J. Indian Chem. Soc.,
Vol. 89, March 2012, pp. 335-348

Synthesis, spectral characterization and solvent H-bonding effects on the electro- and photo-reduction of mixed ligand cobalt(III) complexes

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Manuscript received 31 January 2011, revised 07 June 2011, accepted 20 June 2011

Abstract : Seven new Co^{III} complexes of the type *cis*-β-[Co(dmen)$_2$(R-aniline)Cl]Cl$_2$ where dmen = *N,N'*-dimethylethylenediamine, R = *p*-H, *p*-F, *p*-Me, *p*-Et, *p*-OMe, *p*-OEt and *m*-Me have been synthesized and characterized by elemental analysis, UV-Vis, FT-IR, ^{1}H NMR, TGA and differential pulse voltammetric (DPV) techniques. Further, the electro- and photo-reduction of these Co^{III} complexes has been studied in propan-2-ol/water and 1,4-dioxane/water binary mixtures. The redox potential ($E_{1/2}$) and the photo-reduction quantum yield ($\Phi_{Co^{II}}$) data were correlated with solvent and structural parameters with an aim to shed some light on the mechanism of these reactions. Correlation of $E_{1/2}$ and $\Phi_{Co^{II}}$ with solvent parameters indicated that the reactivity is influenced by both specific and non-specific solute-solvent interactions. The electro- and photo-reduction of these complexes was observed to become increasingly easier with an increase in the dipolarity/polarizability of the medium as evidenced by the Kamlet-Taft correlation. The difference in the relative easiness of the reduction has been explained using the difference in H-bonding properties of the co-solvents.

Keywords : Cobalt(III) complexes, photo-reduction, solvent effect, Hammett equation.

Introduction

The cobalt(III) complexes have been extensively studied and reviewed in recent years due to their applications in bio inorganic chemistry side[1-6]. Therefore, the synthesis, characterization and physicochemical studies of cobalt(III) complexes are the important to elucidate the mechanism of biologically important processes. During the last few years' correlation analysis in the area of solvent effects are also interesting because it explain the effect of different solvents upon rates of chemical change in any considerable process. In general, solvent play the major role of the reaction. Particularly, in binary solvent mixtures as the solute-solvent interaction in these mixtures is more complex than pure solvents. In pure solvents, the composition of the solvation in microsphere is same as in the bulk solvent. But in binary mixture, the composition in this microsphere can be different. The solute can interact to a different degree with the component of the mixture. These solvent effects generally been understood using Linear Free Energy Relationships (LFER)[7] via Kamlet-Taft equation. This multiple regression equation greatly increased our understanding the role of the solvent. Though many reports on the effect of solvent on various types of reactions such as substitution[8,9], redox[10,11], isomerization[12,13] and solvolysis[14,15] of cobalt complexes have been published during the past, such solvent variation studies on the electro-reduction and photo-reduction of these complexes are very scare in literature[16,17] and hence the present study. Structural variation studies are also important for the study and interpretation of chemical reactions and the mechanisms.

The main objective, therefore, of the present work is to investigate the synthesis, spectral characterization and study of solvent effects on the electro- and photo-reduction of a series of mixed ligand cobalt(III) complexes in binary aqua-organic solvent media. The solvent effects on the reaction has been carried out in propan-2-ol/water and 1,4-dioxane/water mixtures of varying compositions and correlation analysis of the data was carried out using linear free energy relationships with an aim to get a better insight into the mechanism of the reaction. The selection of these two organic co-solvents for the study is

based on the fact that propane-2-ol is a typical hydrogen bond donor (HBD) solvent while 1,4-dioxane is a typical non-HBD solvent. Hence by varying the concentration of these solvents in the aqueous binary mixture, the hydrogen bonding property of the mixture can be varied smoothly.

Experimental

Materials : All the chemicals used were of high purity analytical grade (Aldrich, Bangalore or Merck, Mumbai, India). The organic co-solvents, propan-2-ol and 1,4-dioxane used were of spectroscopic grade (Merck, India) and were used as received. Doubly-distilled water was used throughout the work.

Synthesis of Co^{III} complexes : The cobalt(III) complexes, *cis*-β-$[Co(dmen)_2(R\text{-aniline})Cl]Cl_2$ (where dmen = *N,N'*-dimethylethylenediamine and R = *p*-H, *p*-F, *p*-Me, *p*-Et, *p*-OMe, *p*-OEt and *m*-Me) were prepared and purified by the method described for the triethylenetetramine analog[18]. In a typical experiment, acid free $[Co(dmen)_2Cl_2]Cl$[19] (2.9 mmol) was suspended in water (2 ml) and was ground in a mortar with dropwise addition of aniline (2.9 mmol) for 0.5–2 h. Calculated amounts of liquid anilines were added directly while solid anilines were dissolved in 2 ml ethyl alcohol and added. After the addition was completed, the reaction mixture was set aside for about an hour until no further change in colour was noticed. The resultant complex was rinsed with alcohol and ether over a Bucker funnel and was recrystallized twice in acetone/DMF mixture.

Analytical and spectral measurements : The electronic absorption spectra of the Co^{III} complexes were recorded using JASCO, UV-Vis double beam spectrophotometer (V 630, Japan). The FT-IR spectra of the complexes were recorded using KBr disc on a JASCO, FT-IR spectrometer (460 Plus, Japan). ^1H NMR spectra were recorded at Madurai Kamaraj University, Madurai. Elemental (CHN) analysis was carried out at the Central Electrochemical Research Institute, Karaikudi. Conductance measurements were performed using Elico, India Conductivity Bridge. Magnetic measurements were carried out at the Indian Institute of Technology, Chennai.

Electrochemical experiment : The differential pulse voltammetric experiments were carried out with a computer-controlled electrochemical system (CHI643B Electrochemical analyzer). Solutions of the electrolyte, the Co^{III} complexes, were prepared with double distilled water. All electrochemical experiments were performed at 25 ± 0.2 °C using a standard three electrode two compartment configuration with a glassy carbon (GC-3 mm) working electrode, a spiral platinum counter electrode and a Ag | AgCl (KCl sat.) reference electrode. The carbon electrodes were polished between experiments with alumina (0.5 μm) paste. All solutions were deoxygenated thoroughly by purging with nitrogen gas for 15–20 min before commencement of the measurement.

Photolysis experiment : Solutions for photolysis contained the Co^{III} complex (4×10^{-3} *M*) and $NaNO_3$ (0.1 *M*). All the solutions prepared contained binary solvents of varying compositions : propan-2-ol in water and 1,4-dioxane in water [0–40% (v/v) of co-solvent]. Steady photolysis experiments were carried out using a low pressure mercury vapour pen-ray quartz lamp (254 nm). Air-equilibrated solutions were used for photolysis and the temperature control was maintained at 25 ± 1 °C. For quantum yield determinations, photolysis was carried out to within less than *ca.* 15% of the total reaction. The incident light intensities were measured by potassium ferrioxalate actinometry[20]. Quantum yields were calculated by estimating Co^{II} formed by Kitson's method[21].

