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RESEARCH ARTICLE

Modeling Analysis of the Photoreduction of Cobalt(III) Speciation via (Co^{III}-I^-) Ion Pair Formation in Water-1,4-Dioxane Mixtures with XRPD and Voltammetric Studies†

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Abstract: Ion pair charge transfer (IPCT) reaction has been studied on the reduction of Co^{III} centre in coordination compounds with reference to solvent medium and structure of the complex. A series of $Co^{III}(L)_3^{3+}$ (L = $(NH_3)_2$, en, pn, tn and bn) were prepared, characterized and the structures of the complexes were refined using powder XRD data. $Co^{III}(L)_3^{3+}$ crystallizes in distorted monoclinic system with β = 92.93 (1)° to 113.00 (2)°. A combination of powder XRD and cyclic voltammetric technique is shown to be methodologically important and complementary for the understanding of reduction property of Co^{III} centre. The voltammetric measurements of $Co^{III}(L)_3^{3+}$ have shown one irreversible Co(III) → Co(II) reduction of metal centre and the peak positions of the complexes are localized due to strained ligand. Quantum yield for 254 nm excitation of $Co^{III}(L)_3^{3+}$ (L = $(NH_3)_2$, en, pn, tn and bn) in water-1,4-dioxane mixtures (Diox = 0, 5, 10, 15, 20, 25 and 30% (v/v)) were also derived for all the complexes in presence of added iodide ion, in which Co^{III} is reduced via $\{Co^{III}L_3^{3+}, I^-\}$ ion-pair formation. The photoactive state is ion-pair charge transfer transition state and the quantum efficiency is solvent dependent. That is, $\Phi_{Co(II)}$ in water Diox (100:0 (v/v)) is less than that in water Diox (70:30 (v/v)). That is, change in $\Phi_{Co(II)}$ is consistent with observed increase in x_{Diox} of the medium. An elaboration on binary solvent modified $\Phi_{Co(II)}$ in terms of correlation relationships using solvent empirical parameters ε_r, Y, E_T^N, DN^N, α, β and π^* provides a model to understand solvent medium participation. Application of this method involving model equation of the form $Y_S = Y_0 + \sum^n_{i=1} a_i X_i$ helps the binary solvent effect on $\{Co^{III}(L)_3^{3+}, I^-\}$ ion pair into Co^{II} product formation efficiency. The photoreduction proceeds through long-range and short range solvation mechanisms. Regression methods were attempted to quantify the solvation effect.

Keywords: Modeling Analysis, Ion pair charge transfer, Photoreduction, Water-1,4-dioxane mixtures

Introduction

Electron transfer and its components underpin a wide variety of chemistry, biochemistry, and nanotechnology[1]. A common element is that electrons originate in spatially defined regions, tunnel through space and matter and are deposited in another spatially defined region. Simple examples of this include intramolecular electron transfer in which the initial

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and final regions are functional groups on a molecule, intermolecular electron transfer involving the electron transport chains that underpin life.

Experimental

$Co^{III}(L)_3^{3+}$ (L = $(NH_3)_2$, en, pn, tn and bn) were prepared by literature method[2,3] and their purity was spectrally verified. 1,4-Dioxane and KI of analytical grade were used as received. All reagents and organic solvents were analytical grade.

Photolysis experiments

The effect of UV irradiation on samples of $Co^{III}(L)_3^{3+}$ (L = $(NH_3)_2$, en, pn, tn and bn) in water 1,4-dioxane mixed solvent (0-30% (v/v) 1,4-dioxane) was followed by spectrophotometric method. Cobalt(III) complexes are comparatively stable[4] toward UV irradiation and there was no significant amount of Co^{II} present even after 2 days. Therefore, photolysis was performed in presence of iodide ion as reductant.

