:1 (v/v) methanol-water mixture.

Table 10. Values of rate coefficients k_{obs} and ion pair rate coefficient in 1:1(v/v) methanol-water mixture

Salt	10^4[CPXL]	$k_{obs} \times 10^5$	$k_{ip} \times 10^5$
Chloride	1.867	3.18	3.32
Nitrate	1.896	8.56	3,54
Perchlorate	1.370	5.72	3.49
Periodate	1.655	3.71	3.32
Thiocyanate	1.371	7.89	3.64
Azide	1.410	5.78	3.51

As shown from k_{ip} values in table 10; slightly larger rates of aquation were observed in the thiocyanate, nitrate salts while lower rates of aquation for chloride and periodate salts. The slight increase with the rate of aquation for thiocyanate and nitrate ion may be due to the lower stability of the ion-pair as compared to other salts.

5.4. Nucleophilicity of the Counter Ions

Nucleophilic order of the counter ions were determined by the use of Titanium Selenite Ion-Exchanger for the complex $[Co(Py)_4Cl_2]X$.

The inorganic polymer, Titanium selenite[147] contains an exchangable hydrogen ion and high selectivity towards Pb^{2+}.

After shaking the mixture of sample (1 mol) and the inorganic polymer (0.1g) for 18hrs. (was mot completely adsorbed) the supernatant was filtered and titrated with standard 0.1N NaOH in the presence of phenolphthalein. Results are given in Table 11.

Table 11. The meq/g of exchanged hydrogen on Titanium Selenite.

Salt	meq/g
SCN^-	100
NO_3^-	80
Cl^-	75
ClO_4^-	70
IO_4^-	63
N_3^-	60

As shown in table 11 there might be stronger interaction between N_3^- and the complex ion, and weak interaction between SCN^- and the cpmplexion.

The $[Co(Py)_4Cl_2]SCN$ complex was observed to decompose at room temperature after about three months from the date of preparation. This was evidenced by the change of vis-absorption in ethanol (Absorbance 0.288---> 0.182), a colour change from green to light blue and a smell of pyridine. This unstability of the complex is due to the less tendency of the thiocyanates to penetrate the inner sphere. As reported in the literature[78,141] basic anions such as CH_3COO^-, OH^-, OH^-, F^-, N_3^- can penetrate the central cation in a complex which increases the stability of the inner sphere, whereas the, SCN^- and NO_3^- were considered to be weak bases and less able to penetrate the inner sphere of the complex. All the above observations are consistent with the proposed order of nucleophilicity of the counter ions.

5.4.1. IR Analysis of adsorbed molecules

The nucleophilic order of the counterion was determined by using titanium selenite inorganic polymer. This was evidenced by the decreased intensity of the OH peak in the adsorbant molecule. The possible interaction between the polymer and the complex could be electrostatic.

$$\text{Polymer} - OH + [Co(Py)_4Cl_2]X \text{---}> \text{polymer-O-Complex} + HX. \qquad (38)$$

The vibrational spectra of inorganic polymer shows the broad peak near 3400cm^{-1} which is characteristics of the -OH stretching frequency. This vibrational frequency almost disappeared due to the adsorption of the complex on the polymer. The existence of the complex ion on the inorganic polymer was further evidenced from the presence of the characteristic peaks that can be attributed to the complex such as ν(Co-N) at 340-350cm^{-1} and ν(Co-Cl) at 380-390cm^{-1} and pyridine ring vibrations in the range of 650 and 470cm^{-1}.

Additional evidence of adsorption of the complex on the inorganic polymer was obtained from recovering back the complex from the polymer. The adsorbed complex on the inorganic polymer was mixed with 2M solutions of the appropriate acid (HCl, HNO_3, $HClO_4$, HIO_4) in order to regenerate the different salts, and left for about 16 hours. The residue was then separated by filtration and washed several times with water and then the complex was eluted using 5ml of ethanol. The ethanol solution was strongly sensitive at 298nm. The results are shown in table 12.

Table 12. UV absorbance of the ethanol washings at corresponding wavelength.

Salt	A	Concentration (M)x104
NO_3^-	1.868	2.25
Cl^-	1.857	1.74
ClO_4^-	1.621	1.38
IO_4^-	1.120	0.94

The results shown in Table 12 support the suggested nucleophilic order of the counterions. The adsorption of the complex was shown by UV absorption; which indicated that the complex existed as ion-pairs. This was further shown by the IR spectra of the recovered complexes which contained the characteristic peaks. This is probably, because the complex is octahedral and fulfils the eighteen electron rule. If the cobalt(III) from complex forms interaction with the polymer, the symmetry of the complex will be disturbed and forms less stable geometrical configuration of the complex.

As shown in the literature[153] for the complex $Cr(acac)_3$, the central metal was highly screened and adsorption on silica gel was assumed to be through strong interaction with the carbonyl group. This situation may be selective in our case with the only weak interactions between the Co(III) ions and the inorganic polymer.

6. Conclusion

From forgoing research the following conclusions have been drawn.

1. The complex $[Co(Py)_4Cl_2]^+X^-$ is strongly sensitive in UV region. This complex is assumed to be a low spin complex from two absorption bands of visible region.
2. The complexes have a stretching frequencies of 380-390 and 345-346 cm^{-1} for cobalt-chloride and cobalt-nitrogen respectively.
3. The association constant is in reasonable trend with respect to change of dielectric constant of the medium.
4. The rate of aquation of the complex is dependent with dielectric constant of the medium, and indicates that the rate determining step of the reaction depends to some extent on the ionizing power of the medium.
5. Slight variations of rate constants are observed when counterions are varied.
6. The rate of aquation of the complexes obey the dissociative mechanism.
7. The nucleophilic order of the counterions are assumed to be:

   $N_3^- > IO_4^{--} > ClO_4^- > Cl^- > NO_3^- > SCN^-$

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Appendix

Absorbance Vs time for (Co (py) $_4$Cl$_2$)$^+$X$^-$ in water co-solvents:

Ethanol-water (20:80) V/V)

