CHAPTER I

Introduction

The bulk of the experimental investigations on the effect of solvent dynamics on electron transfer (ET) have focused on intramolecular electron transfer reaction\textsuperscript{1-8}, and more recently, on the electron donor-acceptor complexes\textsuperscript{6-8} along with intermolecular ET.\textsuperscript{9-12} Solvent control of intramolecular electron transfer has also been reported for several cases.\textsuperscript{2} However, in the case of intramolecular ET, the relative orientation and distance of the donor and acceptor are fixed by a molecular structure. In contrast, in the case of intermolecular electron transfer the solvent has a profound influence on the geometry and reactivity of the reactants. Therefore, in the latter case, the role of solvent is expected to be more prominent as compared to intramolecular ET. With availability of femtosecond time resolution in spectroscopy, clear role of the solvent-controlled limit has been observed.\textsuperscript{4,13} It has also been pointed out that vibrations can play an active role in the ET process which obscure the role of the solvent.\textsuperscript{5,8} However, Bixon and Jortner argued that the solvent controlled limit is not applicable to ET in the barrierless regime.\textsuperscript{14}

A Study on kinetics and mechanism of charge-transfer reactions in condensed phase is an important and intensively developing branch of theoretical chemistry. Electron transfer, the simplest process of this kind, displays in the purest way the role of solvation effects in chemical kinetics. The rate of electron transfer from donor to acceptor in the solvent is controlled by several factors such as the donor - acceptor separation distance, polarity of solvent, dynamic property of solvent and temperature. The first theoretical formulations of ET rate expression
through these parameters were based on extremely simple continuum models of the solvent. Continuum models remain, even at the present, the most developed and commonly used tools for estimation of solvent effects. As conventional continuum models are unable to take into account the inertial polarization of a nonpolar medium, hence they are inappropriate for investigation of ET reactions in nonpolar solvents. That is why these processes have not been well studied until now.

1.1 Electron Transfer Reactions of Metal Complexes

Outer Sphere Electron Transfer

Electron transfer reactions may occur by either of both of two mechanisms: outer or inner sphere mechanisms. In principle, all outer sphere mechanisms involve electron transfer from reductant to oxidant with the coordination shells or spheres of each staying intact. That is, one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. Such a mechanism is established when rapid electron transfer occurs between two substituted inert complexes.

\[
\begin{align*}
\text{[NC}_4\text{Cl}_4]^{4-} + [\text{Cl}_2\text{NC}_2\text{CN}]^{2-} &\rightarrow [\text{NC}_4\text{Cl}_4\text{CN}]^{2-} + [\text{Cl}_2\text{NC}_2\text{CN}]^{2-} \\
&\text{ (1.1)}
\end{align*}
\]

Inner Sphere Electron Transfer

An inner sphere mechanism is one in which the reactant and oxidant share a ligand in their inner or primary coordination spheres, the electron being transferred across a bridging
group. This is illustrated using the following example. Inner sphere electron transfer is observed at a slower rate than that of outer sphere electron transfer reaction.

\[
\begin{array}{c}
\text{[Co(NH}_3\text{H}_2\text{O})_6\text{Cl]}^{2+} \\
+ \\
\text{[Cr(H}_2\text{O})_6\text{Cl]}^{2+}
\end{array}
\rightarrow
\begin{array}{c}
\text{[Co(H}_2\text{O})_6\text{Cl]}^{2+} + 5\text{H}_2\text{O}
\end{array}
\]

(1.2)

1.2 Photoinduced Electron Transfer Reactions in Metal Complexes

Photoinduced electron transfer (ET) reactions have been investigated both experimentally and theoretically for several decades, there are still several unanswered questions. Those we are currently trying to answer are the following: 1) The absence of inverted region in bimolecular photoinduced ET reaction. The inverted region predicted by Marcus theory has been observed for intramolecular charge separation, charge shift and charge recombination processes, for geminate ion pair, but never for intermolecular ET quenching. 2) The free energy dependence of the charge recombination (CR) in excited donor/acceptor complexes (DACs) or in contact ion pairs (CIPs) departs considerably from theoretical predictions. First, the logarithm of the CR rate constant \( k_{CR} \) exhibits a linear free energy dependence, i.e. \( k_{CR} \) increased with decreasing driving force. Second this dependence has been observed down to very low driving forces and therefore the normal region, predicted by Marcus theory, is not observed. (3) The structure of the various intermediates involved in bimolecular photoinduced ET processes is not known. For example, contact ion pairs (CIP), loose ion pairs (LIP), and free ions have essentially the same absorption spectrum and the only evidence of the existence of some of these species comes from
kinetics. Whenever metal complex is irradiated with UV light, an electron can be virtually moved from metal to ligand (MLCT), ligand to metal (LMCT) or complex metal center to solvent (CTTS). These transitions are responsible in bringing various redox processes of the complexes. In general Cobalt(III) complexes are well known for their LMCT, leading to reduction of metal center and oxidized products.

\[ Co^{III}L_6 + h\nu \rightarrow Co^{2+}_{aq} + \text{Products} \]  

(1.3)

The products are obtained through the formation of a short lived geminate radical pair. It undergoes disproportionation to give redox products.

**Mechanism of Outer Sphere Electron Transfer**

The reaction sequence eqns 1.4 - 1.5 describes the outer-sphere electron - transfer process between two transition metal complexes in solution\(^\text{15}\). The reactants form an ion pair (M(III) and N(II) have opposite charges) or an encounter complex (like-charge reactants) with a common solvation sphere (eqn 1.4).

\[
\begin{align*}
M(\text{III})^n + N(\text{II})^m & \rightleftharpoons [M(\text{III})\text{----}N(\text{II})]^{n+m} \\
&M(\text{III})\text{----}N(\text{II})]^{n+m} \rightleftharpoons [M(\text{II})\text{----}N(\text{III})]^{n+m} \\
&M(\text{II})\text{----}N(\text{III})]^{n+m} \rightarrow \text{Products}
\end{align*}
\]

(1.4 - 1.6)

The electron transfer takes place within this complex to form a successor complex (eqn 1.5), which dissociates to the observed reaction products (eqn 1.6). A composite rate law (eqn 1.7) can be derived for eqns 1.4 - 1.6 if the precursor complex formation is a rapidly established pre-equilibrium and the electron transfer is rate determining (\( k_{-1} \gg k_{e1} \)).

\[
\text{Rate} = k_{e0}K_0[M(\text{III})][N(\text{II})] / 1 + K_0[M(\text{III})], \quad K_0 = k_{1} / k_{-1}
\]

(1.7)
For many systems with like-charged reactants eqn 1.7 reduces to a second-order rate law (eqn 1.8). In a number of instances\textsuperscript{16-20} it has been possible to measure the intramolecular rate constant, $k_{et}$, for the electron transfer within an ion pair.

$$Rate = k[M(III)][N(II)]$$

$$k = k_{et} K_0$$

(1.8)

Oliveira, Giesbrecht, and Toma\textsuperscript{20} have shown that a linear correlation exists between ln$k_{et}$ values for the reductions of $[(NH_3)_5Co(Me_2SO)]^{3+}$ by a series of $[Fe(CN)_3L]^3-$ reductants and their respective reduction potentials. The analogous experiment demonstrating the effect of half-wave potentials of complexes of cobalt(III) (within an ion pair with a common reductant) on the intramolecular electron-transfer rate constant has not been performed to date mainly because the potentials of the Co$^{3+}$/Co$^{2+}$ couple for normal Werner-type complexes are not known.

1.3 **Medium Effect on Outer Sphere Electron Transfer Reactions between Complexes**

The solvent plays an important role in many chemical reactions, especially charge transfer where there is typically a substantial change in electronic distribution between the initial and final states. Surrounding solvent molecules respond to this change and can influence both energetic and dynamics to a substantial degree. The use of different solvents can change the rate constant for electron transfer or cause dramatic shifts in absorption or emission, for example, transition metal complexes have provided useful probes for studying solvent effects. They have easily measured spectroscopic properties and can be varied by making changes in the surrounding ligands. The goal of this account is to summarize results of solvent dependent
studies on metal complexes, especially d⁶ polypyridyl and ammine complexes relying on survey of the literature to late 1996. They will be compared with relevant organic examples and both will be examined critically in light of available theories. There is a rich panoply of solvent-dependent, charge-transfer behavior in these molecules and our goal is to describe them and analyze them systematically with a section at the end for overview and conclusions.

