Chapter - IV

Synthesis, Characterization and Pulse Radiolysis Study of Cis-

dichlorobis(diimine)Cobalt(III) Complexes
Chapter IV

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cis-dichlorobis(diimine)cobalt(III) Complexes

4.1 Introduction

The redox chemistry of metal-polypyridyl complexes has been studied due to their potential applications as anticancer agents, for probing structural changes in DNA and in solar energy conversion.¹-³ Such studies have been restricted to tris-polypyridyl complexes of the type [Ru(bpy)₃]²⁺, [Ru(phen)₃]²⁺, [Co(bpy)₃]³⁺ and [Co(phen)₃]³⁺.¹⁻⁵ The precursors to these tris-polypyridyl complexes are the bis-polypyridyl complexes of the type [Co(NN)₂Cl₂]Cl, where NN denotes polypyridyl ligands have been synthesized, characterized and their interactions with DNA have been recently reported.⁶ The phendione complex is known to cleave plasmid pBR322 DNA upon photoirradiation under aerobic condition.⁶ One of the interests in such molecules is how the electron initially located migrates in the complex, which contains more than one site of electron attack. It is interesting to see in complex containing multiple ligands what is the fate of electron adduct species formed by electron addition. Earlier studies⁷ on tris acetylacetonato Co(III) showed that all the three radical products of water radiolysis viz. e⁻aq, •OH and H⁺ result in reduction of Co(III) to Co(II). Reduction to Co(II) and intramolecular electron transfer between two moieties in the cobalt complexes have also been observed earlier.⁸⁹ In this chapter the synthesis of the complexes type [Co(NN)₂Cl₂]Cl, where NN= 2,2'-bipyridine (bpy) (7), 1,10-phenanthroline (phen) (8) and 1,10-phenanthroline-5,6-dione (phendione) (9) (Scheme I) and their characterization by various analytical techniques are reported. The reactions of (e⁻aq, CO₂⁻, (CH₃)₂COH) radicals with these complexes were studied by kinetic spectrometry method.
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4.2 Experimental

4.2.1 Synthesis of complexes [Co(NN)\(_2\)Cl\(_2\)]Cl

The complexes [Co(NN)\(_2\)Cl\(_2\)]Cl, where NN = 2,2'-bipyridine (bpy) (7), 1,10-phenanthroline (phen) (8) and 1,10-phenanthroline-5,6-dione (phendione) (9), were prepared by reported procedure.\(^6\) Methanolic solutions of respective ligands, bpy (1.56 g; 10 mM), phen (1.80 g, 10 mM) and phendione (2.10 g; 10 mM), were refluxed for 1 h. To this, anhydrous cobalt chloride (0.65 g; 5 mM) in methanol (10 ml) was added while hot. The solution then turned from yellow to dark brown. It was cooled in ice and chlorine gas (generated by mixing potassium permanganate and concentrated hydrochloric acid) was passed.\(^10\) The resulting precipitate was then dissolved in 10\(^{-3}\) M hydrochloric acid (50 ml) by warming at 60 °C for 30 min. After cooling the solution to room temperature, 4 M hydrochloric acid (20 ml) was added and kept overnight. The resulting crystalline complexes were filtered and washed with ethanol and dried in vacuum.

4.2.1.a [Co(bpy)\(_2\)Cl\(_2\)]Cl (7)

Yield: 2.11 g, 44 %. Anal. Calcd. for C\(_{20}\)H\(_{16}\)N\(_4\)Cl\(_3\)Co • 2HCl • H\(_2\)O: C 42.23, H 3.54, N 9.85%. Found: C 41.82, H 3.25, N 9.67%. \(^1\)H NMR (ppm, J = Hz, D\(_2\)O, 25 °C): 9.76 (d, 1H, J = 5.4), 9.01 (d, 1H, J = 5.4), 8.58 (d, 1H, J = 7.8), 8.52 (d, 1H, J = 8.1), 8.43 (m, 2, H), 8.26 (d, 1H, J = 8.1), 8.06 (dd, 2H, J = 7.8), 7.96 (m, 2H), 7.29 (dd, 2H, J = 5.4, 7.8), 7.17 (dd, 2H, J = 5.4, 7.8), 6.99 (d, 1H, J = 5.4). UV–Vis

Scheme I
(H$_2$O, nm) ($\varepsilon$/M$^{-1}$ cm$^{-1}$): 224 (63345), 299 (267221), 309 (26666), 538 (60). IR (cm$^{-1}$): 422, $\nu$(Co-N); 381, $\nu$(Co-Cl); 719, 773. $^{13}$C NMR (ppm, D$_2$O, 25 °C): 157.2, 156.7, 156.6, 153.6, 151.4, 151.0, 150.7, 143.2, 142.9, 142.7, 141.9, 129.3, 129.7, 128.9, 125.6, 125.3, 125.1.