Linear free energy relationships : These relationships are formulated by using empirical constants and are linear with at least one variable, and on the other hand the linearity is not essential and is not strictly maintained in all known equations. In the present study, the effect of solvent on the reduction behavior of the Co^{III} complexes was analyzed using solvent macroscopic properties such as the most popular relative permittivity, ε_r[22], and the donor number[23]. The donor number has proven very useful in coordination chemistry, since it can be correlated with other physical observables such as redox potentials[24].

As it was well established that both specific and non-specific solute-solvent interactions can influence the reactivity[16,17], the experimental data were analyzed using the most celebrated Kamlet-Taft solvatochromic comparison method (eq. (1)) which incorporates both the types of interactions[25].

$$\log k = A_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

where π^* 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, α is the solvent hydrogen bond donor (HBD) acidity which describes the ability of the solvent to donate a proton, β is the solvent hydrogen bond acceptor (HBA) basicity which provides a measure of the solvent's ability to accept a proton (donate an electron pair), in a solute to solvent hydrogen bond, and A_0 is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, a and b measure the relative susceptibilities of the solvent-dependent solute property log k ($E_{1/2}$ or $\Phi_{Co^{II}}$ in the present study) to the indicated solvent parameter. These solvatochromic parameters for the aqueous organic mixtures used in the present study were calculated as described in the literature[26].

The effect of substituent on the reactivity was tested using the Hammett equation[7] :

$$\log k = \log k^0 + \rho\sigma \qquad (2)$$

where k is the rate constant ($E_{1/2}$ or $\Phi_{Co^{II}}$ in the present study). The symbol k^0 denotes the statistical quantity corresponding approximately to k for the unsubstituted compound. The substituent constant, σ, is characteristic of the substituent (in a given position, *meta* or *para*) and independent of the reaction, whereas the reaction constant, ρ, is determined by the reaction and its conditions (reagent, solvent, catalyst, temperature) and is independent of substituent.

Data analysis : Correlation analyses were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using correlation coefficient (r in the case of a simple linear regression and R in the case of multiple linear regression) and standard deviation (sd)[7]. In case of multiple correlation analysis, the percentage contribution (P_x) of a parameter to the total effect on reactivity was computed as reported earlier[27].

Results and discussion

The physical and analytical data of the Co^{III} complexes of the type *cis*-β-[Co(dmen)$_2$(R-aniline)Cl]Cl$_2$ where dmen = *N,N'*-dimethylethylenediamine, R = *p*-H, *p*-F, *p*-Me, *p*-Et, *p*-OMe, *p*-OEt and *m*-Me are given in Table 1. All the Co^{III} complexes gave satisfactory elemental analysis (CHN) confirming to the general composition. The complexes are all diamagnetic as expected. The molar conductance values (Table 1) in water (298 K) identify the species as 1 : 2 electrolytes[28].

Table 1. Physico-chemical properties of the Co^{III} complexes

R[a]	Colour	Elemental analyses (%) : Found (Calcd.)			Molar conductance[b]
		C	H	N	(S cm^2 mol^{-1})
H	Brown	38.90	7.33	15.42	278
		(38.80)	(7.16)	(15.66)	
p-F	Brown	36.28	6.84	15.45	260
		(37.25)	(6.65)	(15.52)	
m-Me	Brown	40.35	7.25	15.68	283
		(40.27)	(7.38)	(15.66)	
p-Me	Brown	40.38	7.42	15.75	255
		(40.27)	(7.38)	(15.66)	
p-OMe	Brown	38.84	7.15	15.15	270
		(38.88)	(7.13)	(15.12)	
p-Et	Brown	41.60	7.62	15.19	281
		(41.65)	(7.59)	(15.18)	
p-OEt	Brown	40.25	7.37	14.70	265
		(40.25)	(7.34)	(14.68)	

[a]Substituent in aniline moiety; [b]in water.

Electronic spectra : The electronic spectra of the Co^{III} complexes were recorded in water and a representative spectrum is shown in Fig. 1. The absorption maxima and

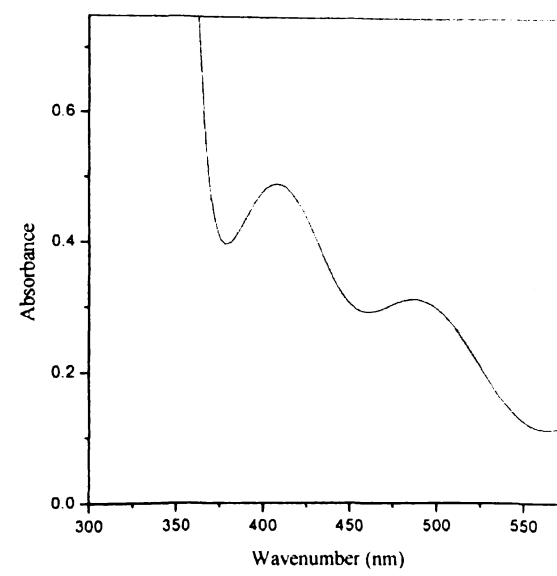


Fig. 1. Electronic spectra of *cis*-β-[Co(dmen)$_2$(*p*-Et-C$_6$H$_4$NH$_2$)-Cl]Cl$_2$ in aqueous solution.

molar extinction coefficients of the Co^{III} complexes are reported in Table 2. It is well established that, regular octahedral $Co^{III}L_6{}^{3+}$ complexes have two UV-Vis spin allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. In tetragonal complexes of the type $Co^{III}L_4X_2$, the first band is split into two, $^1A_{1g} \rightarrow {}^1E_g$ at low energy and $^1A_{1g} \rightarrow {}^1A_{2g}$ at higher energy. In *trans* complexes this splitting is

Table 2. Electronic spectral data for the Co^{III} complexes in water

R[a]	$^1A_g \rightarrow {}^1T_{1g}$ nm (log ε)[b]	Charge transfer nm (log ε)[b]
H	489 (2.52)	406 (2.66)
p-F	486 (2.53)	404 (2.67)
m-Me	486 (2.52)	408 (2.71)
p-Me	485 (2.49)	407 (2.69)
p-OMe	484 (2.51)	405 (2.70)
p-Et	487 (2.49)	408 (2.72)
p-OEt	484 (2.53)	405 (2.67)

[a]Substituent in aniline moiety; [b]ε_{max} in M^{-1} cm^{-1}.

sufficient to completely resolve this band into two components, this is rarely the case in *cis* complexes. Further, ε in *cis* complexes are much greater than the corresponding *trans* values[29]. In the present study, all the Co^{III} complexes show two absorption bands. The absorption bands at *ca.* 405 nm of the complexes were assigned to the MLCT band, while the bands at *ca.* 486 nm were assigned to the first absorption band i.e. due to $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The observed positions and intensities strongly suggest a *cis* rather than a *trans* structure for these complexes[29]. Further, the electronic spectrum of these complexes were found to resemble that for *cis*-β-$Co(trien)Cl_2{}^+$ ion suggesting that these complexes may also posses a *cis*-β arrangement of ligands around the Co^{III} ion[30]. Furthermore, the positions of these bands vary very little through the series of complexes, thus indicating that the ligand field about the Co^{III} ion remains almost constant.

