CHAPTER VII

Novel intercalative Ru(II) / Ru(III) mixed ligand Schiff base complexes with Phen/DPPZ as co-ligands: Synthesis, spectral and redox characterization, antibacterial activity and DNA intercalation

Abstract

Seven new series of complexes of the type \([\text{Ru}^{II}(\text{Phen})(L)(2X-4Y-FPIMP)]\text{ClO}_4 \cdot 2\text{H}_2\text{O}\) where FPIMP = 6-(4-fluorophenyliminomethyl)phenol; X = H, Cl or Br and Y = H or Cl; L = Phen or DPPZ, have been synthesized by adding \([\text{Ru}(\text{Phen})_2(\text{Cl})_2]\cdot 2\text{H}_2\text{O}\) with 2X-4Y-FPIMP and the complex series \([\text{Ru}^{III}(\text{Phen})(L)(2X-4Y-FPIMP)][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}\) have also been prepared by oxidizing \([\text{Ru}^{II}(\text{Phen})(L)(2X-4Y-FPIMP)]\text{ClO}_4 \cdot 2\text{H}_2\text{O}\); with NaClO4 and are characterized by spectral and Cyclic voltammetric studies. These complexes show strong metal to ligand charge transfer (MLCT) transition. In the IR spectral observations, \(\nu(\text{O-H})\), the increase in shift of \(\nu(\text{C-O})\) to 50 – 128 cm\(^{-1}\) and the lower frequency shift of \(\nu(\text{C=N})\) to 15 – 38 cm\(^{-1}\) of the ligands on complexation to ruthenium atom proves the bonding through imine nitrogen and deprotonated phenolic oxygen. Cyclic voltammogram of the complexes in the nitrogen atmosphere show one reversible / quasireversible one electron metal based oxidation Ru\(^{II}/\text{Ru}^{III}\) of Ru(II) complexes and one electron metal based reduction Ru\(^{III}/\text{Ru}^{II}\) of Ru(III) complexes. The ligands and their complexes were tested \textit{in vitro} to their antibacterial activity against Gram-Positive bacteria \textit{Staphylococcus aureus} and Gram-negative bacteria \textit{Proteus mirabilis}. All the Complexes showed activity against both the organisms. The apparent binding constant
for the complex \([\text{Ru(Phen)(DPPZ)(2Br-4Cl-FPIMP)}]\text{ClO}_4^{-} \cdot \text{2H}_{2}\text{O} (6)\) was found in the order of \(10^5 \text{ M}^{-1}\) suggesting an intercalative mode of binding for these complexes.

**Introduction**

Highly organized supramolecular complexes obtained by the self-assembly of polydentate ligands assisted by metal ions are of current interest. They often provide binding sites and cavity for other cations, anions or organic molecules [1]. Recently, the crystal structure of Schiff base \(\text{N,N'bis(salicylidene)benzidine}\) have been reported [2]. The packing of molecules in the crystal structure are found to be dictated by intermolecular interactions. Involvement of these ligands in the development of metal complexes of catalytic importance [4,5] as well as in the self-assembled triple-decker and tetra-decker luminescent materials [6] put them in high demand.

Among the ligands the linear or cyclic Schiff bases obtained by the condensation of primary amines with carbonyl compounds and their metal complexes find a variety of applications including biological, clinical, analytical and industrial, in addition to their important role in catalysis and organic synthesis [6,7]. The central metal ion in these complexes acts as active sites and thereby successfully catalyzes chemical reactions [8]. Metalligand luminescence probes with microsecond decay time have numerous potential applications in the biophysical and clinical sciences. Ruthenium(II) MLCT compounds display long luminescence life time and are extremely photo stable [9,10].

Metal chelates have been used to probe the structure of DNA in solution as agents for mediation of strand scission of duplex DNA and as chemotherapeutic agents. Metal
complexes of 1,10-phenanthroline (phen) or modified phen ligands are particularly attractive for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [11,12]. Ruthenium polypyridyl and phenanthroline complexes have been extensively investigated because of their interesting photochemical [13,14], catalytic [15,16], biological [17,18] and electrochemical [19,20] properties. Ruthenium complexes having phen/bpy along with other co–ligands such as CO, hydride and halides have been extensively studied [21].