4.2.1.b [Co(phen)$_2$Cl$_2$]Cl (8)

Yield: 2.69 g, 51%. Anal. Calcd. for C$_{24}$H$_{16}$N$_4$Cl$_3$Co·3HCl: C 45.30, H 3.01, N 8.80%. Found: C 45.75, H 3.15, N, 8.53%. $^1$H NMR (ppm, $\delta$ = Hz, D$_2$O, 25 °C): 10.18 (d, 1H, $J = 5.7$), 9.49 (d, 1H, $J = 5.4$), 9.21 (dd, 2H, $J = 8.1, 7.2$), 8.75 (d, 1H, $J = 8.4$), 8.62 (d, 1H, $J = 8.4$), 8.49 (dd, 2H, $J = 5.7, 8.1$), 8.44 (d, 1H, $J = 8.1$), 8.40 (d, 1H, $J = 7.2$), 8.28 (d, 1H, $J = 8.1$), 8.21 (d, 1H, $J = 8.1$), 7.60 (dd, 1H, $J = 5.4$). UV–Vis (H$_2$O, nm) ($\varepsilon$/M$^{-1}$ cm$^{-1}$): 226 (59221), 298 (18772), 316 (17272), 548 (55). IR (cm$^{-1}$): 1703, 1728, $\nu$(C=O); 411, $\nu$(Co–N); 716, $\nu$(Co–Cl) 716. $^{13}$C NMR (ppm, D$_2$O, 25 °C): 190.9, 174.1, 157.1, 156.1, 153.8, 153.2, 153.0, 152.1, 151.6, 150.9, 143.4, 141.8, 141.5, 140.9, 139.0, 138.9, 138.2, 132.7, 132.3, 131.0, 130.8, 130.5, 130.0. The crystal structure of the complex was solved previously in our laboratory.  

4.2.1.c [Co(phenidione)$_2$Cl$_2$]Cl (9)

Yield: 1.87 g, 32%. Anal. Calcd. for C$_{24}$H$_{12}$N$_4$O$_4$Cl$_3$Co·HCl: C 46.25, H 2.10, N 8.98%. Found: C 46.10, H 2.34, N 8.53%. $^1$H NMR (ppm, $\delta$ = Hz, D$_2$O, 25 °C): 8.81 (d, 1H, $J = 8.1$), 8.68 (d, 2H, $J = 6.6$), 8.46 (d, 1H, $J = 6.6$), 8.33 (d, 2H, $J = 8.1$), 8.20–6.96 (m, 6H). UV–Vis (H$_2$O, nm) ($\varepsilon$/M$^{-1}$ cm$^{-1}$): 226 (59221), 298 (18772), 316 (17272), 548 (55). IR (cm$^{-1}$): 1703, 1728, $\nu$(C=O); 411, $\nu$(Co–N); 372, $\nu$(Co–Cl) 716. $^{13}$C NMR (ppm, D$_2$O, 25 °C): 190.9, 174.1, 157.1, 156.1, 153.8, 153.2, 153.0, 152.1, 151.6, 150.9, 143.4, 141.8, 141.5, 140.9, 139.0, 138.9, 138.2, 132.7, 132.3, 131.0, 130.8, 130.5, 130.0. The crystal structure of the complex was solved previously in our laboratory.
4.3 Results and discussion

4.3.1 Synthesis and characterization

The complexes \([\text{Co(NN)}_2\text{Cl}_2]\text{Cl}\), where NN = polypyridyl ligand were prepared by methanolic solutions of polypyridyl ligand (1 mM) and anhydrous cobalt chloride (1 mM) in methanol (10 ml) were refluxed for 1 h. Then solution then turned from yellow to dark brown (Scheme 2). It was cooled in ice and chlorine gas (generated by mixing potassium permanganate and concentrated hydrochloric acid) was passed. The resulting precipitate was then dissolved in 10\(^{-3}\) M hydrochloric acid and kept overnight resulting in crystalline solid. The resulting crystalline complexes were filtered and washed with ethanol, dried in vacuum and characterized by elemental analysis, IR, UV–visible, NMR spectroscopy.

\[
\begin{align*}
\text{CoCl}_2 & + 2 \text{NN} & \xrightarrow{\text{Methanol}} & \text{Cl}_2(\text{g}) \text{ at } 0^\circ\text{C} \\
& & \xrightarrow{\text{Cl}_2(g)} & \text{[Co(NN)}_2\text{Cl}_2]\text{Cl}
\end{align*}
\]

\(\text{NN} = \text{bpy, phen and phenedione}\)

Scheme 2. Synthetic scheme of complexes.