**Specific Solvent Effects**

Dielectric continuum theory breaks down for charge transfer in ammine or cyano complexes where there are specific interactions between these ligands and individual solvent molecules. These interactions coexist with continuum effects but tend to dominate when they exist and correlations with dielectric functions normally fail. Correlations are sometimes found with empirical solvent parameters such as, the $E_I$ scale for [Fe(bipy)$_2$(CN)$_2$] and the $z$ scale for [M(bipy)(CO)$_4$] ($M = Mo, W$), demonstrating that charge-transfer transitions having different origins can be influenced in parallel ways by the solvent.

Specific interactions arise from H-bonding or donor-acceptor interactions. In both cases, orbital mixing occurs between individual ligands and solvent molecules. This leads to weak, pseudo-bonding, by electron pair donation and H-bonding to –NH$_3$ or by electron pair donation from the N-based, $\sigma$ (CN) molecular orbital to solvent molecules. The magnitude of the interaction depends on the extent of orbital overlap and energy difference between the interacting orbital, the usual quantities of importance in a quantum mechanical interaction.
Influence of Specific Solvent Effects

The energies involved in specific interactions are sufficient that chemical reactions can be induced by making solvent changes. Intramolecular electron transfer in \(\text{cis-}\{(\text{bipy})_2\text{ClOs}(4,4'\text{-bipy})\text{Ru(NH}_3)_5\}^{4+}\) (eqn 1.9) was induced by exploiting the difference in solvent dependences for the \([\text{Ru(NH}_3)_5]^{3+/2+}\) and \([\text{Os(bipy)}_2\text{Cl}]^{2+/+}\) couples.

\[
\text{cis-}\{(\text{bipy})_2\text{ClOs}^{\text{II}}(4,4'\text{-bipy})\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{\text{III}} \rightleftharpoons \text{cis-}\{(\text{bipy})_2\text{ClOs}^{\text{II}}(4,4'\text{-bipy})\text{Ru}^{\text{III}}(\text{NH}_3)_5\}^{\text{IV}}
\] (1.9)

\(\Delta G^0\) for this equilibrium is highly solvent dependent. In nitromethane (DN = 2.7) oxidation to Os\(^{\text{III}}\) - Ru\(^{\text{II}}\) is favored by 0.20 eV relative to Os\(^{\text{II}}\) - Ru\(^{\text{III}}\). In DMSO (DN = 27.8) specific-solvent effects highly stabilize [Ru\(^{\text{III}}\)(NH\(_3\)_5)\(^{3+}\) and oxidation to Os\(^{\text{II}}\) - Ru\(^{\text{III}}\) is favored by 0.39 V. The isomers coexist in mixtures of CH\(_3\)CN (DN = 14.1) and propylene carbonate (DN = 15.5) where \(\Delta G^0 \approx 0\), and intramolecular electron transfer can be induced by changing the volume fraction of propylene carbonate in solvent mixtures.\(^{21}\)

1.4 Photoinduced Electron Transfer Reactions of Cobalt(III) Complexes

Metal complexes upon irradiation undergo i) substitution and related reactions and ii) Redox reactions. The latter is due to charge transfer between metal centre – ligand or complex – solvent. Photoinduced electron transfer reactions play a vital role in biological, chemical and in the field of molecular electronics. In artificial photosynthesis model systems, molecular assemblies showes long lived charge separated states.\(^{22}\) Such excited states actually correspond to the transient conversion of light into an electrochemical potential, which can be used for
energy storage\(^{23}\) or electricity production.\(^{24}\) In the recent developments in the photosensitized functional assemblies called photochemical molecular devices\(^{25}\) (PMD's), the input is light and
the response can be either a change in the structural feature\textsuperscript{26} or a change in the physicochemical properties.\textsuperscript{27}

It is also interesting to note that two kinds of metal complexes play different roles,\textsuperscript{28} the Ruthenium and Cobalt complexes and also a large number of cyanide - bridged compounds\textsuperscript{29} work as a photosensitizer and a catalyst respectively. The use of these building blocks as ligands has made possible the achievement of magnetic nanowires, and double magnetic nanowires.

The study of inter - component photoinduced electron transfer (PET) and photoinduced energy transfer (PEnt) in multicompontent complexes are interest for a wide variety of applications, varying from mimicking the fundamental steps of photosynthesis\textsuperscript{30} to the development of new materials and devices such as solar cells,\textsuperscript{31} luminescent sensors\textsuperscript{32} and molecular wires.\textsuperscript{33} A great number of studies have been devoted to photochromic compounds because of their potential ability to act as photonic devices such as data storage systems and photo - triggered switches.\textsuperscript{34} The change in electronic distribution due to photon absorption can cause substantial modifications in the chemical and physical properties of a molecule. Among these properties the energy, molecular geometries, polarisabilities, dipole and magnetic moments and related redox and acid base properties can change on passing to excited states. Tremendous advantages of photochemical activation of transition metal complexes are in generation of electronic excited states under very moderate reaction condition. These states are ca.100 kJ mol\textsuperscript{-1} higher in energy that the activation energy of the usual chemical reactions of metal complexes.

Transition metal complexes distinguish themselves from organic compounds both by the number of accessible electronic excited states and their spin multiplicity. Consequently, depending on the wavelength (energy) or irradiation, optical excitation leads to various
electronic excited states of different reactivity. In some favorable instances, this behavior allows tuning of photochemical reactivity and switching between various pathways such as electron transfer due to population of diverse charge transfer states. The great variety of available electronic excited states may be used for photogeneration of transition metal compounds with changed formal oxidation number as well as free ligands and ligand redox product formation.\textsuperscript{35} Photochemical Electron Transfer (PET) leads to an activation of molecules and opens up new synthetic routes because the reactivities of the resulting radical ions differ from those of the ground and excited states of the parent compounds.\textsuperscript{36} A desired pair of radical ions is obtained by generating an auxiliary pair through PET, and then replacing one of its components by a thermal electron transfer between a radical ion and neutral species.\textsuperscript{37} Photo oxidation - reduction reactions are in most cases intramolecular processes in which an internal electron transfer occurs between metal and ligands. Reactions of this type involving reduction of the metal and oxidation of the ligands are rather common in the case of Co\textsuperscript{III} and Fe\textsuperscript{III} complexes.\textsuperscript{38} A typical example is shown in eqn 1.10.

\[ [\text{Co(NH}_3)_2\text{I}^2+] \rightarrow \text{Co}^{2+} + 5\text{NH}_3 + \text{I} \]  \hspace{1cm} (1.10)

A photochemical reaction is generally a very complicated process consisting of several consecutive steps and the first step is the absorption of photons and the formation of electronically excited molecules. Owing to the recent progress in the spectroscopy of transition metal complexes, the spectra of a good number of representative complexes are interpreted.\textsuperscript{39}
1.5 Electron Transfer Reactions Leading to the Formation of Ion - Pair

Electrostatic attraction between charge coordination compounds and oppositely charge counter ions in solution leads to ion pairing. Though ion pairs are loosely bound species, their spectroscopic and photochemical properties may markedly differ from those of the individual components. Upon favorable mutual energetic positions of the redox orbital, additional ion pair charge transfer (IPCT) optical transitions may be observed. Depending on the choice of the components and irradiation wavelength, ion pairs may undergo energy transfer, (leading to the population of non-spectroscopic charge transfer excited states), photoinduced electron transfer (as a thermal reaction from locally excited state of the sensitizer), and optical electron transfer respectively.