Absorbance

Time (min)	Cl^-	NO_3^-	ClO_4^-	IO_4^-	SCN^-	N_3^-
0	0.414	0.383	0.445	0.345	0.274	0.433
30	0.304	0.375	0.435	0.331	0.255	0.403
60	0.397	0.368	0.428	0.321	0.245	0.384
90	0.389	0.360	0.420	0.311	0.237	0.368
120	0.381	0.352	0.410	0.302	0.230	0.354
150	0.372	0.343	0.401	0.294	0.224	0.342
180	0.362	0.334	0.392	0.286	0.219	0.331
210	0.353	0.325	0.383	0.278	0.214	0.320
240	0.344	0.317	0.374	0.270	0.209	0.310
270	0.335	0.309	0.365	0.262	0.205	0.300
300	0.327	0.301	0.357	0.255	0.201	0.290
330	0.319	0.293	0.349	0.248	0.197	0.281
360	0.311	0.285	0.341	0.241	0.193	0.272

Ethanol- water (30:70) (V/V)

Time(Min)	Cl^-	NO_3^-	ClO_4^-	IO_4^-	SCN^-	N_3^-
0	0.454	0.315	0.415	0.488	0.270	0.204
30	0.442	0.304	0.404	0.478	0.249	0.193
60	0.434	0.294	0.392	0.470	0.239	0.183
90	0.425	0.284	0.382	0.462	0.220	0.173
120	0.415	0.274	0.372	0.453	0.208	0.168
150	0.404	0.264	0.362	0.443	0.200	0.163
180	0.394	0.254	0.352	0.433	0.194	0.158
210	0.384	0.244	0.342	0.423	0.188	0.154
240	0.374	0.234	0.332	0.413	0.183	0.149
270	0.364	0.225	0.322	0.403	0.178	0.145
300	0.353	0217	0.312	0.394	0.173	0.141
330	0.344	0.209	0.303	0.385	0.169	0.137
360	0.334	0.202	0.294	0.376	0.165	0.133

Ethanol-Water (40:60) (V/V)

Absorbance

Time(Min) X=	Cl^-	NO_3^-	ClO_4^-	IO_4^-	SCN^-	N_3^-
0	0.482	0.337	0.345	0.293	0.388	0.247
30	0.466	0.329	0.333	0.283	0.332	0.227
60	0.451	0.321	0.325	0.275	0.305	0.215
90	0.437	0.314	0.317	0.267	0.288	0.207
120	02423	0.306	0.309	0.258	0.274	0.199
150	0.409	0.297	0.300	0.250	0.263	0.192
180	0.396	0.288	0.290	0.243	0.253	0.185
210	0.383	0.279	0.280	0.336	0.243	0.179
240	07372	0.271	0.271	0.229	0.233	0.172
270	0.361	0.262	0.262	0.222	0.223	0.166
300	0.350	0.255	0.254	0.215	0.214	0.160
330	0.340	0.247	0.246	0.209	0.205	0.154
360	0.330	0.240	0.239	0.203	0.196	0.148

Ethanol-Water (50:50) V/V)

Absorbance

Time(Min) X=	Cl^-	NO_3^-	ClO_4^-	IO_4^-	SCN^-	N_3^-
0	0.516	0.390	0.534	0.229	0.478	0.278
30	0.506	0.376	0.518	0.220	0.408	0.250
60	0.495	0.362	0.503	0.210	0.369	0.232
90	0.482	0.348	0.484	0.199	0.343	0.217
120	0.468	0.333	0.465	0.186	0.321	0.204
150	0.454	0.318	0.446	0.173	0.303	0.189
180	0.440	0.303	0.428	0.160	0.286	0.176
210	0.426	0.290	0.410	0.148	0.272	0.164
240	0.412	0.277	0.392	0.136	0.261	0.154
70	0.398	0.265	0.374	0.124	0.250	0.146
00	0.384	0.253	0.357	0.112	0.240	0.138
30	0.370	0.241	0.341	0.101	0.232	0.130
60	0.356	0.229	0.325	0.090	0.225	0.123
90	0.342	0.218	0.309	0.079	0.218	0.116
420	0.328	0.207	0.294	0.069	0.211	0.109
450	0.315	0.197	0.279	0.060	0.206	0.103
480	0.303	0.187	0.265	0.052	0.201	0.097
510	0.291	0.178	0.252	0.044	0.196	0.092

2p Propanol-Water (50:50) (V/V)

Absorbance

Time(Min) X=	Cl^-	NO_3^-	CLO_4^-	IO_4^-	SCN^-	N_3^-
0	0.535	0.324	0.374	0.189	0.250	0.242
30	0.522	0.311	0.358	0.180	0.220	0.220
60	0.508	0.301	0.349	0.172	0.193	0.212
90	0.492	0.291	0.338	0.164	0.177	0.204
120	0.475	0.281	0.328	0.157	0.165	0.197
150	0.458	0.271	0.317	0.150	0.157	0.190
180	0.442	0.261	0.306	0.143	0.149	0.183
210	0.426	0.251	0.295	0.137	0.144	0.177
240	0.410	0.241	0.285	0.131	0.139	0.170
270	0.394	0.231	0.275	0.126	0.135	0.164
300	0.378	0.222	0.265	0.121	0.132	0.158
330	0.363	0.213	0.255	0.116	0.131	0.152
360	0.348	0.205	0.245	0.111	0.129	0.146
390	0.333	0.197	0.236	0.106	0.127	0.140
420	0.319	0.189	0.227	0.101	0.125	0.136
450	0.306	0.181	0.218	0.096		
480	0.293	0.174	0.210			
510	0.280	0.167	0.202			

t- Buthanol-Water (50:50) V/V)