Moon et el [22] reported the luminescence intensity of both the Δ- and ∧-[Ru(phen)2DPPZ]2+ complex enhance when they form a complex not only with duplex but with single-stranded DNA, evidencing that the ‘‘light switch effect’’ does not require the intercalation of a large DPPZ ligand. The [Ru(phen)2DPPZ]+;phen = 1, 10-phenanthroline; DPPZ = dipyrido[3,2-a:20,30-c]phenazine), (Figure 7.1) species conceivably interact with the phosphate group by electrostatic interaction.

Figure 7.1 Chemical structures of D- and K-enantiomer of [Ru(phen)2DPPZ]2+
DNA-binding studies of ruthenium(II) complexes containing ancillary ligands bpy or phen of the type [Ru(bpy)(pp[2,3]p$_2$)]($\text{ClO}_4$)$_2$ and [Ru(phen)(pp[2,3]p$_2$)]($\text{ClO}_4$)$_2$ have been reported recently [23].

**Scope of the present work**

Transition metal complexes of 2,2-bipyridyl (bpy), 1,10-phenanthroline (phen) or their modified variants are widely employed in studies of DNA in view of their applications in several research areas, including bioinorganic and biomedicinal chemistries [24–26].

Cisplatin, cis-Pt(NH$_3$)$_2$Cl$_2$ and related Pt(II) complexes are used as anticancer agents in several human cancers particularly testicular and ovarian cancers [27,28]. The action of cisplatin is dependent on the formation of cis-[Pt(NH$_3$)$_2$(OH$_2$)$_2$]$_2^+$ by sequential thermal ligand exchange resulting in the covalent binding to GpG DNA sequences forming intrastrand crosslinks disrupting cellular transcription [29]. However, severe side effects especially nephrotoxicity and acquired resistance limit its widespread use in high doses [30,31]. The development of reagents that can form intrastrand crosslinks with DNA or RNA continues to be a subject of considerable interest in the areas of molecular biology and rational drug design [32]. Barton et al. initiated the binding studies of transition metal complexes with nucleic acids [33] and reported that the cis-[Ru(phen)$_2$Cl$_2$] (phen=1,10-phenanthroline) binds covalently to DNA and exhibits enantiomeric selectivity different from that seen on intercalation [34]. Recently, there has been an interest in the development of cisplatin analogs, which are activated by light providing a means of localizing the action thus reducing the side effects and dosage.
Ruthenium(II) complexes are extremely useful in studying DNA binding of transition metal complexes owing to their intense optical absorption and emission, their ease of preparation and their inertness towards substitution and racemization. Mixed ligand complexes of ruthenium(II) are particularly well suited to explore systematically how such factors as molecular shape and hydrogen bonding stabilize small molecules on DNA [35-39]. The ancillary ligands can be functionalised to tune the DNA binding property as octahedral complexes bind to DNA in three dimensions. Recently reported the complexes \([\text{Ru(NH}_3)_4(\text{diimine})]\text{Cl}_2\) [diimine = bipyridine (bpy), 1,10-Phenanthroline (phen), etc.] interact with DNA through their diimine face, which is supported by the hydrogen bonding of the ammonia co-ligands. Also, when the diimines in these complexes are differently (di/tetra) methyl-substituted 1,10-phenanthrolines [40] and modified 1,10-phenanthrolines [41], the DNA binding affinities are accountable.

Recently, efforts have been directed towards the design of complexes containing modified bpy or phen ligands that bind DNA primarily via base-pair intercalation [42-45].