Fast subsequent thermal reactions have to compete with the back electron transfer in order to achieve high yields of permanent photoredox products. Ion pairs of coordination compounds may find use as photoinitiators for micro imaging and curing applications, as well as photocatalysts for selective organic synthesis.40 Optical electron transfer41 by irradiation using the IPCT absorption band of an ion pair [A⁺; D⁻] primarily leads to the successor pair [A⁺; D⁻]FC in the Frank - Condon excited state. The rate of relaxation of [A⁺; D⁻]FC into its thermally equilibrated ground state [A⁺; D⁻] is limited by the dielectric relativity of the solvent.42

Radiationless deactivation into the ion pair ground state may compete with relaxation,43 but the energetic requirements are rarely met. In general the efficiency of relaxation after IPCT excitation may be assumed to be close to unity. The relaxed successor ion pair [A⁺; D⁻] can react in different ways. The precursor ion pair [A⁺; D⁻] may be regenerated either by luminescence44 (k_lum) or by thermal back electron transfer (k_back). The solvated free species A⁺ and D⁻ formed by
diffusive solvent cage escape (k_{ce}) can undergo subsequent thermal reactions from the bulk solution (k_{p, bulk}). Furthermore, permanent product formation may occur by very rapid in-cage decay of the successor pair components (k_{p, cage}). Photoinduced electron transfer in ion pairs of coordination compounds is of particular interest, since the long wavelength absorption of one of the components e.g. dyestuff, can be exploited. If the excitation of the sensitizer is followed by the fast electron transfer, the subsequent reactions of the successor ion pair [A^+; D^-] can be described by the same kinetic model as depicted. The peculiarity of the photoinduced electron transfer is that, inter - system crossing (ISC) of the excited state sensitizer can occur prior to electron transfer.

The excited state ion pair [*A^+; D^-] (the double asterisk denotes a different spin multiplicity compared with *A^+) and the successor pair [A^+; D^-] are no longer correlated with the ground state ion pair [A^+; D^-] with respect to the spin state. Hence, subsequent reactions from the successor pair (k_{p, cage}, k_{p, bulk}) can efficiently compete with spin-forbidden back electron transfer (k_{back}). Depending on the irradiation wavelength both optical and photoinduced electron transfer from the anion have been shown to occur in the ion pair [Co(NH_{3})_{6}^{3+}; BPH_{4}]. Ion pairing influences kinetics and in some cases the mechanism of the electron transfer reactions. Theoretical model for the effects of ion pairing on the kinetics of these kinds of reactions has been proposed by Marcus and Piotrowiak. The influence of the counter ion dynamics on the reorganization and reaction free energies in several scenarios is considered in these models. Nelson et. al have showed that ion pair formation not only influences the kinetics but depending on the Lewis acidity of the ions participating in the ion association, the formation of an ion - pair can produce a change in the type of reaction. If the ion association is reasonably strong, there is usually little difficulty in separating the properties of the ion pair from the long
range non-specific ion-ion interactions and ion-pair formation. The ions are treated as hard spheres of diameter \('a'\) and only pair wise interaction between them are considered and this collection is known as restricted primitive model (RPM). Very short range interactions involve the mutual exclusion of ions at \(r < a\). However, at distances \(a < r < R\), solvation of the constituent ions must be considered. On this basis, ion pairs may be classified as a (double) solvent separated ion pair (2SIP), when the primary solvation shells of both ions remain essentially intact, as a solvent-shared ion-pair (SIP), if a single solvent layer exists in the space between the ion partners of the pair, or as a contact ion pair (CIP), if no solvent exists between the partners and the ions are in direct contact. The long range electrostatic forces that keep the partners of an ion pair together are non directional.

Once an ion pair is formed, electron density transfer may occur in a second stage.\(^{51}\) Ion pairing proceeded in stages, as a result of competition between ion solvation and the electrostatic attraction between oppositely charged ions. The first stage was the formation of a solvent separated ion pairs (2SIP), where the solvation shells of both cation and anion remained essentially intact. This step occurred at a very fast (diffusion controlled) rate. The common representation of this kind of ion pair specifies two solvent molecules on the line connecting the centres of the partner ions. In the second slower stage, a partial desolvation of the ion-pair (SIP) with a single solvent was shared in the space between the partner ions. In the final slowest stage, the solvent molecules between the partners were eliminated to form a contact ion pair (CIP) that was still solvated outside the region of contact. If a solvent is represented by \(S\), the cation by \(\text{C}^{\circ+}\) and the anion \(\text{A}^{-}\), the stages can be represented as in eqn. 1.11 where the solvation numbers are \(m > p > r > s > y\) and the overall association constant is \(K_A = K_1 + K_1K_2 + K_1K_2K_3\).
\[
\begin{align*}
K_1 & \quad K_2 & \quad K_3 \\
C^{+}S_m + A^{+}S_n & \leftrightarrow S_pC^{+}S_2A^{+}S_q & \leftrightarrow S_rC^{+}SA^{+}S_s & \leftrightarrow S_aC^{+}A^{+}S_y
\end{align*}
\]

(1.11)

The validity of this so called "eigen mechanism" was demonstrated by means of ultrasonic relaxation technique.\textsuperscript{52} Indeed, the concept of stepwise elimination of the solvent between the constituents of an ion-pair is closely related to the motion of outer and inner sphere coordination compounds in solution. In their study of the association of sulfate anion with cobalt(III) amine complexes, Posey and Taube\textsuperscript{53} found that [Co(NH\textsubscript{3})\textsubscript{3}H\textsubscript{2}O]\textsuperscript{3+} formed an outer-sphere species with SO\textsubscript{4}\textsuperscript{2-} virtually instantaneously.

The formation of ion-pairs between [Co(sep)]\textsuperscript{3+} where sep is 1,3,6,8,10,19-octaazabicyclo[6,6,6] eicosane, and some anions can give rise to supramolecular charge-transfer interactions. When the anion is a reducing species such C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-}, a second sphere charge transfer (SSCT) appears in the near - UV or Visible spectral region. The spectroscopic transition in the 200-400 nm regions cannot explain as the sum of the components forming the ion-pairs, but rather is the result of an ion-pair charge transfer transition, IPCT. This kind of contact ion-pair is considered the simplest case of a supramolecule. Since the reactants are already assembled, more informative kinetic and thermodynamic parameters can be evaluated compared to intermolecular ones. Examples of IPCT compounds based on metal complexes are still rare, but the interest in these systems has increased since they are distinguished by interesting photochemical and photocatalytical behaviour.\textsuperscript{54} The excitation at the IPCT band leads to very efficient photoredox reactions in low-energy regions, where each component itself does not show photoredox reactivity. The irradiation of the Co(sep)\textsuperscript{3+}/C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} IPCT reduction induces an electron transfer to the complex and oxidation of oxalate ions to carbon dioxide. When the
photoreaction is carried out in the presence of colloidal platinum, Co(sep)$^{3+}$ plays the role of a photo sensitizer for the evolution of hydrogen from aqueous solutions with oxalate ions as sacrificial agents. Due to this interesting electron transfer sensitizer property, several photochemical studies have been focused on the Co(sep)$^{3+}$ anion system. One of the main aims is the determination of the true quantum yield of the photo process, since light is absorbed both by the ion-pair and complex themselves.

1.6 Linear Free Energy Relationship

The method of Linear Free Energy Relationship (LFER) or correlation analysis is still the simplest and most practical method of predicting the effects of solvents and substituents on the rate and position of equilibrium of chemical reactions and also on spectral absorptions of organic molecules. This is also discussed under Linear Solvation Energy Relationship (LSER). The selection of suitable standard processes to determine empirical parameters of solvent polarity also makes use of number of theoretical considerations. In a certain reaction series, where only small changes are involved in going from one reaction to another, these may be structural, such as a series of differently substituted compounds, or may involve a single reaction carried out in a series of rate and in equilibrium constants occurring in one reaction series can be often related to those in another, closely related series. Thus, plotting the logarithms of rate or equilibrium constants for a second, related series frequently gives a straight line, which can be expressed by eqn. 1.12, in which the subscript $i$ stands for the same structural or solvent-determined variation in the two reaction series and $k_i^B$ and $k_i^A$ are rate or equilibrium constants for two reaction series B and A which are subjected to the same changes in the surrounding medium or the structure.
\[ \log k_i^B = m \log k_i^A + C \] (1.12)

The correlation of data for a new reaction series by means of a linear Gibbs Energy Relationship establishes a similarity between the new series and the reference series. The second use of Linear Gibbs Energy equation is in the prediction of reaction rates or equilibrium constants dependent\textsuperscript{55} on substituent or solvent changes. Let us consider a reaction between a substrate and a reagent in a medium M, which leads, via an activated complex to the products, \((S)_M + (R)_M \leftrightarrow [S, \ldots, R]_M \rightarrow (P)_M\). The designation of one reactant as the substrate and another as the reagent is arbitrary but useful in considering chemical reactivity. The substrate always undergoes some change in the reaction series, but the reagent does not. A catalyst is always considered to be a reagent. In principle, the same considerations as in the above equation can be made for the excitation of a substrate, dissolved in medium M, with photons \((h\nu)\).