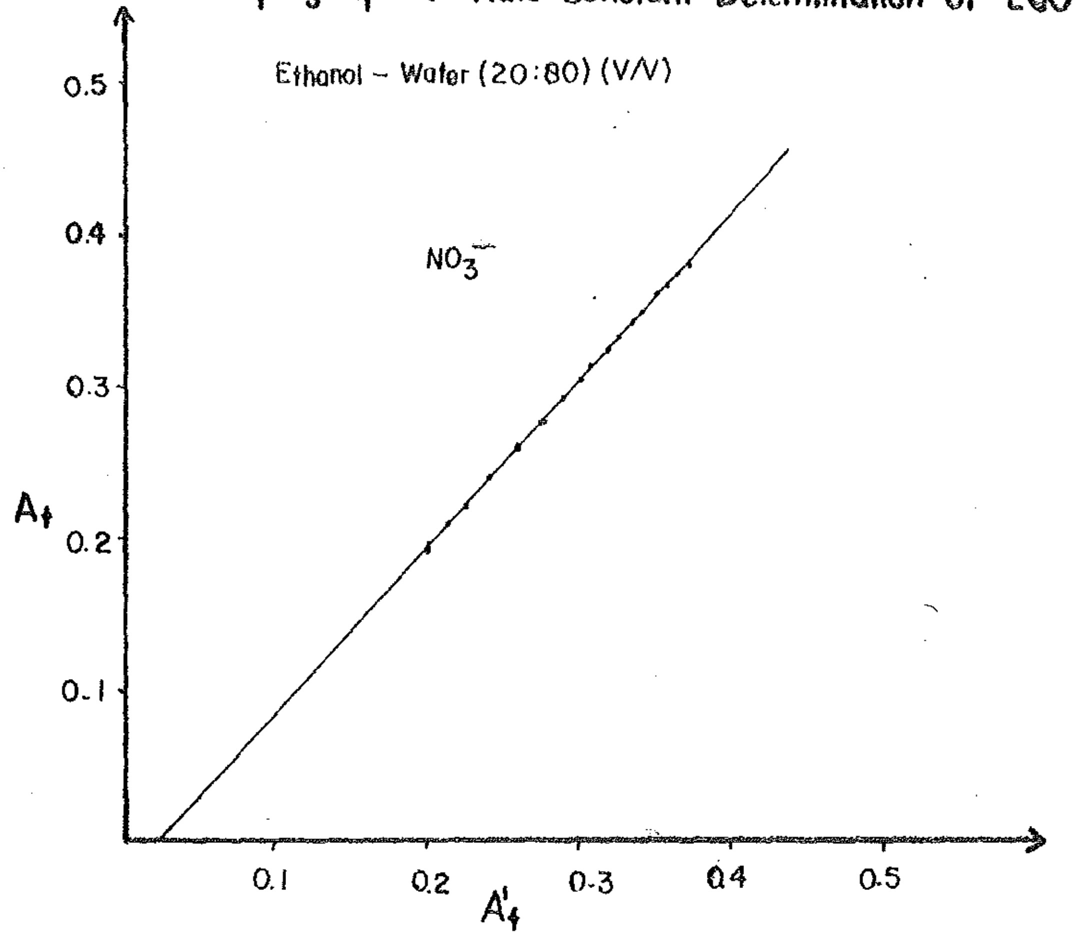
Time(Min) X=	Cl^-	NO_3^-	CLO_4	IO_4^-	SCN^-	N_3^-
0	0.560	0.418	0.537	0.564	0.248	0.366
30	0.541	0.406	0.516	0.555	0.214	0.338
60	0.521	0.397	0.498	0.549	0.194	0.326
90	0.502	0.387	0.486	0.549	0.182	0.314
120	0.485	0.376	0.469	0.535	0.172	0.304
50	0.469	0.365	0.452	0.528	0.162	0.294
180	0.454	0.354	0.435	0.522	0.152	0.285
210	0.439	0.343	0.420	0.516	0.142	0.275
240	0.424	0.332	0.405	0.510	0.133	0.266
270	0.410	0.321	0.390	0.504	0.125	0.258
300	0.396	0.310	0.375	0.498	0.118	0.249
330	0.383	0.300	0.360	0.492	0.112	0.240
360	0.370	0.290	0.345	0.486	0.106	0.231

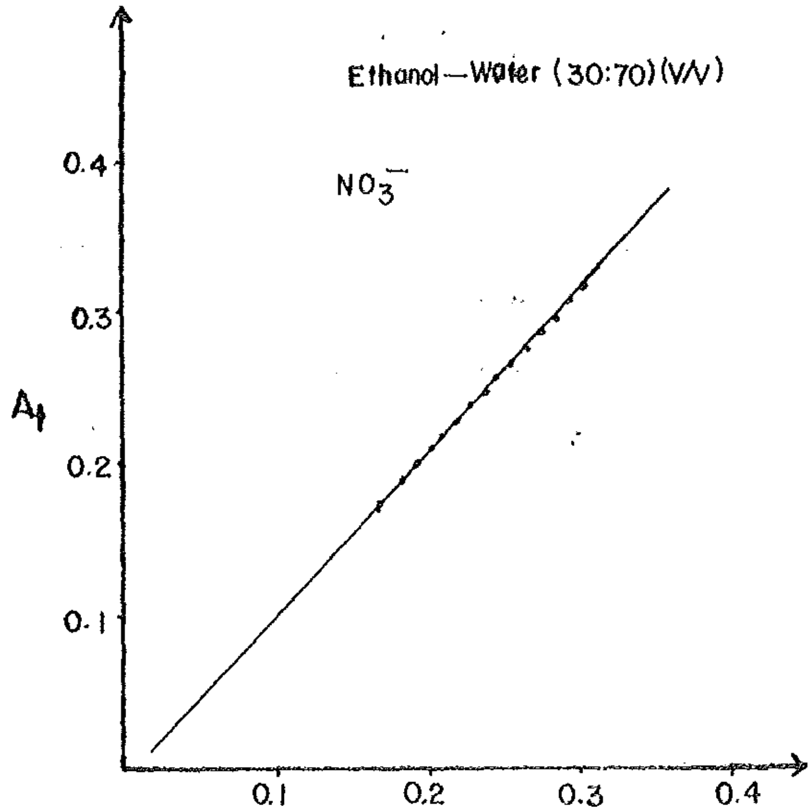
Methanol - Water (50:50) (V/V)