Modeling analysis

Binary solvent medium of varying compositions can have a profound effect on the behavior of photochemistry of ion-pair $\{Co^{III}(L)_3^{3+}, I^-\}$, which can be static or dynamic. To some extent modeling analysis can be used to separate the non-specific and specific solvation effects, as it can also be used to predict the quantitative contributions.

Results and Discussion

X-Ray powder diffraction analysis

Figure 1 is the XRD pattern for $Co^{III}(tn)_3^{3+}$ complex containing pattern range (2θ), deg = 5 - 75 and set up scan increment (2θ), deg = 0.02 with scan time = 1 second. The geometry of the $Co^{III}(tn)_3^{3+}$ was built up in accordance with the constraints of the tn ligand but single phase. The application of X-ray powder diffraction in this work is important as it is an expanded tool, confirms the identity of product and characterizes the unit cell.

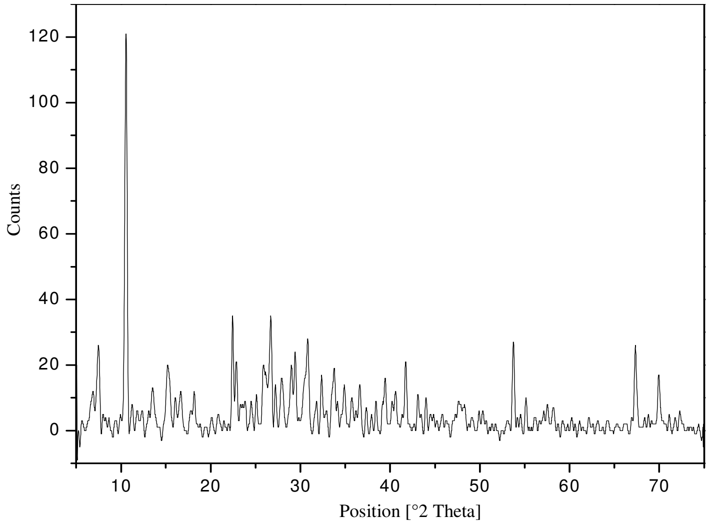


Figure 1. XRD pattern for $[Co^{III}(tn)_3]Cl_3$ complex containing pattern range (2θ), deg = 5-75 and step scan increment (2θ), deg = 0.02,with step scan time = 1s using Generator Settings = 30 mA, 40KV. (a=8.3 A°, b=8.0 A°, c=16.7 A°, β=92.9)

Electrochemical studies

Figure 2 is the successive cyclic peaks of the cyclic voltammograms of $Co^{III}(L)_3^{3+}$ in DMF and in 0.1 M TBAP (υ = 100, 200, 300 mVs^{-1}). The shift of the redox potential of the complexes from simple NH_3 ligand to longer chain bn indicates a binding interaction and the constraints due to coordination make complexes less readily reducible.

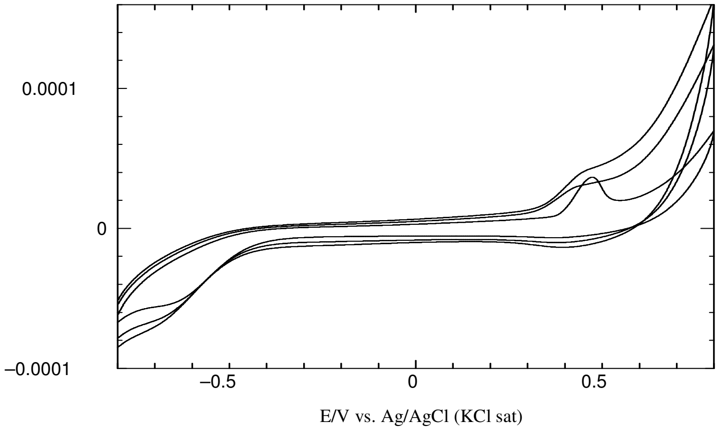


Figure 2. Cyclic voltammograms obtained at a 3.0 mm glassy carbon electrode for $[Co^{III}(tn)_3]Cl_3$ in 0.1 M TBAP with DMF with scan rates 100, 200, 300 mVs^{-1}