Infrared spectra : The FT-IR spectrum of $[Co(dmen)_2(C_6H_5NH_2)Cl]Cl_2$ is shown in Fig. 2. Generally the FT-IR spectrum of $[Co(N)_4X_1X_2]^+$ type molecules shows the IR vibrations at 910–800 cm^{-1} indicates the CH_2 rocking region of the complexes and in general, *cis* complexes exhibit more bands in this region than *trans* complex. In our study, we observed the bands at 838, 860 cm^{-1} corresponds to CH_2 rocking region of the complexes[19]. It conform that N atom of dmen (dmen = *N,N'*-dimethylethylenediamine) molecules coordinated with metal ion. The bands ~1600 cm^{-1} may be due to the anti-symmetric NH_2 bending vibrations. The new strong bands observed in the range of ~500 cm^{-1} may be attributed the M–N stretching[31]. The bands due to NH_2 deformation observed in the ~1300 cm^{-1} region confirm that the structure of the Co^{III} complexes is similar to that of *cis*-β-$[Co(trien)X_2]^{2+}$ ion[32] and also *cis*-β-$[Co(trien)(RC_6H_4NH_2)Cl]^{2+}$ ion[33] proposed earlier.

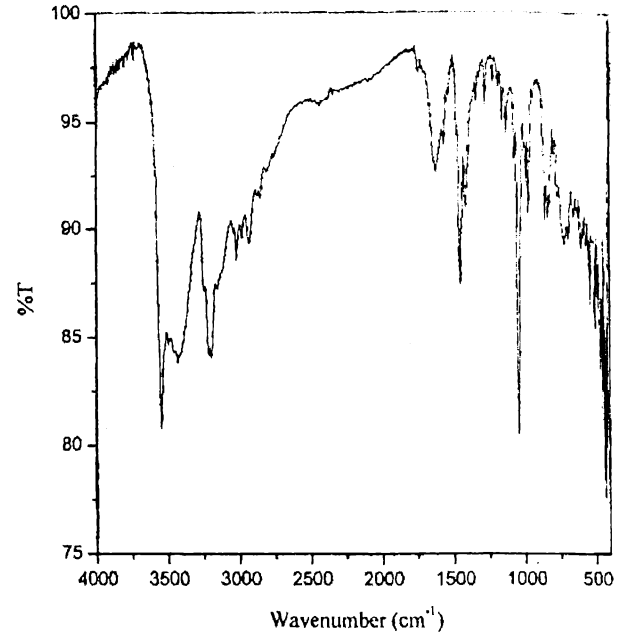


Fig. 2. FT-IR spectrum of *cis*-β-$[Co(dmen)_2(C_6H_5NH_2)Cl]Cl_2$ in KBr disc.

^1H NMR spectra : A representative ^1H NMR spectrum of *cis*-β-$[Co(dmen)_2(p\text{-}Et\text{-}C_6H_4NH_2)Cl]Cl_2$ recorded in DMSO-d_6 is shown in Fig. 3. It is evident from the spectrum that, the signal at ~2.5 ppm belongs to methyl protons at the nitrogen atoms of dmen ligand. The signal at 3.4 ppm belongs to the CH_2 protons of the dmen ligand[34]. The characteristic signals around ~3 ppm confirmed that the Co^{III} complexes exist as *cis*-β isomers rather than *cis*-α one[35]. The downfield shift occurs with the NH_2 protons (aniline moiety) appearing at 6.1 ppm

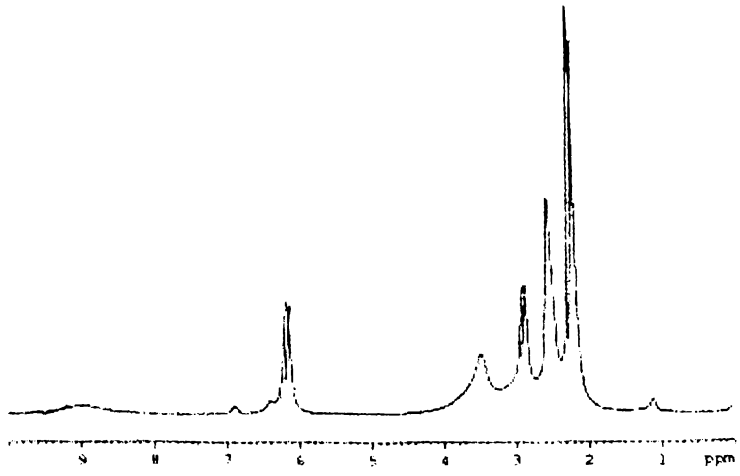


Fig. 3. ^{1}H NMR spectrum of *cis*-β-[Co(dmen)$_2$(*p*-Et-C$_6$H$_4$NH$_2$)Cl]Cl$_2$.

in the ^{1}H NMR spectrum of the [Co(dmen)$_2$(C$_6$H$_5$NH$_2$)-Cl]Cl$_2$ complex, corresponding to 5.1 ppm in the free ligand[36] as expected due to coordination of the aniline nitrogen to the metal ion.

Thermal analysis : Thermal investigation of a representative complex, *cis*-β-[Co(dmen)$_2$(*p*-Et-C$_6$H$_4$NH$_2$)-Cl]Cl$_2$, was made in the temperature interval from room temperature to 1000 °C in stream of nitrogen. The TGA pattern of the complexes is shown in Fig. 4 and the corresponding decomposition patterns are summarized in Table 3. The Co^{III} complex decomposed in a three stage process as shown by the presence of three breaks in the

Table 3. Summary of TGA studies of *cis*-β-[Co(dmen)$_2$(*p*-Et-C$_6$H$_4$NH$_2$)Cl]Cl$_2$

Stages	TGA temp. range (°C)	Mass loss (%) Expt.	Calcd.	Probable leaving group
I	290	14	15.32	Cl$_2$
II	290–425	39	37.64	2dmen
III	425–710	25	26.47	*p*-Et-C$_6$H$_4$NH$_2$