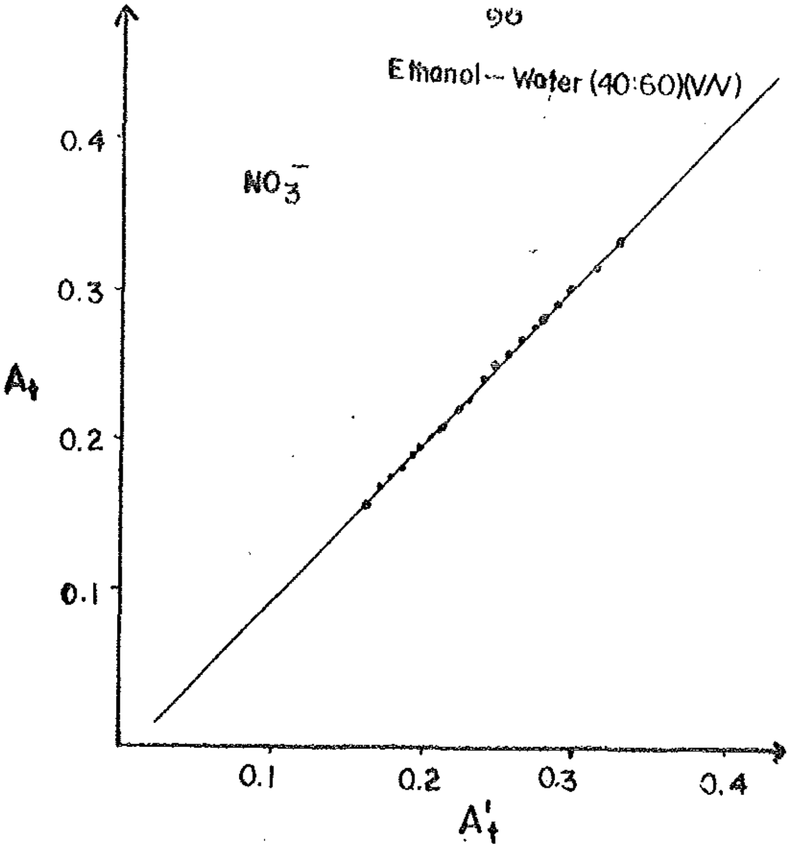
Time(min)	X = Cl^-	NO_3^-	ClO_4^-	IO_4^-	SCN^-	N_3^-
0	0.505	0.451	0.468	0.350	0.220	0.244
30	0.491	0.413	0.433	0.306	0.204	0.200
60	0.479	0.391	0.408	0.281	0.194	0.182
90	0.468	0.371	0.387	0.260	0.184	0.171
120	0.454	0.353	0.368	0.243	0.179	0.161
150	0.441	0.337	0.350	0.228	0.175	0.146
180	0.427	0.322	0.332	0.213	0.170	0.133
210	0.414	0.307	0.316	0.200	0.165	0.121
240	0.400	0.293	0.301	0.187	0.162	0.111
270	0.387	0.281	0.286	0.175	0.157	0.102
300	0.374	0.269	0.271	0.165	0.152	0.093
330	0.361	0.256	0.256	0.155	0.157	0.085
360	0.348	0.244	0.241	0.145	0.152	0.078
420	0.335	0.233	0.226	0.135	0.147	0.072
450	0.324	0.223	0.211	0.128	0.143	0.066
480	0.313	0.213	0.196	0.121	0.139	0.061
510	0.302	0.203	0.183	0.114	0.135	0.056
540	0.291	0.192	0.173	0.106	0.131	0.051
570	0.280	0.184	0.164	0.100	0.128	0.047
600	0.270	0.176	0.155	0.094	0.125	0.043