Elemental analysis of the complexes correlated well with the calculated values and confirmed the stoichiometry. The complexes 7–9 exhibited weak absorption bands at 450–650 nm in the visible region due to d-d transition and ligand based \(\pi-\pi^*\) transition in the UV region 200–350 nm. The molar extinction coefficient \(\left(\epsilon_{\text{max}}\right)\) values for the metal based transition in the visible region are in the range of 50–60 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) and for the ligand based transitions in the order of 10\(^3\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\). Absorption spectra of the complexes 7–9 in water are given in Figure 1–3.
Figure 1. UV-Visible absorption spectra of the complex 7 recorded in water.

Figure 2. UV-Visible absorption spectra of the complex 8 recorded in water.

Figure 3. UV-Visible absorption spectra of the complex 9 recorded in water.
The IR absorption band in the range 1624–1462 cm$^{-1}$ corresponds to ring vibrations of the polypyridyl ligand and band at $\sim$3022 cm$^{-1}$ is due to the $\equiv$C–H vibrations of the aromatic ring hydrogen atom. The $^1$H NMR spectra of the complexes 7–9 in D$_2$O exhibit resonances in the aromatic region due to the polypyridyl ligand.

4.3.2 Pulse radiolysis

Pulse radiolysis studies were carried out using the facility at National Center for Free Radical Research, University of Pune. Details of Pulse radiolysis system$^{11,12}$ are given in Chapter II. The present work was carried out using 50 ns electron pulses at a dose of 10–14 Gy per pulse. Radiation dose was measured using air saturated KSCN dosimeter.$^{13}$ The mechanism of generation of specific radicals such as hydrated electrons ($e_{aq}^-$)$^{14}$, H-atoms, CO$_2$$^-$, and (CH$_3$)$_2$'COH)$^{15}$ are given in Chapter I. The time resolved absorption spectra of the transient species formed on reaction of complexes with $e_{aq}^-$, H-atoms, CO$_2$$^-$, (CH$_3$)$_2$'COH and rate constants of these reactions were determined. These rates are diffusion controlled and comparable with the tris cobalt (III) complexes of phen and bpy.$^{16}$ The reaction of $e_{aq}^-$ with both the complexes were studied and absorption spectra before and after radiolysis were compared.

4.3.2.1 Reaction of $e_{aq}^-$ with [Co(III)(bpy)$_2$Cl$_2$]Cl (7)

The time resolved transient absorption spectra of the anion radical of the bpy complex shows two broad peaks at 360 and 610 nm at 1 $\mu$s (Figure 4). The former peak decays and shows progressive shift to blue region and at 80 $\mu$s the spectrum shows peak at 290 nm. The latter peak shows decay and progressive red shift and at 80 $\mu$s the absorption still shows red shift beyond 680 nm. The decay profile at 360 nm shows absorption beyond 100 $\mu$s. Decay of the transient follows second order kinetics with 2k/el value of $(8.2\pm0.2)\times10^6$ s$^{-1}$ at 360 nm.
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[Graph: Time resolved transient absorption spectra observed in the reaction of \(e^-\) \(_{aq}\) with complex 7 at 1(●), 20(●), 40(▲), and 80(▼) μs after the pulse; B) decay trace at 360 nm [complex 7] = 2 × 10^-4 mol dm^-3, dose/pulse 10 Gy.]

The complex radical anion can decay by 1) aquation 2) de-ligation 3) reduction to give Co(II). Reduction to Co(II) has been observed in the case of tris(acetylacetonato)Co(III)\(^7\) complex. De-ligation has been observed in the case of mixed ligand Co(II) complexes and takes place in millisecond time scale.\(^1^7\) Three sites of electron localization exist in both the complexes studied viz: metal ion, ligands (phen/bpy) and chloride. UV-Visible spectrum of the complex after irradiation indicates that the complex breaks and de-ligation/ aqutation occur.