Mechanism

$Co^{III}(L)_3^{3+}$ complexes with 3+ electric charge are known to give ion-pairs with anions, such as iodide ion. These ion-pairs have characteristic ion-pair charge transfer (IPCT) bands in the UV-Vis region[5]. Light excitation into such IPCT bands causes the promotion of an electron from the anion in the outer coordination sphere to the cobalt(III) center, which is reduced to Co^{II}. The ion pair, for example, $\{Co^{III}(NH_3)_6^{3+}, I^-\}$ system leads to redox decomposition with high quantum yield than that of a neat, simple complex ion (eqs. 1 to 3)

$$\{Co^{III}(NH_3)_6^{3+}, I^-\} + h\nu \rightarrow \{Co^{II}(NH_3)_6^{2+}, I\} \quad \text{IPCT} \quad (1)$$

$$\{Co^{II}(NH_3)_6^{2+}, I\} \rightarrow \{Co^{III}(NH_3)_6^{3+}\},\ I^- \quad \text{IPCT} \quad (2)$$

$$\{Co^{II}(NH_3)_6^{2+}, I\} \rightarrow Co^{2+}_{aq} + 6NH_4^+ + 1/2\ I_2 \quad H^+ \quad (3)$$

Thus, IPCT excitation is followed by either the back-electron transfer reactions within the solvent cage or the separation of the primary photoproducts.

Role of solvent compositions

Table 1 lists the $\Phi_{Co(II)}$ value under different compositions of organic co-solvent together with the respective relative permittivity. $Co^{III}(L)_3^{3+}$ give a considerably high $\Phi_{Co(II)}$ in water diox (70:30 (v/v)) solution, than that observed of efficiency in water - diox (100:0). Figure 3 is a typical Laidler–Eyring plot for $Co^{III}(en)_3^{3+}$ complex in water diox media. All other similar plots are linear and strictly obey the above relationship and the regression result for the typical complex, $Co^{III}(en)_3^{3+}$ is; $\log\Phi_{Co(II)} = (-0.428 \pm 0.041) + (12.43 \pm 1.2)\ 1/\varepsilon_r$, $r^2 = 0.952$, sd = 0.036, Ψ = 0.37, Temp = 300 K, n = 6. A similar trend was observed for the other complexes of $Co^{III}(L)_3^{3+}$ in which the correlation results are r^2 = 0.8962-0.9762, sd = 0.0022-0.0079, Ψ = 0.176-0.354, illustrating the presence of both electrostatic and non-electrostatic interactions of the media to solvation of initial and excited state of the ion-pair $\{Co^{III}(L)_3^{3+}, I^-\}$.

Table 1. Quantum yields for the photoreduction of cobalt(III) – alkylamine complexes in air equilibrated water–1,4-dioxane mixtures at different temperatures

1,4-Dioxane		Temp	$10\Phi_{Co(II)}$				
%(v/v)	x_2	(K)	$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$	$[Co(pn)_3]^{3+}$	$[Co(tn)_3]^{3+}$	$[Co(bn)_3]^{3+}$
0	0	293	5.593	5.473	5.799	5.361	4.113
		300	5.837	5.399	6.084	5.512	4.218
5	0.0109	293	5.649	5.604	5.913	5.407	4.201
		300	5.974	5.517	6.193	5.584	4.313
10	0.0229	293	5.768	5.764	6.084	5.616	4.293
		300	6.089	5.621	6.341	5.699	4.412
15	0.0359	293	5.854	5.815	6.177	5.698	4.381
		300	6.198	5.730	6.462	5.767	4.481
20	0.0502	293	5.939	5.933	6.281	5.743	4.472
		300	6.352	5.844	6.591	5.894	4.583
25	0.0659	293	5.998	6.207	6.415	5.821	4.571
		300	6.417	5.903	6.630	5.969	4.653
30	0.0831	293	6.107	6.515	6.723	5.907	4.659
		300	6.506	6.392	6.802	6.473	4.695