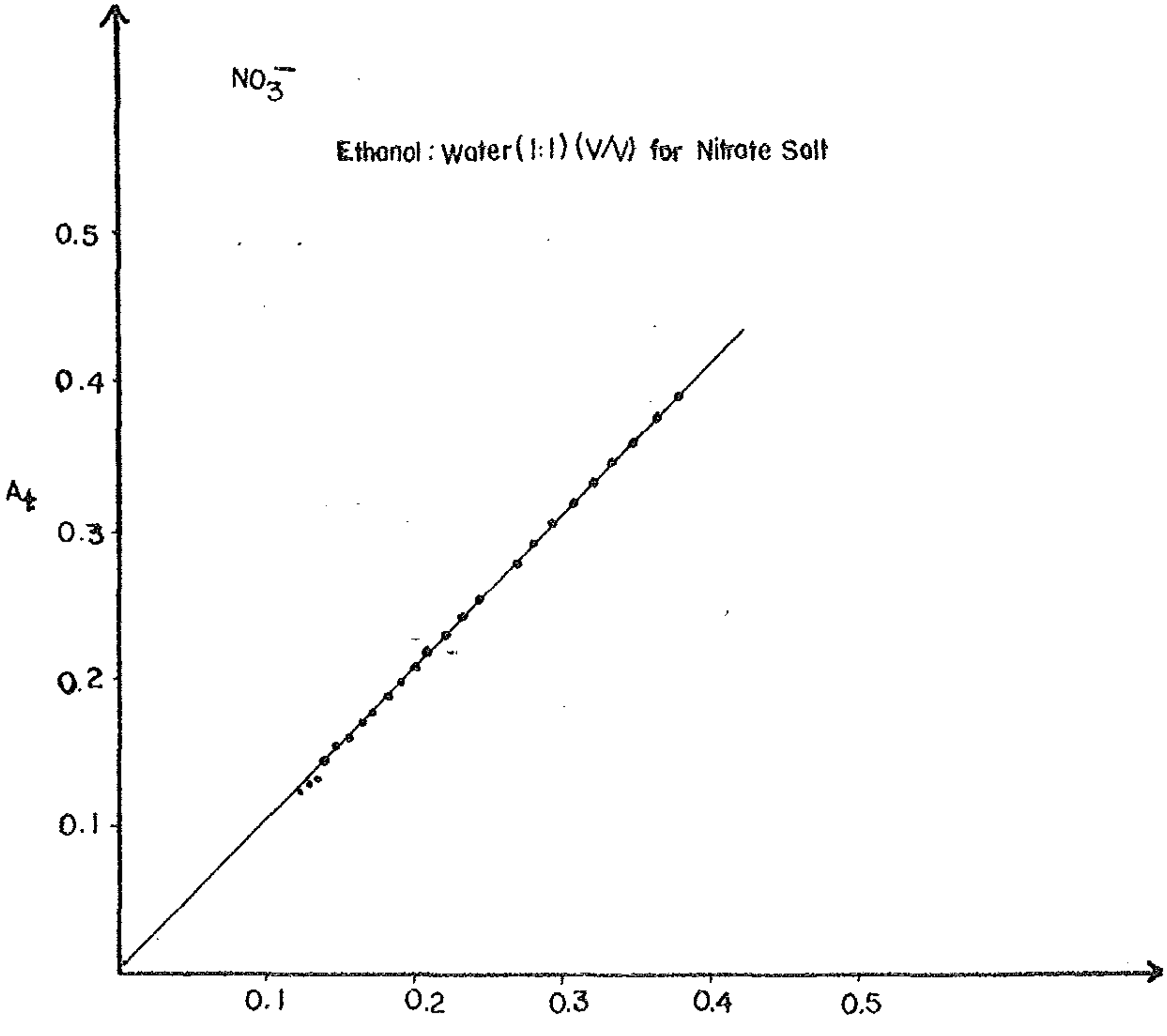
APPENDIX-2

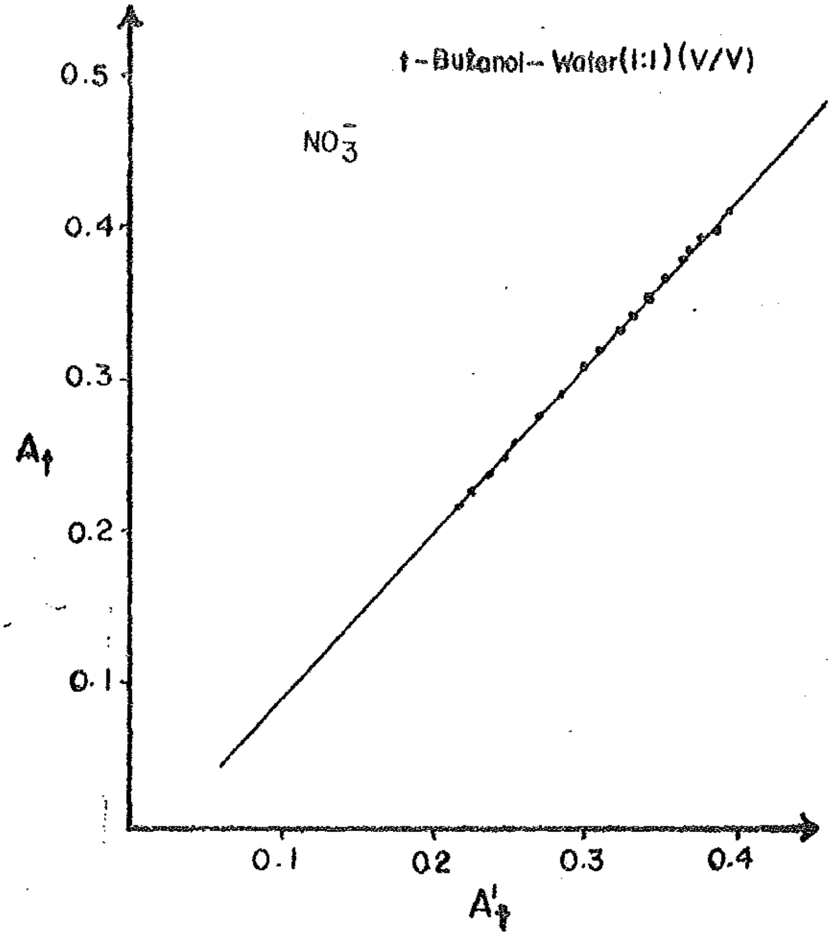
A_t Vs A'_t for Rate Constant Determination of $[Co(Py)_4Cl_2]NO_3$