\((S)_M + h\nu \leftrightarrow (S)_M^*\). Although Linear Gibbs Energy Relationships usually deal with relative reactivities only, in the form of reaction rate and equilibrium data, this approach can be extended to various physical measurements. There are three possibilities of introducing small changes in order to establish a reaction series (i) one can change the substrate by introducing different substituents and this leads, particularly in case of meta- and para-substituted benzene derivatives, to well known Hammett equation: (ii) one can change the reagent (catalyst), as in the case of acid or base - catalyzed reactions, which explains the famous Bronsted-Pederson equation,\textsuperscript{56} which establishes a Linear Free Energy Relationship (LFER) between the strength of acids or bases and their effectiveness as catalyst; (iii) one can change the surrounding medium, while leaving all other reaction partners unchanged. In case the selected reaction is sufficient, this gives us the desired empirical solvent parameters.
Thermodynamically, solvation may be considered in the same general terms as the modifications of the properties of the substrate molecule by substituent changes, the solvating molecules being equivalent to loosely attached\textsuperscript{57} substituents. One important difference between substituents and solvents effects on chemical reactivity is that substituents may change the chemical reactivity of a given substrate in a discontinuous manner only, whereas solvents, especially, solvent mixtures, allow a continuous modification of substrate reactivity. The limitations of the qualitative theory of the influence of the solvent on the reaction rate has led various authors to attempt to dispense with it entirely in favor of solvent parameters based on actual solvent sensitive chemical or physical processes. In general, all these parameters constitute more comprehensive measures of solvent polarity than the relative permittivity or any other single physical characteristic, since they reflect more reliably the complete picture of all intermolecular forces acting between solute and solvent molecules. The solvent-dependent processes used to define solvent polarity parameters may be regarded as probes which permit a purely empirical investigation of solvent effects. In the comparison of various empirical solvent scales, one finds surprisingly, that most of the existing empirical solvent scales agree with each other very well quantitatively and also qualitatively.

1.7 Analysis of Experimental Data using Regression Model Equations

More information about reactivity could be summarized in terms of a very simple mathematical equation that has dominated the development of the correlation analysis in chemistry. The application of the techniques of correlation analysis\textsuperscript{58} has proved strikingly successful and has greatly increased our understanding of the role of the solvent structure on reactivity.
Simple Linear Regression Analysis

In many experiments, it is obvious that the effect on a dependent variable $Y$ changes with respect to an independent variable $X$. The inspection of a series of corresponding values of these variables may suggest to us that $Y$ is related linearly to $X$. In this event, plot of $Y$ against $X$ pattern of the points seems to agree with the linear relationship, within the limits of experimental error, the data can confirm to the eqn 1.13,

$$Y = mX + C \quad (1.13)$$

Where ‘m’ is the slope and $c$ is the intercept should always be calculated by the method of least squares, which also readily provides assessment of the good idea to plot and ponder a graph which is the first step in correlation analysis.

Multiple Linear Regression Analysis

The multiple linear regression of a dependent variable $Y$ with a series of explanatory variables $X_1$, $X_2$, $X_3$, etc... in eqn 1.13 revises the question of significance in an acute form, that is illustrated in eqn 1.14,

$$Y = m_1X_1 + m_2X_2 + m_3X_3 \quad (1.14)$$

There are rather complicated equations for applying the method of least squares to the regression of $Y$ on $X_1$ and $X_2$, and ever more complicated equations for three or more explanatory variables. When a multiparametric equation is encountered, which is said to be successful in correlating a set of reactivity data, it is natural to inquire into physical significance of the various
terms in relation to the reaction mechanism. An explanatory variable is only part of what is necessary. The apparent improvement in correlation coefficient when a new explanatory variable is introduced into the regression must be assessed for significance level is adequate, say better that 95 % , a partial correlation coefficient of perhaps as low as 0.7 may be deemed unacceptable. When several explanatory variables are used, it is almost inevitable that there will be some degree of correlation between one independent variable and another.

Laidler - Eyring Model Relationship

Electrostatic interactions generally make the greatest contribution to the activation energy for ion - ion interactions. The solvent parameter widely used as the measure of the electrostatic interactions between solute and solvent is relative permittivity ($\varepsilon_r$) and is found to change linearly with either mole fraction, volume fraction or mass fraction for solvent mixtures or even harmonically. The influences of $\varepsilon_r$ can be described by the Laidler-Eyring relation$^{59}$ as in eqn 1.15

$$\frac{d\ln k}{d(1/\varepsilon_r)} = \left[ e^2 z^2 (1/r - 1/r^*)/(2kT) \right]$$

(1.15)

Where $k$ is the reaction constant, $z$ the net charge, $r$ the effective radius and $r^*$ the relative radius of the activated species, $k$ the Boltzmann constant, and $T$ is the temperature. This parameter has been used as an indication of dissociative or associative nature of the rate determining step. In substitution reaction of aqua ligands from cis-[Co(BigH)₂(H₂O)]³⁺ with pyridine-2-aldoxime in water - ethanol mixtures, the plot of log $k$ versus 1/ $\varepsilon_r$ was linear with positive slope which shows some indication that the reaction proceeds$^{60}$ through an associative path. The linear least squared plot of log$k_2$ Vs 1/ $\varepsilon_r$ yields a positive slope in all solvent mixtures under investigation.
showing $r^* > r$ which suggests that the electron transfer between Co(NH$_3$)$_5$Ox$^+$ and Fe(CN)$_6^{4-}$ proceeds through an associative path.\textsuperscript{61} That is, ion association is especially attractive in mixed solvents with lowering relative permittivity of the media.

**Grunwald-Winstein Model Expression**

Grunwald and Weinstein\textsuperscript{62} suggested treating solvent effects on rates in terms of the following eqn 1.16,

$$\log k = \log k_0 + mY$$  \hspace{1cm} (1.16)

$log k$ refers to a given solvent, $\log k_0$ to the same reaction in 80% (V/V) aqueous ethanol as a standard solvent, $Y$ is a parameter characteristic of the given solvent and $m$ is a parameter characteristic of the given reaction, which measures its susceptibility to changes in solvent, scales of $Y$ and $m$ were established by taking $Y = 0$ for 80% ethanol and selecting the solvolysis of t-butyl chloride at 25°C as a standard reaction, for which $m$ is defined as 1. $Y$ values are known for various one-component solvents and for various mixtures of organic solvents with water or a second organic solvent. From the nature of the standard reaction, $Y$ values will clearly provide some measure of the ability of the solvent to separate ions. It was therefore, hoped that $Y$ values might be a more generally applicable measure of solvent polarity than relative permittivity. Good linear relationships between $\log k$ and $Y$ are shown by the solvolysis of various halides and secondary sulphonates, i.e., reactions which proceed by an $S_N^1$ mechanism, like the standard reaction.