4.3.2.2 Reaction of \(e^-\) \(_{aq}\) with [Co(III)(phen)\(_2\)Cl\(_2\)]Cl (8)

The time resolved transient absorption spectra of the anion radical of the phen complex shows one broad peak at 420 nm at 1 μs (Figure 5), which decays and shows progressive blue shift and at 80 μs shows peak at 300 nm. The decay profile at 420 nm shows absorption beyond 100 μs. Decay of the transient follows second order kinetics with 2k/el value of (8.1±0.2)×10^6 s^-1 at 420 nm.
4.3.2.3 Reaction of $e^-_{aq}$ with 2,2'-bipyridine and 1,10-phenanthroline

The ligands bpy and phen also react with $e^-_{aq}$.\(^{18}\)

$$e^-_{aq} + bpy/phen \rightarrow (bpy/phen)^{\cdot}\tag{1}$$

The rate constants of $e^-_{aq}$ with ligands were obtained by Mulazzani et al.\(^{18}\) and are $2.5 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for both phen and bpy. The anion radical of phen has a sharp transient absorption peak at 330 and a broad one at 520 nm, at $\sim 1$ $\mu$s time window. The radical anion then protonates at pH 6.2 where experiments have been carried out and the absorption peaks shifts to 360 and 680 nm respectively.

$$\text{(bpy/phen)}^{\cdot -} + \text{H}^+ \leftrightarrow \text{(bpyH}^{\cdot +}/\text{phenH}^{\cdot +})\tag{2}$$

None of these absorption peaks match with those of phen complex. Hence it is concluded that the electron is not localized on the phen ligand but on the complex 7 as a whole. Similarly for bpy, the transient absorption peak for anion radical is seen at 360 nm, which shifts to 320 nm on protonation. For the complex 8 also the transient absorption peaks do not match with those of the anion radical of bpy. Hence it is also concluded that for bpy complex the electron is located on the complex as a whole.
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The phen complex anion decays initially by second order with a rate constant of \(8.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\). For both the complexes the transient absorption decays in ~200 \(\mu\)s time scale. These observations point out to a stable product formation. However, for \([\text{Co(phen)}_3]^3+\) and \([\text{Co(bpy)}_3]^3+\) complexes the ligand radical anion spectra and complex radical anion spectra match and it is reported that the initially produced transient species on electron reaction is likely to be a Co(III) centre containing coordinated aromatic phen/bpy radical. These species then undergo intramolecular electron transfer to form Co(II) species.

4.3.2.4 Reactions of \(e^-_{aq}\) with \([\text{Co(III)(phendione)}_2\text{Cl}_2]\)Cl (9)

Time resolved transient absorption spectrum observed in the reaction of \(e^-_{aq}\) with complex 9 is shown in Figure 6A and 6B. The transient absorption spectrum of the complex indicates the formation of initially ligand radical anion on reaction with \(e^-_{aq}\), which further decays in a few hundred \(\mu\)s. The rate of reaction of \(e^-_{aq}\) with complex was determined by decay of \(e^-_{aq}\) at 700 nm, and was determined to be \((2.2 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\). This rate is diffusion controlled and comparable with other cobalt(III) complexes. The spectra (Figure 6B) shows the absorption peak at 530 nm at later time window which is split into two new peaks at 480 and 560 nm. This may be attributed to intramolecular electron transfer within the complex from one moiety to another in the complex. In the dose per pulse 10–50 Gy the radical anion decays by first order kinetics with rate constant \(1.5 \times 10^4 \text{ s}^{-1}\).
Figure 6. Time resolved corrected transient absorption spectra of radical anion of complex 9, dose/ pulse 10 Gy. [complex 9]: 2x10^-4 mol dm^-3 A: 30–196 μs, B: 100–800 μs.
Figures 7 show the decay trace of complex anion at 530 nm. Since the complex has strong ground state absorption in the region of peak at 340 nm, first order decay constant of \((1.65 \pm 0.2) \times 10^4 \text{ s}^{-1}\) is evaluated from traces at 530 nm. No effect of complex concentration on the decay rate was seen. The complex radical anion can decay by 1) aquation 2) de-ligation 3) reduction to give Co(II). Reduction to Co(II) has been observed in the case of tris acetylacetonato Co (III).\(^7\) De-ligation has been observed in the case of a Co(II) complex and takes place in millisecond time scale.\(^{17}\) Three sites of electron localization exist in the complex studied viz. metal ion, phendione and chloride. UV-Visible spectra of the complex after irradiation indicate (Figure 11) that the complex breaks and de-ligation/aquation occurs.