$[Co(III)] = 3.88x10^{-3}$ M to $5.60x10^{-3}$ M, $[NaNO_3] = 0.1$ M

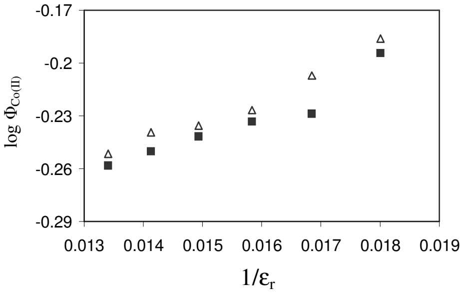


Figure 3. Continuum solvation on the photoefficiency of $Co^{III}(en)_3^{3+}$ complex in different water-1,4-dioxane mixtures at (Δ) 293 and (■) 300 K

Multiparameter calculations

According to the former context the Krygowski – Fawcett expression, illustrates the influence of Lewis acidic and Lewis basic properties of solvent on ion-pair/excited state, that is, $\{Co^{III}(L)_3^{3+}; I^-\}$ / $*\{Co^{III}(L)_3^{3+}; I^-\}$, which can be probed through a consideration of Dimorth - Reichardt's normalized, dimensionless Lewis acidity and Gutmann's normalized donor number Lewis basicity parameters E_T^N and DN^N respectively. From Table 2, summarizing the percentage contribution factor, it follows that the agreement in most cases are satisfactory within the limits of experimental errors demonstrating the sound basis for the effective solvation. The observed values, $P(DN^N) > P(E_T^N)$ significantly exhibit a stronger Lewis basicity of binary mixtures. Hence, the excited state ion pair $*\{Co^{III}(L)_3^{3+,} I^-\}$ is preferentially associated with stronger cage solvation[6]. This sorting effect is amplified by the increase in Diox of mixtures. Quantitative prediction of medium role on photoreduction yield is possible using the Kamlet-Taft solvatochromic parameters through a Linear Solvation Energy Relationship (LSER). The result of tri-parametric analysis for the reduction of $Co^{III}(en)_3^{3+}$ in water-1,4-dioxane mixtures is;log $\Phi_{Co(II)} = 278 + 241\ \pi^* - 466\ \alpha + 26\ \beta$,

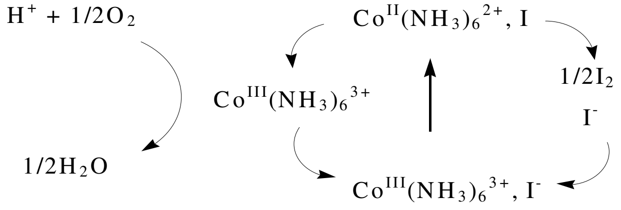
(r^2 = 0.981, sd = 0.06, Ψ = 0.19, n = 6, and Temp = 300). The regression coefficient values along with statistically weighted *P(α), P(β)* and *P(π*)* computed for the cobalt(III) complexes are presented in Table 2.

Table 2. Statistical results, the coefficients and weighted contributions of solvent parameters from Krygowski – Fawcett equation and Kamlet-Taft's equation for the photo reduction of cobalt(III) – alkylamine complexes in water- 1,4-dioxane mixtures at different temperatures