**Swain's Model Biparametric Equation**

Macroscopic dielectric constants alone are unsuitable measures for molecular - microscopic interactions. Bulk solvent property like relative permittivity will poorly describe the
microenvironment around the reacting species, which governs the stability of the intermediate and hence the rate of electron transfer. Therefore, specific solvent effect was analyzed using the empirical solvent parameters of Swain et. al. The most important properties of solvents, affecting the chemical reactivity in processes are their anion - solvating and cation - solvating tendencies. These are symbolized by A and B as the acidity and basicity parameters respectively and they are solvent properties, involved in specific local electrostatic interactions with polar centers in the solutes in solvation. The two solvent vectors A and B in a dual linear free energy relationship for predicted solvent effects were represented by the eqn 1.17

\[ P_j = a_i A_j + b_i B_j + c_i \]  

(1.17)

Where \( P_j \) represents the solvent dependent solute property in solvent \( j \), \( A_j \) and \( B_j \) characterize the solvent \( j \), \( a_i \) and \( b_i \) represent the sensitivity of the reaction to solvent acidity and basicity parameters. \( c_i \) is the predicted value of solute property for the reference solvent \( n \)-heptane. The constants A and B are evaluated by nonlinear least squares by using equal statistical weighting of 1080 data, the four trivial scale - setting subsidiary conditions \( A = B = 0 \) for \( n \)-heptane and \( A = B = 1 \) for water, and the two critical subsidiary conditions \( A = 0 \) for hexamethyl phosphoric triamide and \( B = 0 \) for trifluoroacetic acid.

**Krygowski - Fawcett Model Biparametric Equation**

An empirical model describing the effect of solvent on physicochemical properties measured in solution was described by Krygowski and Fawcett. The main purpose of this model is to describe solvent effects in such a way that all solute - solvent interactions influencing the various physical and chemical properties could be defined in terms of the general concept of the Lewis acidity and basicity of the solvent. It was postulated that the solvent effect on a
physicochemical quantity Q could be represented as a linear function of two independent but complementary parameters describing the Lewis acidity and Lewis basicity of the given solvent. The Reichardt's $E_T^N$ values, which provide an excellent and very sensitive characterization of the micropolarity of solvents, were chosen as measure of Lewis acidity. In addition, Gutmann's donor number (or donicity) $DN^N$ is an empirical semi quantitative measure of the nucleophilic properties of electron pair donor (EPD) solvent, and was chosen as a measure of solvent basicity. Therefore, the solvent effect on a physicochemical quantity could be represented by the eqn 1.18

$$Q = Q_0 + aE_T^N + bDN^N$$ (1.18)

Where $\alpha$ and $\beta$ are regression coefficients describing the sensitivity of the solute property $Q$ to electrophilic and nucleophilic solvent properties, respectively and $Q_0$ is the value of the solvent dependent physicochemical property of the solute under investigation in the gas phase. There is no correlation between the acidity parameter $E_T$ and the basicity parameter $DN$. $\alpha$ and $\beta$ values were determined in the second order substitution reaction $n-C_4H_9Br$ with azide ion as $\alpha = 88\%$ and $\beta = 12\%$. The negative sign $\alpha$ represents a reduction of the reaction rate with increasing lewis acidity of the solvent. In general the sign of a coefficient infers the type of interaction.

**Kamlet - Taft Model Triparametric Relationship**

The solvatochromic comparison method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on many types of physicochemical properties and reactivity. The solvatochromic parameters were intended for use in linear solvation energy relationship (LSER) or, in the case of solute-solute interactions, linear complexation energy relationship of generalized form of eqn 1.19
\[ XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \]  

(1.19)

Where \( XYZ \) is the solute property, generally the logarithm of a rate or equilibrium constant. \( XYZ_0 \) is the regression value of the solute property in cyclohexane as reference solvent. The \( \pi^* \) scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The \( \pi^* \) scale was selected to run from 0.00 for cyclohexane to 1.00 for dimethyl sulfoxide. The \( \alpha \) scale of solvent HBD (hydrogen bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond. The \( \alpha \) scale was selected to extend from zero for non-HBD solvents to about 1.0 for methanol. The \( \beta \) scale of HBA (hydrogen bond acceptor) basicities provides a measure of the solvent's ability to accept a proton in a solute - to - solvent hydrogen bond. The \( \beta \) scale was selected to extend from zero for non-HBD solvents to about 1.0 for hexamethyl phosphoric acid triamide (HMPT). The coefficients a, b and s were obtained by solving the simultaneous equations by commercially available software. These coefficients measure relative susceptibilities of the solvent - dependent solute property \( XYZ \) to the indicated solvent parameters. Kamlet and Taft's triparametric equation explains 70% of the effect of solvent on the hydrolysis of hydroxamic acids.\(^{68}\)

Chemicals and Reagents

Analytical reagent grade chemicals, viz., cobaltous chloride, potassium hexacyanoferrate(II), sodium perchlorate, sodium nitrate, methanol and 1,4 - dioxane were used without further purification in the present investigation. Ethanol obtained was refluxed over lime for 8 hours and distilled. The fraction, collected at 78.3 – 78.5\(^{6}\)C was collected and used. All the solvents were kept out of contact with atmospheric moisture. Solvent mixtures were prepared by volume percentage ( v/v ) and converted into mole fraction, \( x_{os} \) using density data. \( \text{Na}_2\text{H}_2\text{EDTA}, \)
acetone, ammonium thiocyanate, ferric chloride and 1,10 – phenanthroline were GR grade and these were used as such. Doubly distilled water was prepared by distilling twice in an all-glass pyrex unit apparatus with alkaline potassium permanganate.

1.8 Analytical Measurements using Instruments

PXRD X-Ray Powder diffractograms (PXRD) were recorded on a X’PERT PRO-analytical XRD diffractometer using copper K-Alpha radiation (λ = 1.5406 Å). The profile intensities were measured step by step *(0.02° in 2θ)* for a whole time of 1500 s. The VSM loops of the complexes were recorded in a powder form on a Lakeshore – 7404 at sample vibration frequency 825 Hz.

All kinetics experiments were performed with a 5501 CECIL UV – Vis double beam spectrophotometer (Shimadzu model and PerkinElmer model) equipped with a thermo stated cell compartment and a cell holder, using a 1 cm path length quartz cell. The cell compartment was thermostated by circulating water from a water bath regulated to the desired temperature. Absorbance of the solutions was measured using 1 cm length quartz cell.

1.9 Photolysis Assembly

All photolysis experiments were performed in a set-up consisting of mercury vapour lamp, reactor vessel, stirrer and power supply. The irradiation assembly consists of low pressure penray mercury vapour lamp (254 nm), quartz reactor vessel and magnetic stirrer. The photolysis experiments were carried out in a red light using penray mercury lamp which emits
254 nm radiation. The lamp is along with reactor vessel (volume of about 80 ml and a path length of 1.5 cm)

The effect of ligands on the rates and stoichiometries of oxidation-reduction reactions between metal ions in aqueous solution has been investigated extensively. In the majority of these studies no net change in the oxidation state of the ligands takes place. Recently, interest has arisen in the reactions of coordinated ligands, and, in particular, a few studies have been concerned with oxidation-reduction changes of ligands coordinated to substitution-inert complexes.

In the present study, the results are obtained when iodopentammine-cobalt(III) in aqueous solution reacts with various “one-electron” oxidation-reduction reagents-cerium(IV), cobalt(III), iodine atoms, hydroxyl radicals and methyl radicals. The cobalt-containing products derived from the iodopentammine cobalt(III) are aquopentamminecobalt(III), sulfatopentamminecobalt(III), cobalt(II) or mixtures of these species. The retention of the oxidation state of the cobalt(III) center or its reduction to cobalt(II) as the coordinated iodide ion reacts with the external oxidation-reduction reagent is an important feature of the present investigation. As discussed below, it appears that bonding of the iodine to the external “one electron” oxidation-reduction reagent is a necessary condition for the reduction of the cobalt(III) center. Thus, the possible distinction between “one-electron” oxidation-reduction reagents such as cerium(IV) and cobalt(III) which yield aquopentamminecobalt(III) and “one-electron” oxidation-reduction reagents such as iodine atoms, hydroxyl radicals and methyl radicals which yield cobalt(II) has been exploited to yield evidence on the nature of the products formed in the primary step of the reaction between iron(II) and hydrogen peroxide. The discovery of a very efficient reaction between iodopentammine cobalt(III) and iodine atoms provides the possiblity,
which has not yet been exploited, of using this reaction as a diagnostic for the presence of iodine atoms in other systems.