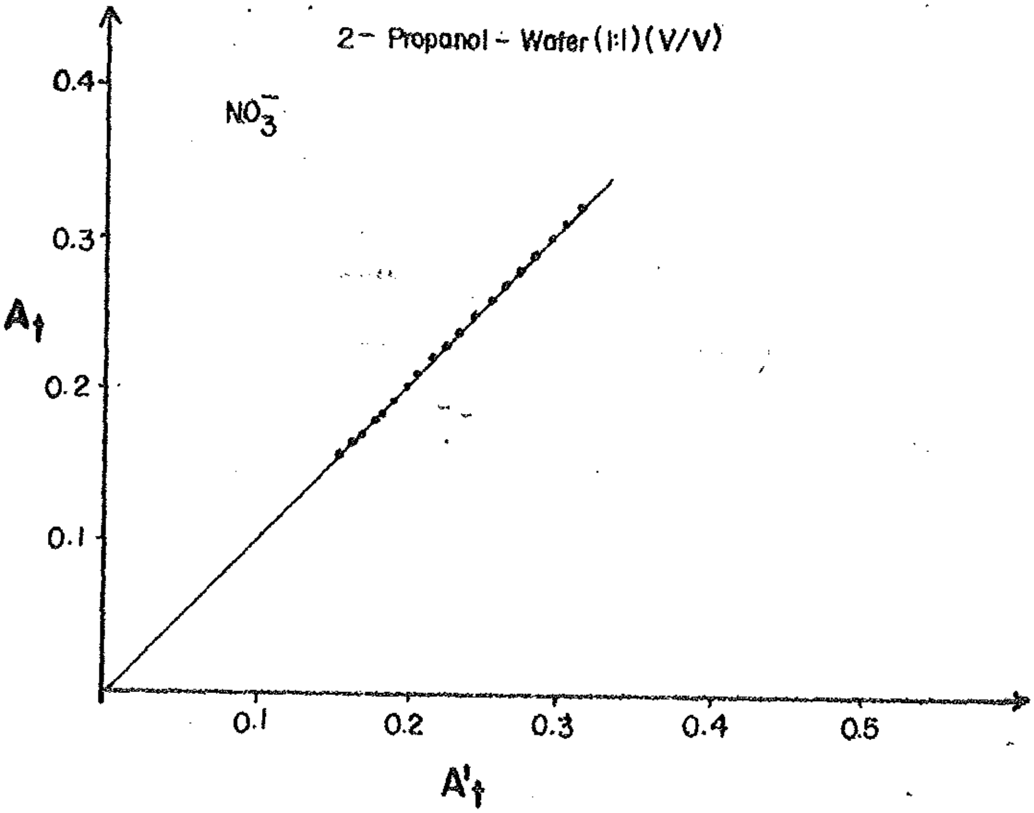



Ethanol -- Water (40:60)(V/V)
NO_3^-
0.4
0.3
0.2
0.1
A_t
0.1
0.2
0.3
0.4
A'_t

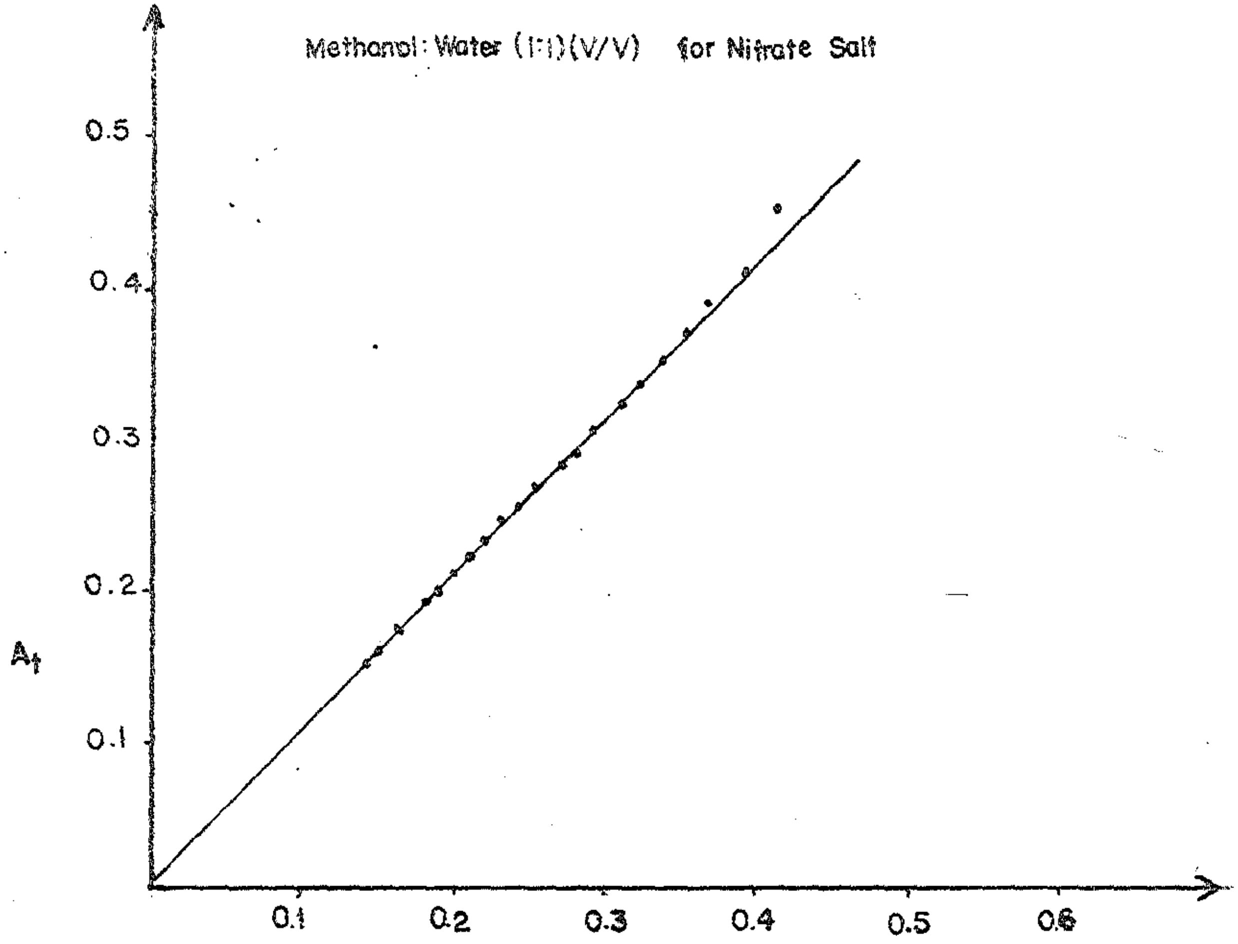

NO_3^-
Ethanol : Water (1:1) (V/V) for Nitrate Salt
0.5
0.4
0.3
0.2
0.1
A_t
0.1
0.2
0.3
0.4
0.5



t-Butanol - Water (1:1) (V/V)
NO_3^-
A_t
0.5
0.4
0.3
0.2
0.1
0.1
0.2
0.3
0.4
A'_t



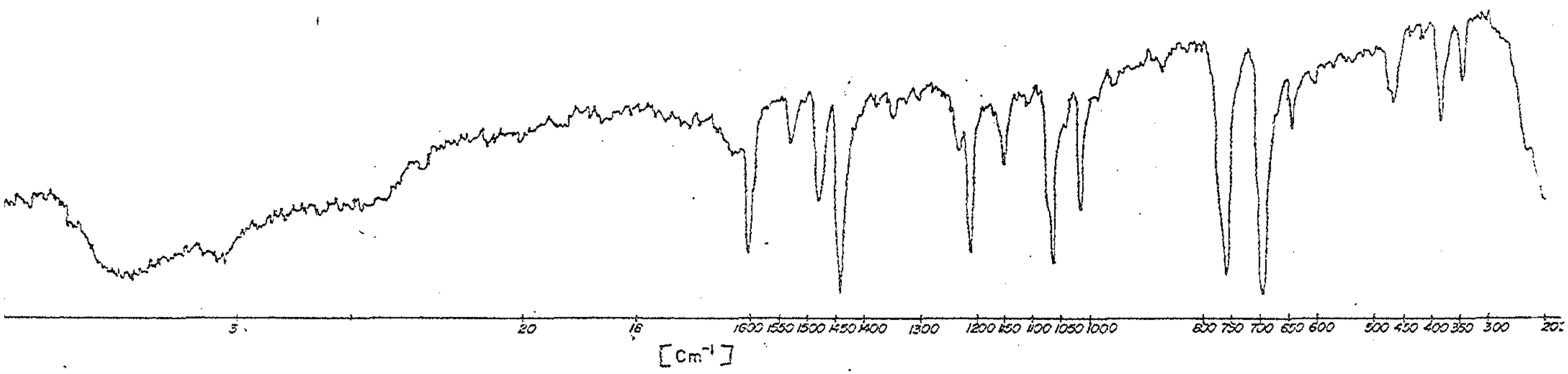
2- Propanol - Water (1:1) (V/V)
NO_3^-
A_t
0.4
0.3
0.2
0.1
0.1
0.2
0.3
0.4
0.5
A'_t