4.3.2.5 Reaction of \(e^-_{aq}\) with 1,10-phenanthroline-5,6-dione

To see whether the ligand phendione also reacts with \(e^-_{aq}\), some experiments were carried out. The time resolved transient absorption spectra of anion radical of phendione are shown in Figure 8 and it matches with the reported one.\(^{24}\)

\[
e^-_{aq} + \text{phendione} \rightarrow (\text{phendione})^-
\]  

(3)

The rate constant of \(e^-_{aq}\) with the ligand determined by us is similar to that obtained.\(^{24}\) The radical anion of phendione has absorption peaks at 340 and 530 nm, which are also seen in the spectra of the radical anion of the complex studied. The
spectral shape and the molar extinction coefficients at these wavelengths also match. Hence it is concluded that the electron is localized in the complex on the phendione moiety. The phendione radical anion decays by first order with a rate constant of \(9.4 \times 10^3\) s\(^{-1}\). The complex anion decay differs from decay of phendione anion due to mechanistic differences. However, both transients are fairly long lived. Dimethyl ketyl radical and \(\text{CO}_2^-\) also give similar transient absorption spectra obtained on the reaction of \(e^-_{\text{aq}}\) with the phendione.\(^{24}\)

**Figure 8.** Time resolved transient absorption spectra of anion radical of phendione, dose/pulse \~ 10 Gy, [phendione]: \(2 \times 10^{-4}\) mol dm\(^{-3}\).

### 4.3.2.6 Effect of benzophenone on \([\text{Co(III)}(\text{phendione})_2\text{Cl}_2]\)Cl (9)

The radical anion formed on reaction with \(e^-_{\text{aq}}\) with complex has transient absorption peaks at 340 and 530 nm (Figure 6) and decays by first order process with a rate constant of \(1.6 \times 10^4\) s\(^{-1}\), probably undergoes intramolecular electron transfer. Hence it is seen that the intramolecular electron transfer in the complex radical anion is fairly slow process. Benzophenone (BP) was used as a scavenger (concentrations of complex and BP: \(2 \times 10^{-4}\) and \(5 \times 10^{-5}\) mol dm\(^{-3}\) respectively) to observe effect of
electron scavenger on the radiolytic process. Benzophenone reacts with $e^{-}_{aq}$ at diffusion controlled rate constant to give BP$^-$ anion and BP$^-$ exists as ketyl (BPH$^*$) radical in acidic conditions.  

$$\text{BP} + e^{-}_{aq} \rightarrow \text{BP}^- \quad k = (2.8 \times 10^{-10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \quad (4)$$

$$\text{BP}^- + H^+ \leftrightarrow \text{BPH}^* \quad pK = 9.2 \quad (5)$$

On the basis of competition kinetics since the rates of electron reaction with BP and complex are almost equal, about 25% of $e^{-}_{aq}$ generated would react with BP. However, conductivity results show better protection of the complex. In experiments with BP, it is seen that conductivity does not change significantly after irradiation. This observation points out to the reduction of radiation damage to the complex in the presence of BP.

4.3.2.7 Reactions of H-atoms with [Co(III)(phendione)$_2$Cl$_2$]Cl (9)

Figure 9 shows the time resolved transient absorption spectra obtained on the reaction of H-atoms with the complex. The rate constant for the reaction of H-atom with the complex is evaluated to be $(3.5 \pm 0.3) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (lifetime ~ 1.3 $\mu$s) from the growth of 440 nm peak. This is about 5 times lower than that of the reaction of complex with $e^{-}_{aq}$. In this reaction absorption peak is observed at 340 nm, and is attributed to H-atom addition to the phendione moiety. The species decays by first order rate of $(6.1 \pm 0.2) \times 10^3 \text{ s}^{-1}$. The kinetics of decay differs from that seen in the reaction with $e^{-}_{aq}$.

The adduct eventually gives cobalt (II) in the course of time (>1 ms). The difference in decays of two peaks at 340 and 500 nm shows that two species exist which are attributed to 1) H-atom adduct 2) other generated by electron transfer from H-atom to give complex anion radical. As a rough estimate ~35% H-atoms give anion radical by electron transfer.
4.3.2.8 Reactions of dimethyl ketyl radical with [Co(III)(phendione)$_2$Cl$_2$]Cl (9)

The time resolved transient absorption spectra obtained on the reaction of dimethyl ketyl radicals with the complex using both the methods of their generation are identical with that obtained with the reaction of e’aq with the complex (Figure 6). The rate constant for the reaction of dimethyl ketyl radical with the complex is evaluated to be $(1.2 \pm 0.1) \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ (lifetime $\sim 4 \mu$s) from the growth of 530 nm peak. The 530 nm peak decays slowly by first order rate of $(7.8 \pm 0.2) \times 10^3$ s$^{-1}$.

No effect of concentration of 2-propanol was seen on the transient absorption spectra and kinetics.