**Photolysis of Co(NH₃)₄I⁺⁺**

With the geometrical arrangement used, the light flux arriving at the 1 cm silica cell was 9.3 X 10⁻⁵ einstein/min./l, the extinction coefficients of Co(NH₃)₄I⁺⁺ and I₂ at 2537 Å are such that even after 80% disappearance of the complex, 90% of the light is absorbed by the unreacted Co(NH₃)₄I⁺⁺. Photolysis of 3.46 X 10⁻³ M Co(NH₃)₄I⁺⁺ in 0.1 M HClO₄ yielded, after 25 minutes, a solution 1.69 X 10⁻³ M in I₂ (measured spectrophotometrically at 460 mμ) and 3.48 X 10⁻³ M in Co(III), a result that indicates that the photochemical reaction proceeds according to the stoichiometry given by equation 1.20)

\[
2Co(NH₃)₄I⁺⁺ + 10H⁺ = 2Co⁺⁺ + 2I + 10NH₄⁺ \tag{1.20}
\]

By following the decrease in optical density at 580 mμ (where Co(NH₃)₄I⁺⁺ has an absorption maximum) it was established that the photochemical reaction obeys zero order kinetics up to 80% reaction. The quantum yield, measured by determining the concentration of Co(II) after 10 minutes of irradiation, was 1.94.

**1.10 Literature Survey of some Important Systems**

**The Reaction with Fe(II)-H₂O₂**

When hydrogen peroxide is added to a solution of Co(NH₃)₃I⁺⁺, Co(NH₃)₃OH₂⁺⁺ is formed quantitatively at a measurable rate. However, in the presence of iron(II) the reaction appears to be complete upon mixing the reagents and the stoichiometry is drastically altered, with large amounts of Co(II) being formed. The experiments were performed by adding 5 ml of a
solution hydrogen peroxide of the desired concentration to a 50 ml volumetric flask containing 40 ml of a solution of Co(NH$_3$)$_3$I$^{4+}$, Fe(II) and HClO$_4$ of the desired concentrations. Thiosulfate was added to reduce the iodine formed; the solution was made up to volume and examined spectrophotometrically to determine the reaction products. The optical density at 388 nm (where Co(NH$_3$)$_3$I$^{4+}$ has a maximum with extinction coefficient 2700, as compared to extinction coefficients 11 and 0.16 for Co(NH$_3$)$_3$OH$_2$$^{+3}$ and Co(II) respectively) indicated that in all instances the Co(NH$_3$)$_3$I$^{4+}$ has reacted completely.

From the nature of acid dependence of the rate of chloride release, it might be inferred that the reaction proceeds through two simultaneous paths: (i) an acid-independent dissociative path and (ii) an acid-dependent conjugate base path. The reaction scheme shown in eqn 1.22 yields the rate expression, which is consistent with rate being acid independent at high acid concentration ($k_{app} \rightarrow k_1$). Values of $k_1$ and $k_2K_a$ have been calculated by the least-squares method using the experimental data.

According to reaction scheme (eqn 1.22) the acid dependence of chloride release from the amine complexes would depend upon the $pK_a$ values of the coordinated amines. However, the magnitude of $k_2$ would depend upon the $\pi$-bonding ability of the amido base. In view of the very
rapid reaction of the hydroxide ion with these complexes, it was not possible to obtain reliable values of pKₐ and hence k₂ of any of these complexes experimentally. Basolo, et al., have estimated that the pKₐ of Co(en)₂NH₃Cl²⁺ is certainly greater that 15. Examination of the pKₐ values of series of amines shows that the pKₐ of aniline decreases to 4.58 as compared to 9.24 for that of ammonia, owing to the electron-withdrawing phenyl group as the substituent.

In view of the above considerations, as a reasonable estimate, a pKₐ value of greater than 10 may be assigned to the complex Co(en)₂(NH₂C₆H₅)Cl²⁺. The m-toluidine and p-toluidine complexes would be expected to have pKₐ values of the same order as that of the aniline complex. The pKₐ values of these aromatic amine complexes, being considerably lower than that of the corresponding ammonia complex, are expected to produce kinetically significant concentration of the amido bases even in acid media, particularly at relatively higher temperatures (50 °C), thus increasing the contribution of the conjugate base path toward chloride release. Using this estimated value of pKₐ > 10 for these aromatic amine complexes, k₂ is found to be of the order of 10³ sec⁻¹, k₂Kₐ being of the order of 10⁸ mol sec⁻¹ for the Sₐ¹ dissociation of the conjugate bases of the complexes, this order appears to be quite reasonable.

The effect of substituting a methyl group in phenyl ring on the rate of chloride release (k₁) may now be examined. Since the inductive effect cannot be suitably transmitted to the cobalt atom through the fully protonated nitrogen atom, the acid-independent k₁ values of the three complexes should be equal. For the aniline and p-toluidine complexes this is found to be the case. The slightly lower k₁ value of the m-toluidine complex might be due to a steric or some other unknown factor. Substituent effects are expected to be more significantly reflected in the k₂ values of these complexes, since the nature and position of the substituent in the phenyl ring would make the Co-N π bond less or more effective. Higher k₂Kₐ values for the chloro-p-
toluidine complex might be the result of higher $k_2$ values, which might again be due to the para-orienting effect of the methyl group. However, with the approximately estimated values of $k_2$ this aspect need not be discussed further.

1.11 Experimental Section

Synthesis of Cobalt(III) Aryl Amine Complexes

Series I: Preparation of $[\text{Co}^{\text{III}}(\text{en})_2(\text{L})\text{I}_2\cdot \text{H}_2\text{O}]$ Complexes (where $\text{L} = \text{RC}_6\text{H}_4\text{N}\text{H}_2$; $\text{R} = m-$OMe, $p-$F, $H$, $m-$Me, $p-$Me, $p-$OEt and $p-$OMe)

Trans-iodo(R-aniline)bis(1,2-diaminoethane)cobalt(III) iodide series was prepared from trans-[Co(en)$_2$I$_2]$I by the literature method$^{82}$. Two grams of trans[Co(en)$_2$ I$_2]$I was made into paste with 3 or 4 drops of water and then ground with equimolar amount of R-aniline (where $\text{R} = m-$OMe, $p-$F, $H$, $mm$ Me, $p-$Me, $p-$OEt or $p-$OMe). A calculated amount of liquid R-aniline was added directly, but solid aniline dissolved in 1-2 ml of alcohol was added slowly. The mixture was ground and R-aniline was added in drops for 2 hours. The mixture was allowed to stand overnight. Finally, the solid was washed with ethanol and ether over a Buckner funnel. The R-aniline series of complexes in general were prepared by changing the concentration and addition time from the starting material.

Anal: Calculated compositions of trans-[Co(en)$_2$(m-OCH$_3$C$_6$H$_4$N$\text{H}_2$I)]I$_2$.H$_2$O : C $-$ 18.85, H $-$ 3.88, N $-$ 10.01, Co $-$ 8.41 ; Found : C $-$ 19.1 , H $-$ 3.2, N $-$ 9.8, Co $-$ 8.2 : Electronic absorption data in close agreement with the reported values. $\lambda_{\text{max}}$ : $\epsilon_{\text{max}}$ (232 : 8890 $M^{-1} cm^{-1}$; 344 : 4955 $M^{-1} cm^{-1}$, 465 : 5010 $M^{-1} cm^{-1}$ and 601 : 1280 $M^{-1} cm^{-1}$), $\lambda_{\text{min}}$ : $\epsilon_{\text{min}}$ (337 :
Calculations of the energy levels of trans-[Co(en)$_2$(p-FC$_6$H$_4$NH$_2$)]I$_2$.H$_2$O: C = 17.43, H = 3.51, N = 10.19, Co = 8.55; Found: C = 17.8, H = 2.9, N = 10.0, Co = 8.4. Electronic absorption data in close agreement with the reported values.