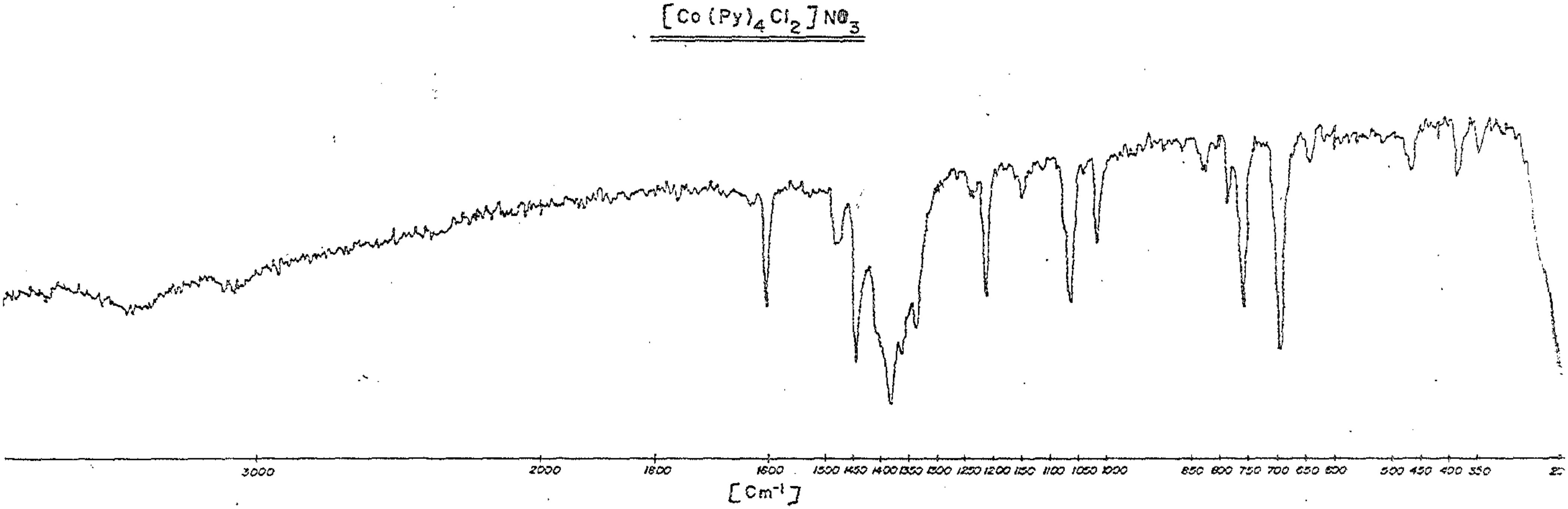
Methanol: Water (1:1)(V/V) for Nitrate Salt