4.3.2.9 Reactions of CO$_2^{\cdot-}$ radical with [Co(III)(phendione)$_2$Cl$_2$]Cl (9)

Figure 10 shows the time resolved transient spectra obtained on the reaction of $\text{CO}_2^{\cdot-}$ radicals with the complex. The rate constant for the reaction of $\text{CO}_2^{\cdot-}$ radicals with the complex is evaluated to be $(2.3\pm0.2) \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ from the growth of 530 nm peak. The species decays by first order rate of $(9.3 \pm 0.2) \times 10^3$ s$^{-1}$. 

Figure 9. Time resolved transient absorption spectra obtained in the reaction of H-atom with complex 9, dose/pulse $\sim 12$ Gy. [complex 9]: $2 \times 10^{-4}$ mol dm$^{-3}$. 

\[ \text{Figure 9.} \text{ Time resolved transient absorption spectra obtained in the reaction of H-atom with complex 9, dose/pulse $\sim 12$ Gy. [complex 9]: $2 \times 10^{-4}$ mol dm$^{-3}$.} \]
It is seen from the figure that absorption at ~ 380 nm grows as that at 300 and 530 nm decreases. To ascertain the effect of formate ion concentration on this peak, the formate concentration was changed from 0.1 to 0.25 mol dm$^{-3}$. This resulted in increase of transient absorption at 380 nm as that at 530 nm decreased. This is attributed to the replacement of chloride ligand by formate ions during the course of reduction.

**Figure 10.** Time resolved transient absorption spectra obtained in the reaction of CO$_2$ radical with complex 9, dose/pulse 12 Gy. [complex 9]: 2×10$^{-4}$ mol dm$^{-3}$.

Similar radical insertion reaction have been observed in Co(III) aquo-ammonia complexes where "CH$_3$, acetate radicals replace H$_2$O to generate Co-C σ-bond. Breznia and Hoffman have estimated the half life for ligand replacement in [Co(NH$_3$)$_5$CO$_2$] complex to be ~ 2 μs and half life for dissociation for all the NH$_3$ groups to be ~ 500 μs. In the present case we find that lifetime for ligand replacement i.e. Cl$^-$ by formate ions, is ~ 200 μs. While that for dissociation of phendione groups was well above 10 ms. This fact could be attributed to the stronger ligand field offered by phendione ligand as against weaker ligand ammonia. Hence breakdown of
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the complex is delayed. Since water and 2-propanol are weaker ligands than Cl\textsuperscript{−}, replacement by solvent does not result in spectral shift.

A summary of spectral and kinetic parameters of the reaction rate constant of hydrated electron (e\textsubscript{aq}\textsuperscript{−}) with complexes 7–9 and H-atoms, (CH\textsubscript{3})\textsubscript{2}\textsuperscript{*}COH and CO\textsubscript{2}\textsuperscript{−} radicals with complex 9 are tabulated in Table 1.

Table 1. Rate constants of hydrated electron (e\textsubscript{aq} \textsuperscript{−}) with complexes 7–9 and H-atoms, (CH\textsubscript{3})\textsubscript{2}\textsuperscript{*}COH and CO\textsubscript{2}\textsuperscript{−} radicals with complex 9 at Temp. 300 K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant (dm\textsuperscript{3}mol\textsuperscript{−1}s\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(bpy)\textsubscript{2}Cl\textsubscript{2}]Cl pH= 6.2 (7)</td>
<td>7.6(±0.2)x10\textsuperscript{10}</td>
</tr>
<tr>
<td>[Co(phen)\textsubscript{2}Cl\textsubscript{2}]Cl pH= 6.2 (8)</td>
<td>6.9(±0.2)x10\textsuperscript{10}</td>
</tr>
<tr>
<td>*[Co(bpy)\textsubscript{3}]\textsuperscript{3+}</td>
<td>8.8\times10\textsuperscript{10}</td>
</tr>
<tr>
<td>*[Co(phen)\textsubscript{3}]\textsuperscript{3+}</td>
<td>7.5\times10\textsuperscript{10}</td>
</tr>
<tr>
<td>#2,2'-Bipyridine</td>
<td>2.5\times10\textsuperscript{10}</td>
</tr>
<tr>
<td>#1,10-Phenanthroline</td>
<td>2.5\times10\textsuperscript{10}</td>
</tr>
<tr>
<td>[Co(phendione)\textsubscript{2}Cl\textsubscript{2}]Cl (9) + e\textsubscript{aq} pH= 6.2</td>
<td>(2.2 ± 0.2)x10\textsuperscript{10}</td>
</tr>
<tr>
<td>[Co(phendione)\textsubscript{2}Cl\textsubscript{2}]Cl (9) + (CH\textsubscript{3})\textsubscript{2}\textsuperscript{*}COH</td>
<td>(1.2 ± 0.1)x10\textsuperscript{9}</td>
</tr>
<tr>
<td>[Co(phendione)\textsubscript{2}Cl\textsubscript{2}]Cl (9) + CO\textsubscript{2}\textsuperscript{−}</td>
<td>(2.3 ± 0.2)x10\textsuperscript{9}</td>
</tr>
<tr>
<td>[Co(phendione)\textsubscript{2}Cl\textsubscript{2}]Cl (9) + #H</td>
<td>(3.5 ± 0.3)x10\textsuperscript{9}</td>
</tr>
<tr>
<td>phendione + e\textsubscript{aq} pH= 6.2</td>
<td>$^5$(3.2 ± 0.2)x10\textsuperscript{10}, $^6$(3.0 ± 0.2)x10\textsuperscript{10}</td>
</tr>
</tbody>
</table>