$\lambda_{\text{max}}: \epsilon_{\text{max}} = 233: 8740 \text{ M}^{-1} \text{ cm}^{-1}$, 287: 5085 $\text{ M}^{-1} \text{ cm}^{-1}$, 350: 3910 $\text{ M}^{-1} \text{ cm}^{-1}$, 462: 1850 $\text{ M}^{-1} \text{ cm}^{-1}$, 601: 650 $\text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{min}}: \epsilon_{\text{min}} = 266: 4115 \text{ M}^{-1} \text{ cm}^{-1}$ and 315: 3060

Calculated compositions of trans-[Co(en)$_2$(C$_6$H$_5$NH$_2$)]I$_2$.H$_2$O: C = 17.9, H = 3.76, N = 10.46, Co = 8.78; Found: C = 18.1, H = 3.2, N = 10.2, Co = 8.4; Electronic absorption data in close agreement with the reported values.

$\lambda_{\text{max}}: \epsilon_{\text{max}} = 231: 8715 \text{ M}^{-1} \text{ cm}^{-1}$, 345: 2700 $\text{ M}^{-1} \text{ cm}^{-1}$, 461: 1850 $\text{ M}^{-1} \text{ cm}^{-1}$ and 601: 1005 $\text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{min}}: \epsilon_{\text{min}} = 315: 255 \text{ M}^{-1} \text{ cm}^{-1}$ and 413: 160 $\text{ M}^{-1} \text{ cm}^{-1}$

Calculated compositions of trans-[Co(en)$_2$(m-CH$_3$C$_6$H$_4$NH$_2$)]I$_2$.H$_2$O: C = 19.29, H = 3.97, N = 10.25, Co = 8.60; Found: C = 19.4, H = 3.5, N = 10.0, Co = 8.4; Electronic absorption data in close agreement with the reported values.

$\lambda_{\text{max}}: \epsilon_{\text{max}} = 233: 8740 \text{ M}^{-1} \text{ cm}^{-1}$, 287: 2990 $\text{ M}^{-1} \text{ cm}^{-1}$, 346: 2275 $\text{ M}^{-1} \text{ cm}^{-1}$, 464: 1270 $\text{ M}^{-1} \text{ cm}^{-1}$ and 601: 270 $\text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{min}}: \epsilon_{\text{min}} = 271: 2705 \text{ M}^{-1} \text{ cm}^{-1}$ and 316: 2000 $\text{ M}^{-1} \text{ cm}^{-1}$

Calculated compositions of trans-[Co(en)$_2$(p-CH$_3$C$_6$H$_4$NH$_2$)]I$_2$.H$_2$O: C = 19.29, H = 3.97, N = 10.25, Co = 8.60; Found: C = 18.7, H = 3.7, N = 10.0, Co = 8.1; Electronic absorption data in close agreement with the reported values.

$\lambda_{\text{max}}: \epsilon_{\text{max}} = 233: 8740 \text{ M}^{-1} \text{ cm}^{-1}$, 286: 6020 $\text{ M}^{-1} \text{ cm}^{-1}$, 353: 4600 $\text{ M}^{-1} \text{ cm}^{-1}$, 455: 1075 $\text{ M}^{-1} \text{ cm}^{-1}$ and 601: 160 $\text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{min}}: \epsilon_{\text{min}} = 267: 4940 \text{ M}^{-1} \text{ cm}^{-1}$ and 320: 3525 $\text{ M}^{-1} \text{ cm}^{-1}$

Calculations of the energy levels of trans-[Co(en)$_2$(p-OC$_2$C$_6$H$_5$C$_6$H$_4$NH$_2$)]I$_2$.H$_2$O: C = 20.16, H = 4.09, N = 9.82, Co = 8.24; Found: C = 19.7, H = 3.6, N = 9.6, Co = 8.1; Electronic absorption data in close agreement with the reported values.

$\lambda_{\text{max}}: \epsilon_{\text{max}} = 232: 8740 \text{ M}^{-1} \text{ cm}^{-1}$, 331: 2125 $\text{ M}^{-1} \text{ cm}^{-1}$, 468: 2315 $\text{ M}^{-1} \text{ cm}^{-1}$ and 601: 1340 $\text{ M}^{-1} \text{ cm}^{-1}$, $\lambda_{\text{min}}: \epsilon_{\text{min}} = 293: 2145 \text{ M}^{-1} \text{ cm}^{-1}$ and 3822: 1525 $\text{ M}^{-1} \text{ cm}^{-1}$
Calculated compositions of trans-[Co(en)$_2$(p-OCH$_3$C$_6$H$_4$NH$_2$)]I$_2$.H$_2$O: C = 18.85, H = 3.88, N = 10.01, Co = 8.41; Found: C = 19.3, H = 3.9, N = 9.7, Co = 8.2. Electronic absorption data in close agreement with the reported values. $\lambda_{\text{max}}$: $c_{\text{max}}$ (233: 8740 $M^{-1} \text{cm}^{-1}$, 328: 2210 $M^{-1} \text{cm}^{-1}$, 470: 2385 $M^{-1} \text{cm}^{-1}$ and 601: 1795 $M^{-1} \text{cm}^{-1}$), $\lambda_{\text{min}}$: $c_{\text{min}}$ (284: 2235 $M^{-1} \text{cm}^{-1}$ and 387: 1760 $M^{-1} \text{cm}^{-1}$).

The general formula of the complex from elemental analysis data is [Co(en)$_2$(RC$_6$H$_4$NH$_2$)]I$_2$.H$_2$O. Anal: calculated composition: $C_{\text{min-max}}$ = 17.43-20.18, $H_{\text{min-max}}$ = 3.51-4.09, $N_{\text{min-max}}$ = 9.82-10.46, $Co_{\text{min-max}}$ = 8.24-8.78. Found: $C_{\text{min-max}}$ = 17.8-19.7, $H_{\text{min-max}}$ = 2.9-4.09, $N_{\text{min-max}}$ = 9.6-10.4, and $Co_{\text{min-max}}$ = 8.1-8.4.

**Synthesis of Cobalt(III)Alkyl Amine Complexes**

**Series II [Co$^{III}$($N_x$I$_y$)]n$^{+0}$ Complexes**

**Preparation of trans-[Co(NH$_3$)$_4$I$_2$]**

It was prepared and purified by the described method$^{76}$. Air is bubbled for five hours through a solution of 5 grams of Co(CH$_3$COO)$_2$ 2H$_2$O with 5 grams of NaNO$_2$ in 50ml of 20% NH$_3$. The solution is concentrated to a small volume with occasional addition of solid NaHCO$_3$ and then chilled. A large excess of alcohol is added to cause precipitation. The precipitate is filtered off, washed with alcohol-ether, and dried in a vacuum desicator. This is cis-dinitrotetraamine cobalt(III) nitrite, which is not contaminated with the trans compound. It is very easily hydrolyzed. This is added in small portion to conc. HI maintained at -10$^\circ$C to give the yield of iodide.
Anal: Calculated compositions of trans-[Co(NH$_3$)$_4$I$_2$]I: C = 0, H = 2.4, N = 11.2, Co = 11.7; Found: C = 0, H = 2.2, N = 10.8, Co = 11.3. Electronic absorption data in close agreement with the reported values. $\lambda_{\text{max}}: C_{\text{max}}$ (346: 1375 M$^{-1}$ cm$^{-1}$), $\lambda_{\text{min}}$ (398).

Preparation of trans-[Co(en)$_2$I$_2$]I

Preparation of trans-[Co(en)$_2$I$_2$]I. Trans-diiodobis(1,2-diaminoethane) iodide was prepared and purified by the literature$^{77,78}$ method. About 15 grams of cobaltous chloride was dissolved in 45 ml of water and to this solution 10 ml of 20% solution of 1, 2-diaminoethane was added with stirring. A vigorous stream of air was passed through the solution for 10 hours. Aeration was stopped and 33 ml of concentrated hydroiodic acid was added slowly. The solution was evaporated on a water-bath until a crust formed over the surface. The solution with solid was allowed to cool overnight and green coloured crystals appeared, which were filtered and washed by chilled ethanol and ether respectively. The solid was kept in an oven at 105°C for half an hour. A pale green trans complex was obtained. The complex was recrystallized from 20% dilute hydroiodic acid. The purity of complex was checked by elemental and spectral analyses.