Literature reveals that the interactions of polypyridyl/phenanthroline ruthenium complexes with DNA, the cationic complexes have been found to bind with DNA in an intercalative, electrostatic or surface interaction fashion [46,47]. To observe the influence of the ligand planarity of complex on DNA binding affinity and antibacterial activity, we designed, synthesized and characterized new complexes derived from supramolecular Schiff bases (described in chapter V) as shown in figure 5.2. (published in Acta Cryst.) [48], phen and derivatives (DPPZ) as co-ligands.
Experimental

The instruments employed for recording the UV-Vis, IR & NMR spectra and Cyclic Voltammetry are described in Chapter II.

Synthesis of Schiff base ligands

Synthesis of Schiff bases employed to prepare Ru(II) & Ru(III) complexes have been described in Chapter V (Scheme 5.1).

Synthesis of starting complexes

Starting complexes for the synthesis of the ruthenium(II)/ruthenium(III) complexes were prepared by the following reported procedure.

Synthesis of cis-[Ru(Phen)(L)Cl₂] . 2H₂O (L = Phen or DPPZ)

Commercial RuCl₃.3H₂O (1.0 mmol), 1,10-phenanthroline or DPPZ (2.0 mmol) and lithium chloride (1.0 mmol) were heated at reflux in reagent grade DMF (10 ml) for 8h. The reaction mixture was stirred magnetically throughout the period. After the reaction mixture was allowed to cool at room temperature, reagent grade acetone (50 ml) was added and the resultant solution was kept overnight at 0°C. Filtering the red to red-violet solution yielded dark green microcrystalline product. The solid was washed three times with water and ether and then dried in vacuo.
Synthesis of cis-[Ru\textsuperscript{II}(Phen)(L)(2X-4Y FPIMP)]ClO\textsubscript{4}. 2H\textsubscript{2}O (L = Phen or DPPZ) (scheme 7.1)

The starting complex, [Ru(phen)\textsubscript{2}Cl\textsubscript{2}].2H\textsubscript{2}O or [Ru(phen)(DPPZ)Cl\textsubscript{2}].2H\textsubscript{2}O (1.0 mmol) was dissolved in dry ethanol (40 ml) and AgNO\textsubscript{3} (2.0 mmol) was added. The mixture was stirred for 30 min. and the deposited AgCl was removed by filtration and to the filtrate was added the appropriate hydrazone (1.0 mmol) and NaOAc (1.0 mmol). The resulting solution was refluxed for 1h on a water bath. It was then allowed to cool to room temperature and a saturated aqueous solution of NaClO\textsubscript{4} (10 ml) was added. The complex precipitated as a deep brownish red crystalline solid, which was collected by filtration, washed with cold water and dried \textit{in vacuo} over CaCl\textsubscript{2}. Recrystallising from 1:1 acetonitrile-benzene gave dark red crystals of [Ru(Phen)\textsubscript{2}(2X-4Y FPIMP)]ClO\textsubscript{4}.2H\textsubscript{2}O and [Ru(Phen)(DPPZ)(2X-4Y FPIMP)]ClO\textsubscript{4}.2H\textsubscript{2}O.
Scheme 7.1 Synthesis of Ru(II) Schiff base complexes
“Phen” as co-ligand.

\[
\text{[Ru}^{II}(\text{Phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}} + \text{NaClO}_4 \rightarrow \text{Ru(II) Schiff base complexes}
\]
Synthesis of [Ru$^{III}$](Phen)(L)(2X-4Y FPIMP)](ClO$_4$)$_2$. 2H$_2$O (L = Phen or DPPZ) (Scheme 7.2)

[Ru$^{II}$](Phen)(L)(2X-4Y FPIMP)]ClO$_4$. 2H$_2$O (100 mg) was dissolved in acetonitrile (25 ml) and excess ceric ammonium nitrate solution was added to it. The mixture was stirred vigorously for 2h. and the color changed from deep brown to bluish green. The green solution was then filtered to remove any insoluble matter. The volume of the oxidized solution was reduced under vacuum. An aqueous solution of NaClO$_4$ was added to the concentrated solution and the mixture was kept in a refrigerator for 2h. The green solid complex that obtained was filtered under vacuum and washed with ice-cold water followed by cold methanol. The solid mass was finally dried in vacuo over CaCl$_2$. 
Scheme 7.2 Synthesis of Ru(III) Schiff base complexes “Phen” and “DPPZ” as co-ligands.
Antibacterial Screening

The \textit{in vitro} antibacterial screening effects of the investigated compounds were tested against the bacteria \textit{Staphylococcus aureus} and \textit{Proteus mirabilis} by the well diffusion method according to the procedure described in the chapter III.