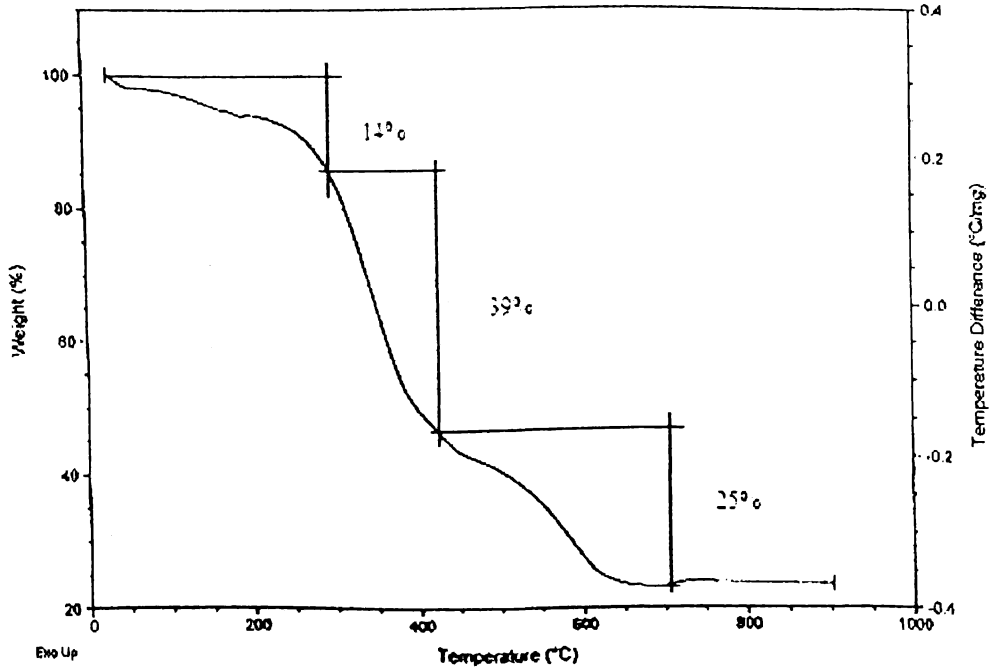
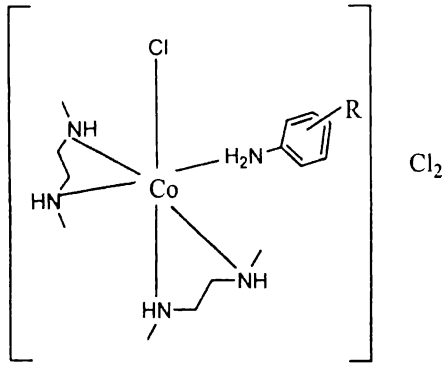


Fig. 4. TGA spectrum of *cis*-β-[Co(dmen)$_2$(*p*-Et-C$_6$H$_4$NH$_2$)Cl]Cl$_2$.

TGA graph. The complex was found to be thermally stable up to 100 °C. Above 100 °C a rapid decomposition occurs with a mass loss corresponding to the loss of organic moiety and loss of two chlorine atoms present outside the coordination sphere (stage I). The mass loss of 39% and 25% for stages II and III, respectively, are recorded and are accounted by the loss of dmen (dmen = *N,N'*-dimethylethylenediamine) and *t*-Bu-$C_6H_4NH_2$ ligand in two stages. The procedural decomposition temperature for stage III is close to 710 °C and the decomposition ends at 900 °C. The close agreement between the observed and calculated values of percentage mass loss indicated that the proposed formula for the complex is correct.

Based on the foregoing results and discussion the following structure for the Co^{III} complexes, with a *cis*-β configuration, has tentatively been proposed.



where R = *p*-H, *p*- F, *p*-Me, *p*-Et, *p*-OMe, *p*-OEt, *m*-Me

Electro-reduction study : The solvent and substituent effects on the electro-reduction of a series of Co^{III} complexes of the type *cis*-β-[Co(dmen)$_2$(R-aniline)Cl]Cl_2 where dmen = *N,N'*-dimethylethylenediamine, R = H, *p*-F, *m*-Me, *p*-Me, *p*-Et, *p*-OMe and *p*-OEt, in varying concentrations of organic co-solvents (propan-2-ol and 1,4-dioxane) in water was investigated. Attempts have been made to analyze the effect of solvent and structure on the redox potentials ($E_{1/2}$) of the complexes using simple and multiple regression equations.

Differential pulse voltammetric (DPV) technique was used to study the redox behavior of these complexes. A representative DPV curve is shown in Fig. 5. All the other Co^{III} complexes exhibit a similar DPV pattern under present experimental conditions. The redox potential data for all the complexes in water are given in Table 4. Generally the redox potentials are better expressed by $E_{1/2}$ than by the anodic peak E_{pa} or cathodic peak E_{pc} potentials, because both E_{pa} and E_{pc} change with scan rate, whereas $E_{1/2}$ is independent of the scan rate[37]. The redox potential ($E_{1/2}$) of the Co^{III}/Co^{II} couple was determined according to the following equation[38].

$$E_{1/2} = (E_{pa} + (E_{pc})/2 \quad (3)$$

The voltammograms of all the Co^{III} complexes exhibited a reversible cathodic and anodic peak in the 0.1 to -0.6 V range which is probably due to the Co^{III}/Co^{II} couple[39]. The separation values between the anodic and cathodic peak potentials (ΔE_p) show the quasi reversible (*p*-Me and *p*-OMe) and irreversible (H, *p*-F, *m*-Me, *p*-Et, and *p*-OEt,) nature of the Co^{III}/Co^{II} redox couple[40].

Table 4. Electrochemical data ($E_{1/2}$, V) from DPV for the Co^{III} complexes *cis*-β-[Co(dmen)$_2$(R-aniline)Cl]Cl_2 in water at 25 ± 0.2 °C

R[a]	E_{pc} (III/II)	E_{pa} (II/III)	$E_{1/2}$	ΔE_p
H	0.104	-0.380	-0.138	484
p-F	0.084	-0.472	-0.194	556
m-Me	0.028	-0.428	-0.200	456
p-Me	-0.076	-0.228	-0.152	152
p-OMe	-0.320	-0.588	-0.454	268
p-Et	-0.128	-0.560	-0.344	432
p-OEt	0.100	-0.553	-0.227	653

[a]Substituent in aniline moiety.

Effect of solvent : The electro-reduction of the Co^{III} complexes has been studied in varying amounts of the organic co-solvent in water ranging from 0 to 40% v/v of co-solvent. The electrochemical data as a function of co-solvent percentage are collected in Table 5. The results indicate that in both the solvent mixtures the $E_{1/2}$ value for the Co^{III}/Co^{II} couple becomes more positive with an increase in the co-solvent concentration in the mixture. The general pattern of the voltammograms remains unaltered with change in the composition of the solvent mixture which indicated that the added organic co-solvent does not alter the nature of the mechanism of the redox reaction. However, the change in composition of the sol-