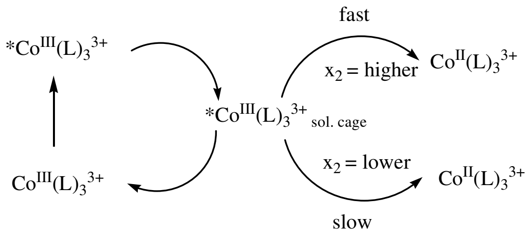
Complex	Temp	$Q = Q_o + \alpha E_T^N + \beta DN^N$			$XYZ = XYZ_o + s\pi^* + a\alpha + b\beta$			
	(K)	R^2	α	β	R^2	s	a	b
$[Co(NH_3)_6]^{3+}$	293	0.993	-0.27	0.22	0.985	-61.24	18.30	-59.30
	300	0.995	-0.45	0.88	0.998	-162.74	50.37	-150.34
$[Co(en)_3]^{3+}$	293	0.997	0.84	-5.59	0.999	170.09	-40.81	237.64
	300	0.944	0.88	-5.60	0.954	318.13	-96.58	315.04
$[Co(pn)_3]^{3+}$	293	0.985	0.34	-3.02	0.988	111.06	-30.27	133.51
	300	0.985	-0.34	0.38	0.978	-85.25	25.45	-83.14
$[Co(tn)_3]^{3+}$	293	0.949	-0.50	1.19	0.916	-104.46	32.7	-93.5
	300	0.954	1.09	-6.53	0.959	298.89	-83.7	339.4
$[Co(bn)_3]^{3+}$	293	0.999	-0.22	-0.41	0.999	-53.07	15.38	-53.02
	300	0.995	-0.46	0.87	0.996	-183.80	58.89	-157.70

$P(E_T^N) = 10\text{-}54;\ P(DN^N) = 46\text{-}90;\ P(\pi^*) = 37\text{-}46;\ P(\alpha) = 9\text{-}15;\ P(\beta) = 39\text{-}53$

In conclusion, some I_3^- is generated and some $Co^{III}(NH_3)_6^{3+}$ is regenerated. Light excitation of the $\{Co^{III}(NH_3)_6^{3+}, I^-\}$ ion pair in the presence of dioxygen leads to oxidation of I^- to I_3^-. The net reaction is Co(III) photoassisted oxidation of I^- by dioxygen, which is illustrated in Scheme 1. The problem of photoinduced donor-acceptor electron transfer in mixed solvent media is analyzed to obtain an understanding of the relationship between solvent properties and transition state[7]. Product formation due to fast and slow processes are shown in Scheme 2. Appropriate fitting of $\Phi_{Co(II)}$ values in correlation model equations containing solvent empirical parameters in six mixtures of water-1,4-dioxane yields exciting results. A few important conclusions can be deduced from this work.



Scheme 1. Formation of geminate radical pair upon excitation of $\{Co^{III}; I^-\}$ ion pair in water-1,4-dioxane solvent mixture leading to the oxygen assisted production of iodine.



Scheme 2. Product formation due to fast and slow processes

Conclusions

1. All the cobalt(III) complexes under investigation belong to distorted monoclinic system, probably, due to the strain in the ligand. This was ascertained from XRPD studies.
2. Metal centered irreversible reduction, $Co^{III} \rightarrow Co^{II}$ was found to be influenced by the chelate ligand. Cyclic voltammetric measurements establish this reduction peak shifted to more negative potential (when L = $(NH_3)_2$, E_{PC} = 90 mV and if L = bn, E_{PC} = -700 mV).
3. $Co^{III}L_3^{3+}$ complexes are reduced efficiently by iodide ion in mixed solvent media, on the contrary, in neat water and in the absence of reducing agent they show some stability when exposed to 254 nm light.
4. Solvent-assisted reduction is more evident taking into account non-specific and specific salvation interactions.
5. Regression equations between log $\Phi_{Co(II)}$ and solvent empirical parameters ($1/\varepsilon_r$, Y, E_T^N, DN^N, α, β and π^*) give better fit of experimental data leading to appropriate results on medium participation.
6. The investigation presented here arrive an important, long standing problem, on complicated solvation influences on reactions. Proper mathematical analytical models can yield reasonable results about solvent effects.

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