Results and discussion

All the complexes are amorphous powder, insoluble in water and ether, sparingly soluble in solvents such as CHCl$_3$, CH$_2$Cl$_2$, MeCN but completely soluble in DMF and DMSO.

Electronic spectra

The electronic absorption spectral bands of the complexes were recorded over the range 200-800 nm in DMSO together with tentative assignments [49] (Table 7.1) are discussed in detail.

Ru(II) complexes (Figure 7.2-7.5) exhibit two bands. The band in the region 446-449 nm is assigned to the MLCT transition and another intense band at ca. 265-268 nm to the $^1A_{1g} \rightarrow ^1T_{1g}$. These results are in good agreement with assignments made for octahedral ruthenium complexes [50]. Ru(III) complexes (Figure 7.6&7.7) are characterized by intense $\pi-\pi^*$ ligand transitions in the UV region (265-271 nm) [51] and metal-to-ligand charge transfer (MLCT) transition in the visible region. The broad MLCT absorption bands appear between 434-447 nm. Similar cases were observed between
[Ru(bpy)$_2$(dppz)]$^{2+}$ (448 nm) and [Ru(dppz)$_3$]$_2$$^{2+}$ (455 nm) [52] and the band positions are similar to those observed for other octahedral ruthenium(III) complexes [53,54].

**FTIR Spectra**

The IR bands for the metal complexes (Figure 7.6&7.7) derived from Schiff bases of FPIMP (Figure 5.10&5.11), which are most useful to determine the mode of coordination and are listed in Table 7.2. The IR spectra of the free Schiff base ligands show a strong band in the region 1617-1637 cm$^{-1}$ that is characteristic of the azomethine group. Coordination of the Schiff bases to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine frequency. The band due to azomethine nitrogen $\nu$(C=N) shows a modest decrease in the stretching frequency for the complexes and is shifted to lower frequencies, appearing around 1602-1622 cm$^{-1}$, which indicates the coordination of the azomethine nitrogen [55,56]. Also, there is an upward shift in the stretching frequency of phenolic oxygen in the complexes $\nu$(C-O) from 1427-1452 cm$^{-1}$ to 1502-1555 cm$^{-1}$ [57]. This fact is further supported by the disappearance of the $\nu$(O-H) band in the range 3415-3434 cm$^{-1}$ for all the complexes, indicating the subsequent deprotonation of the phenolic proton prior to coordination. Bands in the 519-539 and 465-490 cm$^{-1}$ regions are ascribed to the formation of Ru–O and Ru–N bonds, respectively [58] which further supports the coordination of the azomethine nitrogen and the phenolic oxygen. In addition these complexes showed peak between 1949-1960 cm$^{-1}$ characteristic to $\nu$ (C≡O) [59,60]. Also the characteristic bands due to triphenylphosphine / arsine were observed in the expected regions [61].
EPR Spectra

The representative EPR spectra of ruthenium(III) complex [Ru(Phen)(DPPZ)(2Br-4Cl-FPIMP)](ClO\textsubscript{4})\textsubscript{2}·2H\textsubscript{2}O (7) have been recorded in DMSO solution at LNT and the ‘g’ values \(g_x = 2.36\), \(g_y = 2.04\), \(g_z = 1.90\) with \(g_{av} = 2.1\) which is derived from \(<g>^* = [1/3g_x^2+1/3g_y^2+1/3g_z^2]^{1/2}\) indicate a rhombic distortion. These values fit very well with the values obtained for other similar ruthenium(III) octahedral complexes [62-66].

Cyclic Voltammetry

The redox behaviour of the complexes (Figure 7.8-7.11) were investigated by cyclic voltammetry. Voltammetric data versus Ag/AgCl reference electrode in DMSO solution at a scan rate, 100 mV/s are presented in table 7.3.