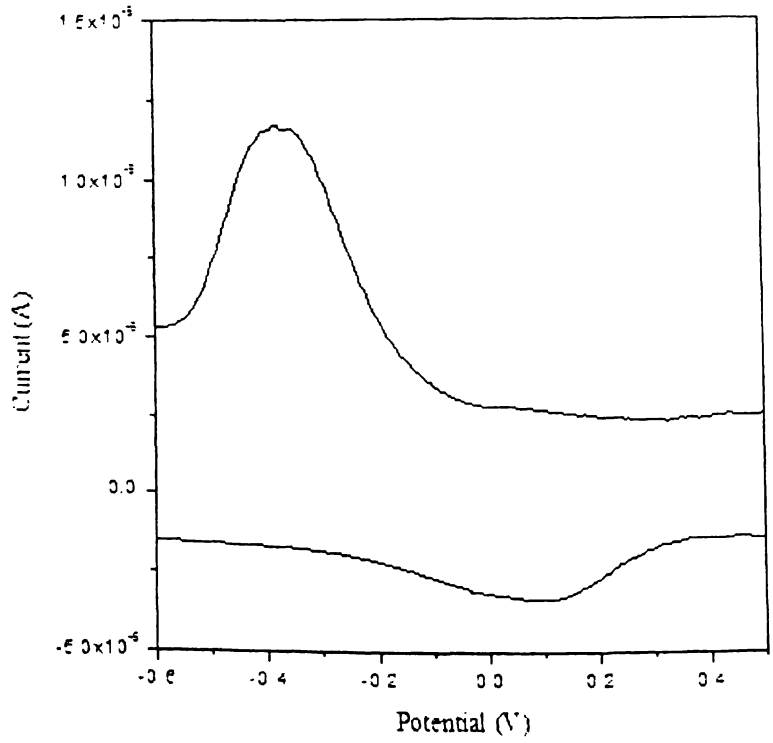


Fig. 5. Differential pulse voltammogram of *cis*-β-[Co(dmen)$_2$(C$_6$H$_5$NH$_2$)Cl]Cl$_2$ in water.

vent mixture influences the lenience of the redox process. The variation of $E_{1/2}$ with the mole fraction of the organic co-solvent (x_2) in the binary mixture is depicted in the following correlation relations.

Table 5. Electrochemical data ($E_{1/2}$, V) from DPV for the Co^{III} complexes *cis*-β-[Co(dmen)$_2$(R-aniline)Cl]Cl$_2$ in varying percentages of propan-2-ol/water and 1,4-dioxane/water medium

R[a]	0	5	10	15	20	25	30	35	40
				% of propan-2-ol (v/v)					
H	-0.138	-0.132	-0.125	-0.119	-0.113	-0.108	-0.103	-0.097	-0.091
p-F	-0.194	-0.183	-0.174	-0.162	-0.154	-0.152	-0.150	-0.143	-0.139
m-Me	-0.200	-0.192	-0.189	-0.182	-0.175	-0.163	-0.159	-0.152	-0.148
p-Me	-0.152	-0.136	-0.124	-0.119	-0.110	-0.082	-0.060	-0.053	-0.045
p-OMe	-0.454	-0.446	-0.432	-0.416	-0.400	-0.387	-0.373	-0.360	-0.355
p-Et	-0.344	-0.323	-0.316	-0.300	-0.284	-0.282	-0.272	-0.266	-0.256
p-OEt	-0.227	-0.218	-0.210	-0.202	-0.198	-0.194	-0.184	-0.182	-0.179
				% of 1,4-dioxane (v/v)					
H	-0.138	-0.131	-0.125	-0.121	-0.113	-0.109	-0.104	-0.099	-0.094
p-F	-0.194	-0.192	-0.187	-0.179	-0.172	-0.169	-0.165	-0.158	-0.154
m-Me	-0.200	-0.189	-0.184	-0.176	-0.166	-0.162	-0.152	-0.136	-0.133
p-Me	-0.152	-0.138	-0.120	-0.112	-0.102	-0.096	-0.088	-0.084	-0.070
p-OMe	-0.454	-0.440	-0.420	-0.410	-0.402	-0.389	-0.378	-0.359	-0.345
p-Et	-0.344	-0.318	-0.312	-0.308	-0.294	-0.280	-0.280	-0.272	-0.270
p-OEt	-0.227	-0.212	-0.206	-0.204	-0.200	-0.198	-0.186	-0.182	-0.172

[a]Substituent in aniline moiety.

$$E_{1/2}\,(V) = 0.34\,x_2 - 0.13 \quad (4)$$

(Co-solvent = propan-2-ol; R = H; r = 0.99; sd = 0.002)

$$E_{1/2}\,(V) = 0.35\,x_2 - 0.13 \quad (5)$$

(Co-solvent = 1,4-dioxane; R = H; r = 0.98; sd = 0.005)

The difference in the observed slope values indicates a difference in the participation of the co-solvents in the solvation process.

For all the complexes, in both the aquo-organic solvent media, the correlation of $E_{1/2}$ with the inverse of the relative permittivity of the medium through Laidler-Erying[22] is satisfactory ($0.98 \geq r \geq 0.92$; figure not shown) with positive slopes. In both propan-2-ol/water and 1,4-dioxane/water media the positive slopes of the correlation indicate that $E_{1/2}$ increases with an increase in concentration of the co-solvent in the mixture. Thus, the addition of propan-2-ol or 1,4-dioxane to the mixture makes the reduction of Co^{III} to Co^{II} easier. Likewise, the correlation of $E_{1/2}$ values with normalized donor number, DN^N, of the solvent mixture is also satisfactory ($0.99 \geq r \geq 0.94$) in both the solvent media. The DN^N values employed in the present study were calculated as described earlier[23]. Either an increase in concentration of propan-2-ol or a decrease in concentration of 1,4-dioxane in the mixture increases the donicity of the mixture[38]. For a given complex in propan-2-ol/water medium, the $E_{1/2}$ shifts towards more positive potentials with an increase in DN^N. In other words with rise in the concentration of the organic co-solvent in the mixture the reduction of Co^{III} to Co^{II} becomes easier. However, in the case of 1,4-dioxane/water, for a given complex, the $E_{1/2}$ shifts towards more negative potentials with decrease in DN^N. In other words with rise in the concentration of the organic co-solvent in the mixture the reduction of Co^{III} to Co^{II} becomes easier.

Satisfactory quantitative descriptions of medium effects should take into all non-specific and specific solvent-solute interactions into considerations. This kind of dual dependency of reactivity on solvent composition is illustrated by the Kamlet-Taft solvatochromic comparison method[25]. This method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on reactivity. Thus, the experimentally measured redox potential data, $E_{1/2}$ for the Co^{III}/Co^{II} couple were correlated with the solvatochromic parameters α, β and π*. The $E_{1/2}$ values for the solvent mixtures investigated show an excellent correlation with Kamlet-Taft parameters with an observed variance of ~97% in both the solvent mixtures. The goodness of these fits was confirmed by the linearity of the plots of experimentally measured $E_{1/2}$ values versus calculated $E_{1/2}$ values (Figs. 6 and 7). The statistical results of the correlation and the weighted percentage contributions of the solvatochromic parameters are presented in Table 6.