*Value from reference *\textsuperscript{18}, *This work, *\textsuperscript{5} Values from ref.*\textsuperscript{16} *\textsuperscript{6} Values from ref.*\textsuperscript{18}

4.3.3 Conductivity measurements

The dichloro complex anions can decay by aquation with release of chloride ions. To ascertain whether such a process occurs on irradiation, conductivity measurements were carried out. The complex solutions were given 3 electron pulses, and conductivities were measured for the unirradiated and irradiated solutions. In case of both the irradiated complexes the conductivity increases almost three times (Table 2). This observation points out to replacement of chloride ions in the complexes by
the water molecules i.e. aquation. The following reactions can be put forth to explain both aquation and de-ligation of the complexes on irradiation:

\[
\text{[Co(III)(bpy/phen/phenedione)_2Cl_2]^+ + e}^{-}_{aq} \rightarrow \text{[Co(III)(bpy/phen/phenedione)_2Cl_2]^*} \quad (6)
\]

\[
\text{[Co(III)(bpy/phen/phenedione)_2Cl_2]^* + H_2O} \rightarrow \text{[Co(III)(bpy/phen/phenedione)_2(H_2O)_2]^{2+} + 2Cl}^{-} \quad (7)
\]

Release of one chloride ion may also be possible (reaction 9), which might result in reduction of Co(III) to Co(II). The Co(II) species then dissociate to give free ligand and free Co(II) ions.

\[
\text{[Co(III)(bpy/phen/phenedione)_2Cl_2]^* + H_2O} \rightarrow \text{[Co(II)(bpy/phen/phenedione)_2(H_2O)_2]^{2+} + Cl}^{-} \quad (8)
\]

\[
\text{[Co(II)(phen/phenedione)_2(H_2O)Cl]^{2+}} \rightarrow \text{Co(II) + 2 phen/phenedione + Cl}^{-} \quad (9)
\]

Qualitative spot tests carried out using nitroso-R salt show presence of Co(II) in irradiated solutions for the phen complex. Such intramolecular electron transfer reactions have been previously observed in Co(III) complexes.\(^{9,25}\)

Intramolecular electron transfer reactions have been previously observed in a Co(III) complex\(^{8}\) and the rate of following intramolecular electron transfer reaction was measured to be \(k = 2.6 \times 10^{3} \text{ s}^{-1}\).

\[
\text{[(NH}_3)_5\text{Co}^{\text{III}}\text{O}_2\text{CC}_6\text{H}_4\text{N}_2\text{O}_2^- \text{p}] \rightarrow \text{Co}^{2+}_{aq} + 5\text{NH}_4^+ + \text{p}^- \text{O}_2\text{CC}_6\text{H}_4\text{N}_2\text{O}_2^- \quad (10)
\]

These rates are slower or equal to the rates of the analogous intermolecular reactions of the type\(^{25}\)

\[
\text{Co}^{\text{III}}\text{(NH}_3)_3\text{X} + \text{p}^- \text{O}_2\text{CC}_6\text{H}_4\text{N}_2\text{O}_2^- \rightarrow \text{Co}^{2+}_{aq} + 5\text{NH}_4^+ + \text{X} + \text{p}^- \text{O}_2\text{CC}_6\text{H}_4\text{N}_2\text{O}_2^- \quad (11)
\]

\((X = \text{NH}_3 \text{ or } -\text{O}_2\text{CC}_6\text{H}_3)\)

\(k = (0.12 \pm 0.04) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) for \(X = \text{NH}_3\) and \(k = (0.21 \pm 0.05) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) for \(-\text{O}_2\text{CC}_6\text{H}_5\)
Table 2: Conductivity measurements before and after irradiation in milli mhos.
Dose: 10–15 Gy, pH: 6.2, [complex] = 2×10^4 mol dm^{-3} [Benzophenone (BP)] = 5×10^{-3} mol dm^{-3}