Ruthenium(II) complexes display an irreversible (Ru\textsuperscript{III}/Ru\textsuperscript{II}) oxidative response with peak-to-peak separation \(\Delta E_p = 151-398\) mV [67] and two reductive responses—an irreversible (Ru\textsuperscript{II}/Ru\textsuperscript{I}) and reversible/quasi-reversible (Ru\textsuperscript{I}/Ru\textsuperscript{0}) with peak-to-peak separation \(\Delta E_p = 192-220\) mV and 10-132 mV respectively [68]. But ruthenium(III) complexes showed only reductive responses two irreversible reductions [(Ru\textsuperscript{III}/Ru\textsuperscript{II}); \(\Delta E_p = 274-316\) mV] & [(Ru\textsuperscript{II}/Ru\textsuperscript{I}); \(\Delta E_p = 306-308\) mV] and two quasi-reversible reductions [(Ru\textsuperscript{I}/Ru\textsuperscript{0}); \(\Delta E_p = 112-132\) mV] & [(Ru\textsuperscript{0}/Ru\textsuperscript{I}); \(\Delta E_p = 150-168\) mV] and are readily assigned as successive metal centered couples only [69]. In addition, Ru(II) complexes showed Ru\textsuperscript{II}/Ru\textsuperscript{I} ligand based reduction with cathodic peak potential \(E_{pc}\) between −0.503 to −566 V. Also, Ru(II) complexes with “phen” as co-ligands also showed the reductive response (Ru\textsuperscript{0}/Ru\textsuperscript{I}), but which is absent when “phen” is replaced with “dppz”. The stability of different oxidation states of ruthenium can be tuned by proper
modification of the ligand substitution. Among various electronic and structural parameters which influence the $E_{1/2}$ values of ruthenium, the $\pi$-acceptor quality of the ligands appears to be the most dominating feature. A change in the ligating atoms, either from hard to soft or vice versa, can greatly alter the redox potential of the central metal.

**Antibacterial activity studies**

The recent reports have been shown that the ruthenium based complexes are not only having catalytic activity and also very good medicinal properties [70-73] and so the synthesized Schiff base ligands & their ruthenium chelates were screened *in vitro* for their microbial activity against two human pathogenic bacterial species using the well diffusion method (Figure 7.12&7.13). These compounds were found to exhibit considerable activity against Gram +ve (*S. aureus*) and Gram -ve (*P. mirabilis*). The test solutions were prepared in acetonitrile and the results are summarized in Table 3.4. Blank experiments with RuCl$_3$.3H$_2$O and the Ru(III) precursors were carried out under identical experimental conditions and show the inability of these complexes to inhibit the bacterial growth. The effectiveness of an antimicrobial agent in sensitivity is based on the zones of inhibition. The diameter of the zone is measured to the nearest millimeter (mm).

The obtained results are summarized below,

- The ruthenium chelates are more toxic compared to their parent ligands against the same microorganisms under identical conditions [74].
- The toxicity of ruthenium chelates increases on increasing the concentration [75].
The increase in the antibacterial activity of metal chelates may be due to the effect of the metal ion on the normal cell process.

A possible mode of the toxicity increase may be considered in light of Tweedy’s chelation theory [76].

Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible $\pi$-electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of central metal atom, which subsequently favours its permeation through the lipid layers of cell membrane.

Furthermore the mode of action of the compounds may involve formation of a hydrogen bond through the azomethine (\(\text{>C N}\)) group with the active centers of cell constituents, resulting in interference with the normal cell processes [77].

The variation in the effectiveness of the different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells [78,79].