Anal: Calculated compositions of trans-[Co(en)$_2$I$_2$]I: C = 8.6, H = 2.9, N = 10.0, Co = 10.5; Found: C = 8.1, H = 2.6, N = 10.4, Co = 10.1. Electronic absorption data in close agreement with the reported values. $\lambda_{\text{max}}: C_{\text{max}}$ (236.9: 8118 M$^{-1}$ cm$^{-1}$ and 416.9: 8835 M$^{-1}$ cm$^{-1}$), $\lambda_{\text{min}}: C_{\text{min}}$ (334: 5175 M$^{-1}$ cm$^{-1}$).
Preparation of [Co(dien)]I₃

For the preparation of the above complex, two stage preparation was performed, that is, [Co(dien)]I₃ was obtained from Co(dien)(NO₂)₃. A solution was prepared by adding 10.5 grams (0.036 mol) of cobalt(II) nitrate hexa hydrate, 11 grams (0.16 mol) of sodium nitrite, 2.9 grams (0.072 mol) of sodium hydroxide, and 8.7 grams (0.145 mol) of acetic acid to 15 ml of water. The solution was aerated with simultaneous addition of mixture of 3 ml of diethylene triamine in 12 ml of water. The solution was added very slowly, as rapid addition does not yield the compound. The pH (5 or 6) should be checked after amine has been added and is adjusted if necessary. The formation of a green precipitate indicates that the amine is being added too rapidly or the pH is too high. After aeration for one hour, the solution was filtered and the yellow precipitate was washed several times with water followed by ethanol.

Ten grams (0.033 mol) of trinitro(diethylene triamine)coblat(III) was gently heated with 250 ml of concentrated hydroiodic acid until nitrogen(IV) oxide evolution ceased. The resulting solution was cooled and allowed to stand overnight. The fine brown crystals of triiodo(diethylene triamine)cobalt(III) were removed by filtration on a Buckner funnel and washed with cooled acetone until the washings become colourless. The washings and little of acetone were added to the mother liquor to give a final volume of about 1 litre. A second crop of crystals can be recovered after 2 to 3 days.

Anal: Calculated compositions of [Co(dien)]I₃: C – 8.9, H – 2.4, N – 7.8, Co – 10.9; Found: C – 8.3, H – 1.9, N – 7.3, Co – 10.3: Electronic absorption data in close agreement with the reported values. \( \lambda_{max} : C_{max} (292.38 : 19250 \text{ } \text{M}^{-1} \text{ } \text{cm}^{-1} \text{ } \text{and} \text{ } 352.1 : 15125 \text{ } \text{M}^{-1} \text{ } \text{cm}^{-1}) \), \( \lambda_{min} : C_{min} (320 : 6872 \text{ } \text{M}^{-1} \text{ } \text{cm}^{-1}) \).
Preparation of [Co(trien)I₂] I

It was prepared by the procedure published earlier. A solution of 75 grams (0.50 mole) of triethylene tetramine in 525 ml water was added, with stirring, to a solution of 160 grams (0.67 mole) of cobalt(II) chloride hexa hydrate in 500 ml of water contained in a two-liter flask. A vigorous stream of air, previously washed with a dilute solution of sodium hydroxide, was passed through the solution for approximately eleven hours. About 350 ml of concentrated hydroiodic acid was added, and then the solution was concentrated on a steam-bath until finely divided crystals began to separate. The solution was kept overnight at room temperature, the bluish-purple crystalline product was collected on a filter and washed with a small amount of cold water followed by alcohol and ether.

Anal: Calculated compositions of [Co(trien)I₂] I : C – 12.4, H – 3.1, N – 9.6, Co – 10.1 ; Found : C – 12.0 , H – 3.5, N –10.1, Co – 9.7 : Electronic absorption data in close agreement with the reported values. λ_{max} : ε_{max} (289.36 : 18700 M⁻¹ cm⁻¹ and 352.1 : 13200 M⁻¹ cm⁻¹), λ_{min} : ε_{min} (320 : 8142 M⁻¹ cm⁻¹)

Preparation of [Co(tetren)I]I₂

It was prepared by the literature method. An aqueous solution of 24 gram of CoCl₂ 6H₂O in 75 ml of water and 20 ml of 30% H₂O₂ was added drop wise for nearly 20 minutes to a stirred solution of 19 gram of tetren in 50 ml of water, with cooling in an ice bath. The mixture was then allowed to stand at room temperature for 10 minutes and then 75 ml of hydroiodic acid was added slowly with stirring in an ice bath. The crude product was collected by filtration from
the cooled mixture, and the crystals were washed with 95% cooled methanol and dried in desiccators. The product was recrystallized by dissolving it in the minimum amount (5g/150ml) of hydroiodic acid. The crystals obtained from the cooled solution were washed and dried as above.

Anal: Calculated compositions of [Co(tetren)]I₂: C – 15.4, H – 3.7, N – 11.3, Co – 9.5; Found: C – 14.9, H – 3.2, N – 10.8, Co – 9.0: Electronic absorption data in close agreement with the reported values. \( \lambda_{\text{max}} : C_{\text{max}} \) (286.35 : 14025 \( M^{-1} cm^{-1} \) and 355.1 : 9625 \( M^{-1} cm^{-1} \), \( \lambda_{\text{min}} : C_{\text{min}} \) (320 : 5225 \( M^{-1} cm^{-1} \))

Materials and Methods The IR spectra of the complexes were recorded on a Thermo Niccollet-6700 FT-IR instrument (KBr pellet technique). Electronic absorption spectral studies were undertaken using HITACHI model U-1800 single beam spectrophotometer with a quartz cell. The VSM spectra of the complexes were recorded in a powder form on a Lakeshore-7404 at sample vibration frequency 82.5 Hz. A crystallography study was performed on the prepared cobalt(III) complexes by rotating anode diffractometer (XRD-PHILIPS-PANALYTICAL, Netherland) using Cu-Kα irradiation.
1.12 Aim of the Investigation

In this investigation two series of cobalt(III) complexes were synthesized and characterized. The first series of complexes contains aryl amines as the sixth ligand and the second series contains alkyl amine ligands. The general formula of the first series is [Co^{III}(en)_2(L)]^{2+} complexes (where L = RC_6H_4NH_2; R = m-OMe, p-F, H, m- Me, p-Me, p-OEt and p-OMe) and the second series is [Co^{III}(N)_x(I)_y]^{n+/0} complexes (where (N)_x = (tetren), (NH_3)_4, (tren), (dien), and (en)_2). All the complexes were synthesized, recrystallised and characterized using elemental, spectral, magnetic studies like vibrating sample magnetometer (VSM) analysis and Powder X-Ray Diffraction Analysis. The electron transfer reaction between [Co^{III}(en)_2(L)]^{2+}/[Co^{III}(N)_x(I)_y]^{n+/0} and [Fe^{IV}(CN)_6]^{4-} as well as photoredox reaction using 254 nm wavelength low pressure mercury vapour lamp were carried out in neat water and in binary mixed solvents with water and methanol (MeOH)/1,4-dioxane (Diox). Generally, the compositions of the mixtures are: water/organic co-solvent = 100/0, 95/5, 90/10, 85/15, 80/20, 75/25 and 70/30 (v/v) mixtures. The solvents were chosen because these two can act as hydrogen bond donor/hydrogen bond acceptor solvents. The organic co-solvents can be used to prepare a series of binary mixtures of varying relative permittivity. The electron transfer (ET) rate constants and the quantum yield values were subjected to linear and multiple regression analyses to understand the solvation characteristics on the reactivities of the metal complexes. Cobalt(III) complexes can undergo an interesting redox reactions in the above mentioned conditions, therefore, the above two series with two different solvents were chosen for this investigation.
1.2 References