Appendix 3

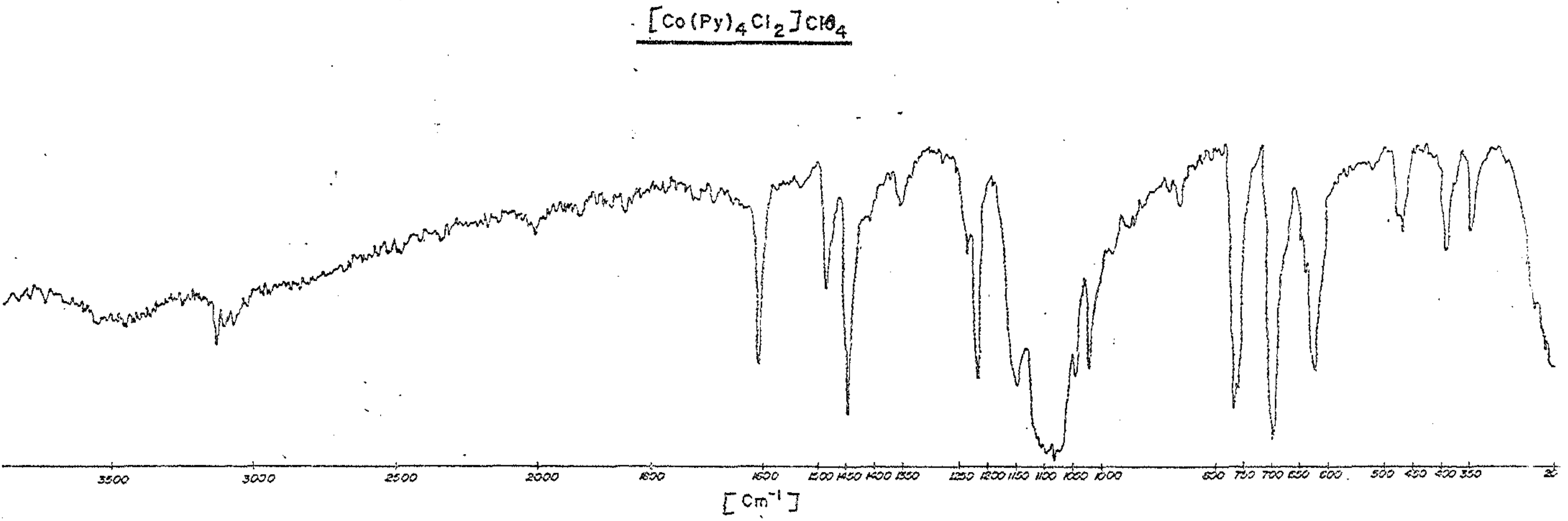
$[Co(Py)_4Cl_2]Cl$



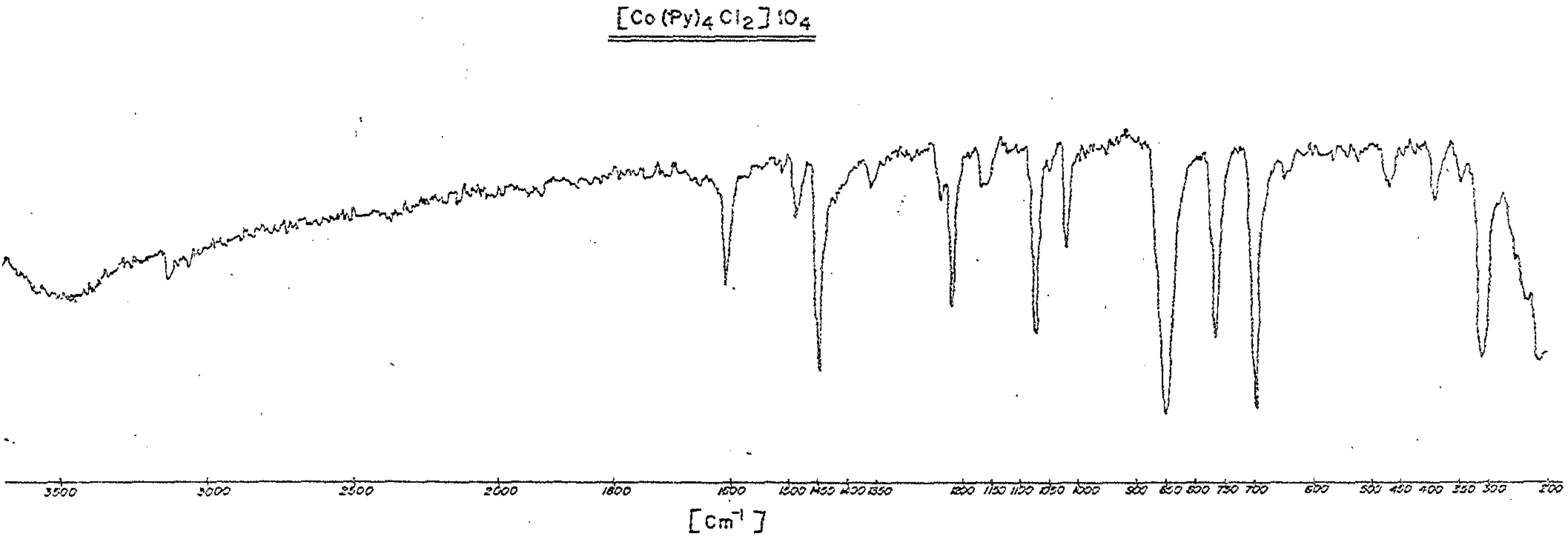
IR spectrum of $[Co(PY)_4Cl_2]Cl$



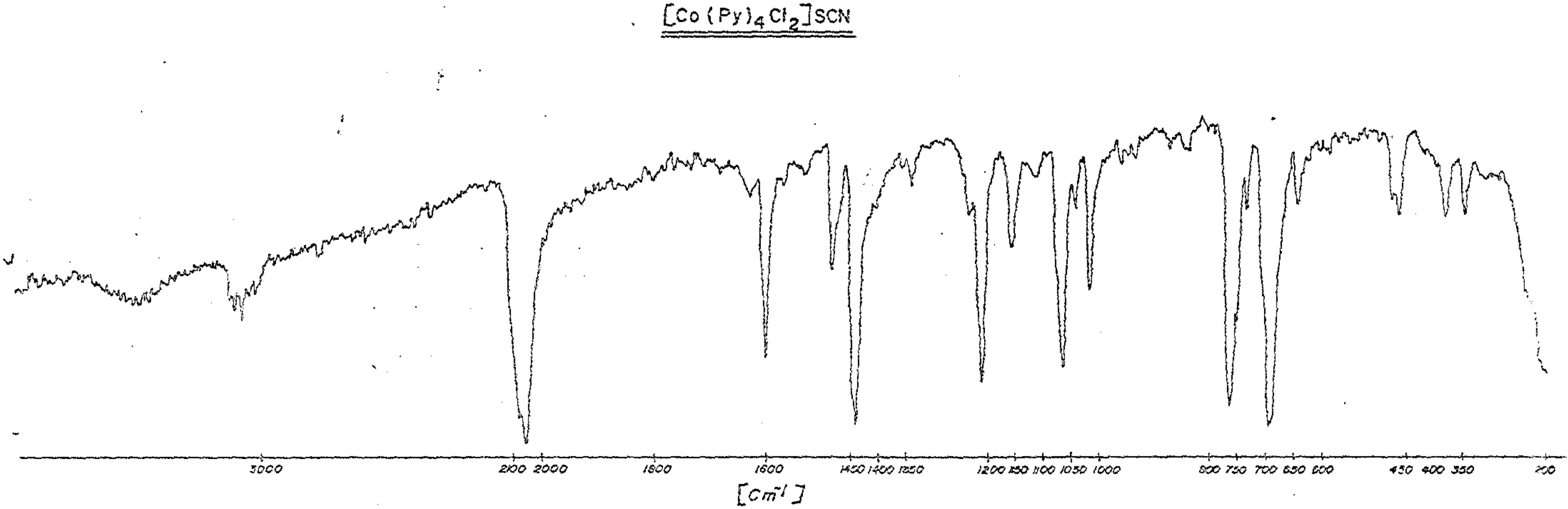
IR spectrum of $[Co(Py)_4Cl_2]NO_3$



: IR spectrum of $[Co\ (Py)_4\ Cl_2]\ ClO_4$



IR spectrum of [Co (Py)$_4$ Cl$_2$] Io$_4$



IR spectrum of [Co (Py)$_4$ Cl$_2$] SCN

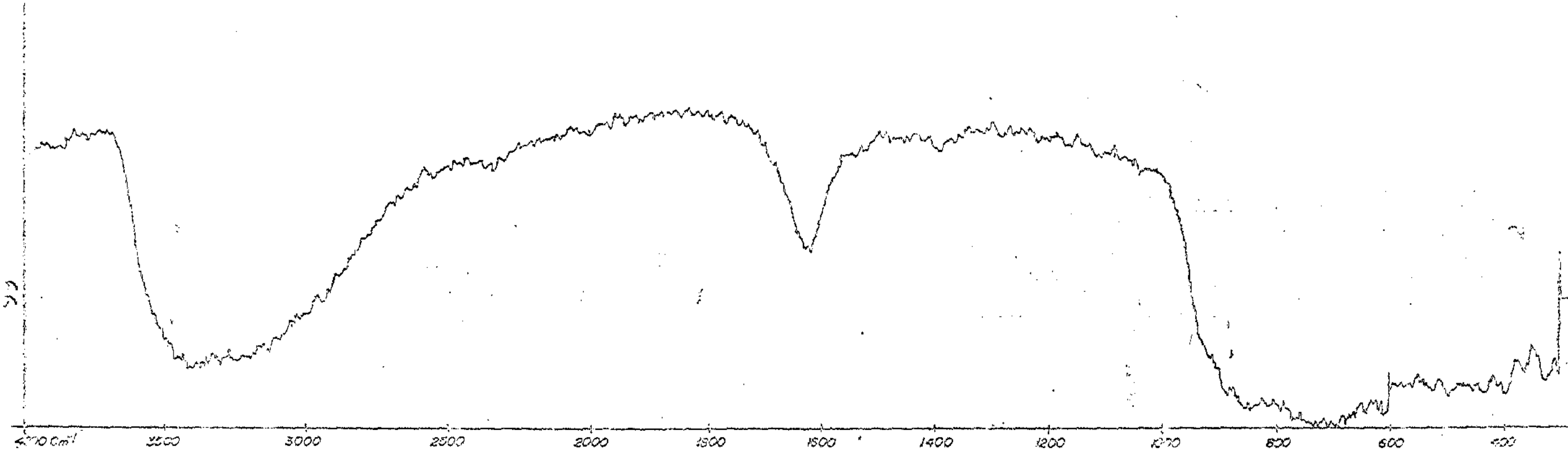


Fig. IR Spectrum of Inorganic Polymer (Titanium Selenite)