Though complexes of this type were found to have potential antibacterial activity against the bacterial microbes, they could not reach the effectiveness of the conventional bacterial control Ampicillin.
DNA binding studies

Absorption titration

The experiments involving the interaction of the complexes with DNA were carried out in Tris buffer (5 mM Tris and 50 mM NaCl, pH 7.2). Absorption titration experiment was performed by maintaining the metal complex concentration constant (2 µM) and varying the concentration of nucleic acid from (0 to 20 µM). While measuring the absorption spectra, equal amount of DNA was added to both complex solution and the reference solution to eliminate the absorbance of DNA itself. From the absorption data, the intrinsic binding constant $K_b$ was determined using the following equation through a plot of $[\text{DNA}] / (\varepsilon_A - \varepsilon_f)$ Vs [DNA], of the straight line (Figure 7.14)

$$[\text{DNA}] / (\varepsilon_A - \varepsilon_f) = [\text{DNA}] / (\varepsilon_b - \varepsilon_f) + 1 / K_b (\varepsilon_b - \varepsilon_f)$$

Where $\varepsilon_A$, $\varepsilon_f$ and $\varepsilon_b$ correspond to $A_{\text{obsd}} / [\text{Ru}]$, the extinction coefficient for the free ruthenium complex (5) and the extinction co-efficient for the complex in the fully bound form respectively.

Electronic absorption spectroscopy is one of the most powerful experimental techniques for probing metal ion–DNA interactions. Binding of the macromolecule leads to changes in the electronic spectrum of the metal complex. Base binding is expected to perturb the ligand field transition of the metal complex. Intercalative mode of binding usually results in hypochromism and bathochromism due to the strong stacking interaction between an aromatic chromophore and the base pairs of DNA. The extent of
hypochromism parallels the intercalative binding strength. On the other hand, metal complexes, which bind non-intercalatively or electrostatically with DNA may result in hyperchromism or hypochromism. The electronic spectrum of complex $[\text{Ru(Phen)(DPPZ)(2Br-4Cl-FPIMP)}]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ (6) at $25^\circ\text{C}$ in the presence of varying amounts of DNA and in the absences of DNA was carried out, the intensity of the intraligand band at 284 nm decreases with increasing concentration of DNA. Addition of DNA also leads to changes in the position of absorption bands. The 284 nm band is red shifted by 2 nm and 389 nm band is red shifted by 12 nm in the presence of 20 µM DNA. The DNA binding constant of complexe have been estimated to be $1.01 \pm 0.20 \times 10^5 \text{ M}^{-1}$ through spectroscopic titration and these values are higher than the reported for $[\text{Ru(bpy)}_2(\text{PPIP})]^{2+}$ ($4.3 \times 10^4 \text{ M}^{-1}$) and also comparable to that of $[\text{Ru(phen)}_2(\text{PPIP})]^{2+}$ ($1.1 \times 10^5 \text{ M}^{-1}$) [80]. The hypochromism observed in complex 1 and complex 2 in the presence of DNA is indicative of intercalative binding of complex 1 and complex 2 to DNA. It is known that the ancillary ligand “phen” can intercalate in between the base pairs. Hence, it is clear that the intercalative binding of complex (6) to DNA is due to insertion of the ligand FPIMP in between the base pairs of DNA.
References


Figure 7.2 UV Spectra of [Ru (Phen)$_2$ (2Cl-4Cl-FPIMP)] ClO$_4$. 2H$_2$O

Figure 7.3 UV Spectra of [Ru (Phen) (DPPZ) (2Cl-4Cl-FPIMP)] ClO$_4$. 2H$_2$O
Figure 7.4 UV Spectra of \([\text{Ru (Phen) (DPPZ) (2Br-4Cl-FPIMP)}] \text{ClO}_4 \cdot 2\text{H}_2\text{O}\)

Figure 7.5 UV Spectra of \([\text{Ru (Phen) (DPPZ) (2Cl-4Cl-FPIMP)}] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\)
Figure 7.6 FTIR Spectrum of [Ru (Phen) (DPPZ) (2Cl-4Cl-FPIMP)](ClO$_4$)$_2$·2H$_2$O

Figure 7.7 FTIR Spectrum of [Ru (Phen) (DPPZ) (2Br-4Cl-FPIMP)]ClO$_4$·2H$_2$O
Figure 7.8 Cyclic voltammogram of 
[Ru (Phen)$_2$ (2H-4H-FPIMP)] ClO$_4$·2H$_2$O