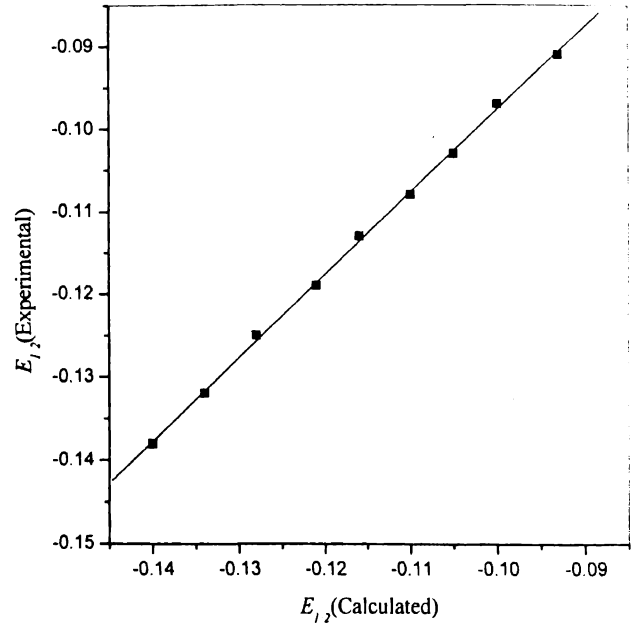


Fig. 6. Experimentally determined redox potential values for *cis*-β-$[Co(dmen)_2(C_6H_5NH_2)Cl]Cl_2$ plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 6.

Such an excellent correlation of the experimental data with the Kamlet-Taft solvatochromic parameters indicates the operation of both specific and non-specific solute-solvent interaction mechanisms in the present system. The observation of this multiple regression analysis leads to the following preliminary conclusions. The weighted percentage contributions indicated that the specific properties, as indicated by P_α and P_β play a dominant role in propan-2-ol/water medium and specific properties and non-

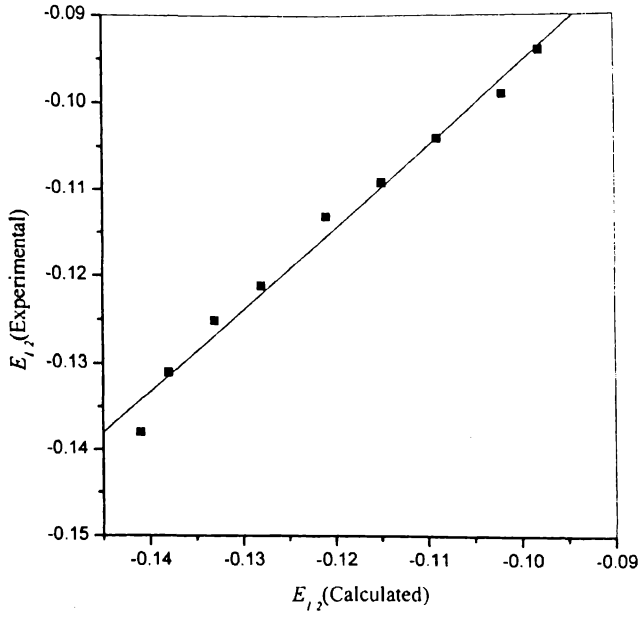


Fig. 7. Experimentally determined redox potential values for *cis*-β-$[Co(dmen)_2(C_6H_5NH_2)Cl]Cl_2$ plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 6.

specific properties, as indicated by P_α and P_β and P_{π^*} play an equal role in 1,4-dioxane/water medium in governing the electro-reduction of the complexes. The weighted percentage contributions indicate that in the case of propan-2-ol/water medium, the HBD properties play appreciable roles in governing the reactivity. The signs of the majority of the coefficients of the α terms are positive indicating that the solvation of the intermediate, through H-bonding properties, is greater than that of the reactant. Hence, an increase in the concentration of the co-solvent in the mixture stabilizes the intermediate and consequently makes the reduction of Co^{III} to Co^{II} easier. On the other hand, in the case of 1,4-dioxane/water medium, since 1,4-dioxane is a typical HBA solvent, its contribution towards reactivity was found to be appreciable, as indicated by the β term. The majority sign of the coefficients of this term was observed to be negative indicating better solvation of the reactant than of the intermediate through dioxane's HBA properties. Hence an increase in the concentration of the co-solvent in the mixture should have made the reduction of Co^{III} to Co^{II} more difficult. However, the appreciable contribution of the dipolarity/polarizability of the medium makes the reduction easier. Owing to these two opposite effects the increase in the $E_{1/2}$ values in this mixture is observed to be less.

There exists a dynamic exchange of solvent molecules between the solvation shell of the excited state and the bulk. As the concentration of organic co-solvent in the

Table 6. Statistical results and weighted percentage contributions for the correlation of the redox potential ($E_{1/2}$) for $Co^{III/II}$ couple with Kamlet-Taft's solvatochromic parameters α, β and π* in propan-2-ol/water and 1,4-dioxane/water medium

R[a]	$100R^2$	*sd*	*a*	*b*	*s*	P_α	P_β	P_{π^*}
			Propan-2-ol/water (v/v)					
H	99	0.001	0.44	-0.06	-0.90	24	3	73
p-F	99	0.001	3.71	1.07	-2.51	44	12	44
m-Me	98	0.002	1.39	1.47	-0.71	37	35	28
p-Me	97	0.008	-2.52	-1.68	-0.69	50	30	20
p-OMe	99	0.004	3.16	2.44	-1.96	38	27	35
p-Et	99	0.003	4.69	1.89	-3.05	43	16	41
p-OEt	98	0.002	1.39	-0.09	-1.59	37	2	61
			1,4-Dioxane/water (v/v)					
H	98	0.002	21.5	-41.3	-61.8	14	25	61
p-F	99	0.001	5.82	-77	-40.3	4	52	44
m-Me	98	0.003	6.65	-47.8	-32.3	7	44	49
p-Me	94	0.007	36.3	-72.5	-105	14	26	60
p-OMe	98	0.005	11.8	-32.3	-38.4	12	38	50
p-Et	92	0.008	69.6	-100	-187	16	21	63
p-OEt	95	0.004	7.02	57.6	4.32	11	79	10[a]

[a]Substituent in aniline moiety.

mixture increases, more organic solvent molecules are introduced into the solvation shell, increasing the hydrophobic environment of the excited state. Increase in hydrophobicity of the medium stabilizes the intermediate through solute-solvent interactions (as enumerated in the Kamlet-Taft correlation) and consequently increases the redox potential i.e. makes the reduction of Co^{III} to Co^{II} easier. This is demonstrated by the results of eqs. (4) and (5). As the solute-solvent interaction varies in these mixtures, the extent of lenience of the reduction differs.

In both the medium, the dipolarity/polarizability, as indicated by $P_{\pi*}$, play a appreciable role in governing the electro-reduction of the complexes. The majority of the sign of this coefficient is negative indicating that the value of $E_{1/2}$ would increase with decreasing dipolarity/polarizability of the medium. As the concentration of organic co-solvent in the mixture increases the dipolarity/polarizability of the medium decreases and thus, the reduction of Co^{III} to Co^{II} becomes relatively easier.