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Before irradiation*</th>
<th>After irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(bpy)_2Cl_2]Cl (7)</td>
<td>0.103</td>
<td>0.346</td>
</tr>
<tr>
<td>[Co(phen)_2Cl_2]Cl (8)</td>
<td>0.162</td>
<td>0.376</td>
</tr>
<tr>
<td>[Co(phendione)_2Cl_2]Cl (9)</td>
<td>0.227</td>
<td>0.484</td>
</tr>
<tr>
<td>[Co(phendione)_2Cl_2]Cl with BP</td>
<td>0.210</td>
<td>0.242</td>
</tr>
</tbody>
</table>

*immediately after dissolution

4.3.4 Steady state optical absorption

Steady state optical absorption spectra (Figure 11) show that for phen and phendione complex, the O.D. of the irradiated solution decreases drastically indicating the breakdown of the complex further corroborated by the increase in the conductivity.

Extraction of the irradiated complex in chloroform shows the same spectrum as that of phen, and detection of Co(II) by nitroso-R reagent support the conclusion, that phen complex dissociates completely. Similarly it observed in phendione complex. On the other hand for bpy complex, the absorption blue shifts on irradiation and may probably be due to the formation of reduced species of the bpy complex. Free bpy was not found in irradiated solutions after extraction in chloroform.

This indicates that the [Co(III)(bpy)_2Cl_2]^+ complex gets reduced to [Co(II)(bpy)_2]^{2+} complex and the reaction can be expressed by following equations:

\[
[Co(III)(bpy)_2Cl_2]^+ + e^{-}_{aq} + 2H_2O \rightarrow [Co(II)(bpy)_2(H_2O)_2]^{2+} + 2Cl^{-} \quad (12)
\]

Reaction 11 also explains the increase of conductivity on irradiation for bpy complex.
Figure 11. UV-Visible absorption spectrum of A and B: complex 7, C and D: complex 8 and E and F: complex 9 in water in UV and Visible region.
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ACE-  
a: 200 μM complex, immediately after dissolution,
b: 200 μM complex, 12 hrs for bpy and phen complex and 10 hrs for phendione after dissolution,
c: 200 μM complex, after irradiation dose 15 Gy,

BDF-  
d: 40 μM complex, immediately after dissolution,
e: 40 μM complex, 12 hrs for bpy and phen complex and 10 hrs for phendione after dissolution,
f: 40 μM complex, after irradiation dose 15 Gy.

4.4 Conclusion

Complexes of the type [Co(NN)$_2$Cl$_2$]Cl where NN = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 1,10-phenanthroline-5,6-dione (phendione) have been synthesized and characterized by various physical methods. The reaction of hydrated electron (e$^-$$_{aq}$) with these complexes have been studied by electron pulse radiolysis and their rate constant with the complexes 7–9 were determined to be $(7.6 \pm 0.2) \times 10^{10}$, $(6.9 \pm 0.2) \times 10^{10}$ and $(2.2 \pm 0.2) \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. Rate constant of H-atoms, (CH$_2$)$_2$COH and CO$_2$ with the [Co(III)(1,10-phenanthroline-5,6-dione)$_2$Cl$_2$]Cl have been determined to be $(3.5 \pm 0.2) \times 10^9$, $(1.2 \pm 0.2) \times 10^9$ and $(2.3 \pm 0.2) \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ respectively. Time resolved transient absorption spectra show two peaks at 360 and 610 nm for the bpy complex and at 420 nm for phen complex. For both the bpy and phen complexes the transient absorption decays in ~ 200 μs. These peaks do not match with those of respective anion radicals of the ligands. Based on these observations it is concluded that in the anion radicals of both the complexes the electron is localized on the complex as a whole. The transient absorption spectra of phendione complex show two peak at 340 and 530 nm, which match with those of phendione anion radical. Steady state absorption spectra on irradiation indicates breakdown of the phen and phendione complex to free ligand, free Co(II) and Cl$^-$ ions and in the case of bpy complex gets reduced and [Co(II)(bpy)$_2$(H$_2$O)$_2$]$^{2+}$ complex is formed and Cl$^-$ ions are released. Increase in conductivity on irradiation in all the complexes can be attributed to aquation/de-ligation from these complexes. In the presence of benzophenone conductance of the
irradiated solution does not significantly increases indicating protection of complex. This shows that benzophenone may be able to intercept the intramolecular electron transfer leading to aquation/de-ligation of the complex on irradiation.

4.5 References

    2007, 92, 599.
    1979, 83, 439.