Effect of structure : The effect of substituents in the aniline moiety on the redox potentials of Co^{III}/Co^{II} couple was studied with *para*- and *meta*-substituted aniline ligands in propan-2-ol/water and 1,4-dioxane/water medium. The $E_{1/2}$ values failed to conform to the usual Hammett or its modified equations[41]. The plot of $E_{1/2}$ versus Hammett's substituent constants, σ, is a scatter gram. This deviation from Hammett's plot may be due to the fact that the substituents present in the *para*- and *meta*-position of the aniline ligand have no significant effect on the electro-reduction of these complexes as they are far away from the metal centre.

Photo-reduction study : The solvent and substituent effects on the photo-reduction of a series of Co^{III}-aniline complexes, of the type *cis*-β-[Co(dmen)$_2$(R-aniline)Cl]Cl$_2$ where dmen = *N,N'*-dimethylethylenediamine, R = H, *p*-F, *m*-Me, *p*-Me, *p*-Et, *p*-OMe and *p*-OEt, in varying concentrations of organic co-solvent, propan-2-ol/water and 1,4-dioxane/water was investigated. Attempts have been made to analyze the effect of solvent and structure on the photo-reduction quantum yields ($\Phi_{Co^{II}}$) of the complexes using simple and multiple regression equations.

The quantum yields, $\Phi_{Co^{II}}$ measured at 254 nm for the photo-reduction of all the cobalt(III)-aniline complexes in various propan-2-ol/water and 1,4-dioxane/water mixtures, are collected in Table 7. It is evident from the results that $\Phi_{Co^{II}}$ increased as the mole fraction of the

Table 7. Quantum yields ($10^2\Phi_{Co^{II}}$) for the photo-reduction of [Co(dmen)$_2$(R-aniline)Cl]Cl$_2$ in air-equilibrated propan-2-ol/water and 1,4-dioxane/water mixtures at 25 ± 1 °C

R[a]	0	5	10	15	20	25	30	35	40
				Propan-2-ol % (v/v)					
H	7.3	7.4	7.6	7.7	7.9	8.2	8.2	8.4	8.7
p-F	11.6	11.8	11.9	12.1	12.3	12.6	12.6	12.7	12.9
m-Me	9	9.1	9.4	9.5	9.7	9.8	10	10.1	10.3
p-Me	9.5	9.6	9.6	9.7	9.8	9.9	10	10.1	10.2
p-OMe	8.2	8.4	8.6	8.7	8.8	9	9.1	9.2	9.4
p-Et	14.2	14.4	14.5	14.6	14.9	15	15.2	15.4	15.5
p-OEt	13.6	13.8	13.9	14	14	14.2	14.4	14.6	14.8
				1,4-Dioxane/water (v/v)					
H	7.3	7.6	7.8	8.0	8.3	8.5	8.7	9.0	9.3
p-F	11.6	11.7	11.8	11.8	11.9	12.0	12.1	12.2	12.3
m-Me	9.0	9.1	9.2	9.3	9.4	9.5	9.7	9.8	9.8
p-Me	9.5	9.6	9.8	10.1	10.2	10.4	10.5	10.7	10.9
p-OMe	8.2	8.4	8.4	8.7	8.9	9.1	9.3	9.4	9.6
p-Et	14.2	14.5	14.5	14.6	14.8	15.0	15.1	15.1	15.2
p-OEt	13.6	13.8	14.1	14.2	14.4	14.7	14.9	15.1	15.4

[a]Substituent in aniline moiety.

organic co-solvent increased in the mixture. This may be due to the reduction of metal centre by the ligand (LMCT) and the solvent (solvent-to-metal charge transfer). This argument is in line with that suggested by Weit *et al.*, for the photo-reduction of cobalt(III)-am(m)ine complexes[42]. Therefore, attempts have been made to analyze the effect of solvent and substitution on the photo-reduction quantum yields of the cobalt(III)-aniline complexes using linear and multiple regression equations.

Effect of solvent : The correlation of photo-reduction quantum yields with inverse of relative permittivity of the medium through Laidler-Erying[22] equation is only satisfactory ($0.99 \geq r \geq 0.95$ for both medium). The positive slope indicates that the excited state is less polar than the reactant. Such an excited state will more easily be attained in a medium of lower relative permittivity and hence the increase in quantum yield with increase in the proportion of organic co-solvent is observed. Similarly, the experimental data also correlates satisfactorily with donor number ($0.99 \geq r \geq 0.95$ in both the media). The DN^N values employed in the present study were calculated as described earlier[23].

The simplicity of idealized electrostatic models for the description of salvation of ions and dipolar molecules, considering solvents as nonstructured continua, has led to the use of physical constants, such as relative permittivity, ε_r, refractive index, n, or functions thereof, as macroscopic solvent parameters for the evaluation of medium effects. However, solute-solvent interactions take place on a molecular microscopic level within a structured discontinuum consisting of individual solvent molecules, capable of mutual solvent-solvent interactions. For this reason, and because of neglecting specific solute-solvent interactions, the electrostatic approach to medium effects often failed in correlating observed solvent effects with physical solvent parameters. In reality, satisfactory quantitative descriptions of medium effects have taken into account all non-specific and specific solvent-solvent-solute interactions. The separation of solvent polarity into non-specific and specific solvent-solvent-solute interaction mechanism is purely formal, but, if this separation can be reasonably done, the resultant parameters may be used to interpret solvent effects through such multiple correlations, thus providing information about the type and magnitude of interactions with the solvent[24].

The dual dependency of reactivity on solvent composition is tested using Kamlet-Taft equation[25]. The $\Phi_{Co^{II}}$ values in different propan-2-ol/water and 1,4-dioxane/water mixtures show an excellent correlation via Kamlet-Taft equation with an observed variance of *ca.* 98%. The goodness of these fits was confirmed by the linearity of the plots of experimentally measured $\Phi_{Co^{II}}$ values versus calculated $\Phi_{Co^{II}}$ values (Figs. 8 and 9). The statistical results of the correlation and weighted percentage contributions of the solvatochromic parameters are given in Table 8.

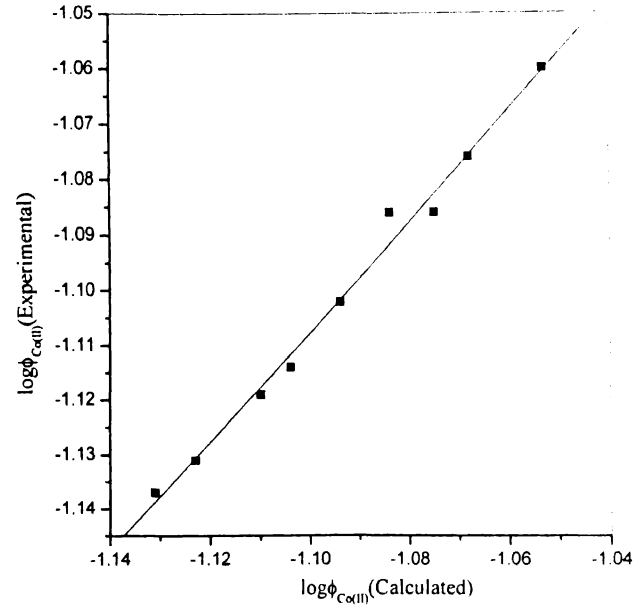


Fig. 8. Experimentally determined log $\phi_{Co^{II}}$ values for *cis*-β-$[Co(dmen)_2(C_6H_5NH_2)Cl]Cl_2$ plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 8.

The results indicate that, (i) The specific and non-specific solute-solvent interactions, as indicated by P_α, P_β and P_{π^*} play almost equal role in propan-2-ol/water medium and non-specific solute-solvent interactions, as indicated by P_{π^*} play a major role in 1,4-dioxane/water medium in governing the reactivity of the complexes. (ii) In the case of propan-2-ol/water medium, the sign of the coefficients '*a*' of the triparametric equation is randomly

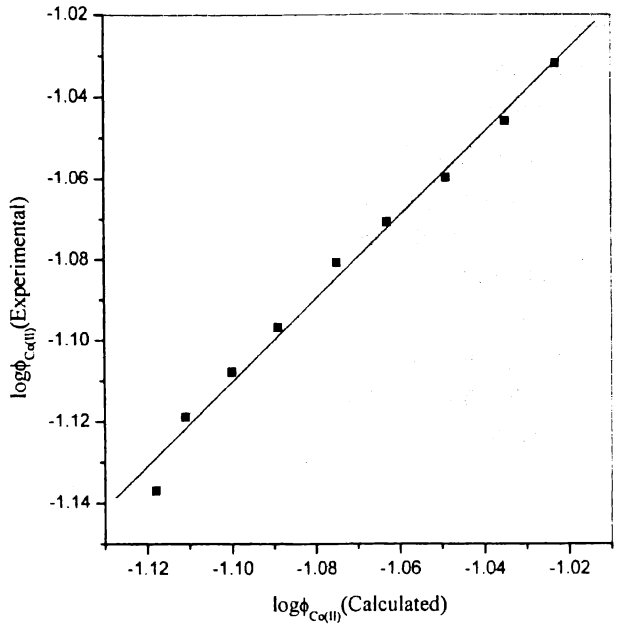


Fig. 9. Experimentally determined log $\phi_{Co^{II}}$ values for *cis*-β-[Co(dmen)$_2$($C_6H_5NH_2$)Cl]Cl_2 plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 8.

observed. This may be due to the fact that the medium interacts in a complex manner with the reactant/excited state[43]. On the other hand, in the case of 1,4-dioxane/water medium, since 1,4-dioxane is a typical HBA solvent, its contribution towards reactivity was found to be appreciable, as indicated by the β term. The majority sign of the coefficients of this term was observed to be negative indicating better solvation of the reactant than of the intermediate through dioxane's HBA properties. Hence an increase in the concentration of the co-solvent in the mixture should have made the reduction of Co^{III} to Co^{II} more difficult. However, the appreciable contribution of the dipolarity/polarizability of the medium makes the reduction easier. (iii) The dipolarity/polarizability of the mixture also plays an appreciable role in explaining the observed solvent effect as it is evidence from the percentage contribution values. The majority of the sign of the coefficient of this term is negative which shows that decrease in dipolarity/polarizability will stabilize the less polar excited state, to a greater extent, with increase in the proportion of organic co-solvent and consequently increases the $\Phi_{Co^{II}}$. Parallel observations has been made earlier for the photo-reduction of cobalt(III) complexes in aquo-organic solvent media[16,17].

Effect of structure : The effect of structure of the ligand on $\Phi_{Co^{II}}$ was studied by changing the *para*- and *meta*-

Table 8. Statistical results and weighted prcentage contributions for the correlation of photo-reduction quantum yield ($\Phi_{Co^{II}}$) with Kamlet-Taft's solvatochromic parameters α, β and π* in water/propan-2-ol/water and 1,4-dioxane/water mixtures

R[a]	$100R^2$	*sd*	*a*	*b*	*s*	P_α	P_β	P_{π^*}
			Propan-2-ol/water (v/v)					
H	98	0.003	-2.31	-2.64	-0.97	38	39	23
p-F	98	0.002	1.05	0.03	-1.26	36	1	63
m-Me	97	0.003	-0.41	-1.41	-1.27	11	36	53
p-Me	99	0.001	0.64	1.34	6.09	6	11	83
p-OMe	99	0.001	-0.60	-1.84	-1.40	14	38	48
p-Et	98	0.001	0.89	1.10	-0.42	36	40	24
p-OEt	98	0.001	-0.78	0.15	0.21	64	11	25
			1,4-Dioxane/water (v/v)					
H	98	0.004	25.1	-68.3	-79.9	12	30	58
p-F	99	0.001	11.9	12.2	-21.8	22	20	58
m-Me	99	0.001	33.7	-38.4	-87.1	17	18	65
p-Me	98	0.002	3.75	-103	-45.3	2	57	41
p-OMe	98	0.003	14.3	-104	-68.7	7	45	48
p-Et	95	0.002	28.5	-32.2	-73.5	17	18	65
p-OEt	99	0.001	19.4	-0.35	-42.9	23	1	76

[a]Substituent in aniline moiety.

substituent in the aniline moiety in propan-2-ol/water and 1,4-dioxane/water medium. The $\Phi_{Co^{II}}$ failed to conform to the usual Hammett equation. The plot of log $\Phi_{Co^{II}}$ versus Hammett's substituent constants, σ is a scatter gram[41]. This deviation from Hammett's plot may be due to the fact that the substituents present in the *para*- and *meta*-position of the aniline ligand have no significant effect on the electro-reduction of these complexes as they are far away from the metal centre.

Conclusion : The foregoing results and discussions indicated that the seven new cobalt(III) complexes have been prepared and characterized by elemental analysis, UV-Vis, FT-IR, ^{1}H NMR, thermal studies and differential Pulse Voltammetric techniques. The results of the spectral studies revealed that these complexes posses a *cis*-β arrangement of ligands around the Co^{III} ion. The electro- and photo-reduction of the cobalt(III) complexes are highly influenced by the solvent properties. The electro- and photo-reduction of Co^{III} to Co^{II} becomes increasingly easier with an increase in the percentage of the organic co-solvent in the mixture. The solvent effects on the reduction of these complexes are conveniently described by the Kamlet-Taft relationship. The electro- and photo-reduction of these complexes indicated that there is no significant effect of the structure on the reactivity of propan-2-ol/water and 1,4-dioxane/water medium.

Acknowledgement

We are grateful to the University Grants Commission, New Delhi for its financial assistance under Major Research Project Scheme. Also, the authors thank Dr. S. Abraham John, Associate Professor in Chemistry, Gandhigram Rural Institute-Deemed University, Gandhigram, for providing the electrochemical work station.

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