Figure 7.9 Cyclic voltammogram of 
[Ru (Phen)$_2$ (2Cl-4Cl-FPIMP)] ClO$_4$·2H$_2$O
Figure 7.10 Cyclic voltammogram of 
[Ru (Phen)$_2$ (2Br-4Cl-FPIMP)] ClO$_4$ · 2H$_2$O

Figure 7.11 Cyclic voltammogram of
Figure 7.12 Zone of inhibition of $$[\text{Ru(Phen)}_{2}(\text{2Br-4Cl-FPIMP})]^{2+} \cdot 2\text{H}_2\text{O}$$ against *Staphylococcus aureus*
Figure 7.13 Zone of inhibition of [Ru (Phen) (DPPZ) (2Cl-4Cl-FPIMP)](ClO_4)_2 \cdot 2H_2O against *Proteus mirabilis*

Figure 7.14 Plot of [DNA]/(\(\varepsilon_a - \varepsilon_f\)) vs [DNA] for the absorption spectral titration of DNA (2, 4, 6, 8, 10, 12, 14, 16 & 18 \(\mu\)M) with [Ru (Phen) (DPPZ) (FPIMP – 4Cl 6Cl)](ClO_4)_2 \cdot 2H_2O (2 \(\mu\)M)
Table 7.1 Electronic spectral data

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<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}^*$ (nm)</th>
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<td>(1) $[\text{Ru (Phen)}_2(2\text{H-4H-FPIMP})] \text{ClO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>265 a, 448 b</td>
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<td>(2) $[\text{Ru (Phen)}_2(2\text{Cl-4Cl-FPIMP})] \text{ClO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>266 a, 447 b</td>
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<td>(4) $[\text{Ru (Phen)}(\text{DPPZ})(2\text{Cl-4Cl-FPIMP})] \text{ClO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>268 a, 446 b</td>
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<tr>
<td>(5) $[\text{Ru (Phen)}(\text{DPPZ})(2\text{Cl-4Cl-FPIMP})] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$</td>
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<td>(6) $[\text{Ru (Phen)}(\text{DPPZ})(2\text{Br-4Cl-FPIMP})] \text{ClO}_4 \cdot 2\text{H}_2\text{O}$</td>
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<td>(7) $[\text{Ru (Phen)}(\text{DPPZ})(2\text{Br-4Cl-FPIMP})] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$</td>
<td>271 a, 447 b</td>
</tr>
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* In dimethyl sulphoxide

a $\pi-\pi^*$ transition
b Charge Transfer transition
Table 7.2 FT-IR spectral data (cm$^{-1}$) of the ligands and Ru$^{III}$/Ru$^{II}$ complexes

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<th>Compound</th>
<th>$v_{(C=N)}$</th>
<th>$v_{(C–O)}$</th>
<th>$v_{(O–H)}$</th>
<th>$v_{(Ru–O)}$</th>
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<td>3430</td>
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<td>–</td>
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<td>465</td>
</tr>
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<td>1504</td>
<td>–</td>
<td>524</td>
<td>469</td>
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<td>528</td>
<td>465</td>
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</tr>
<tr>
<td><a href="ClO$_4$">Ru (Phen) (DPPZ) (2Br-4Cl-FPIMP)</a>$_2$.2H$_2$O</td>
<td>1622</td>
<td>1510</td>
<td>–</td>
<td>520</td>
<td>490</td>
</tr>
</tbody>
</table>
Table 7.3 Electrochemical redox data of Ru\(^{II}\)/ Ru\(^{III}\) complexes *

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal based oxidation / reduction (mV)</th>
<th>Ligand based reduction (mV)</th>
<th>Metal based reduction (mV)</th>
<th>Metal based reduction (mV)</th>
<th>Metal based reduction (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(^{III})/Ru(^{II})</td>
<td>(\Delta E_p)</td>
<td>(E_{1/2})</td>
<td>(E_{pc})</td>
<td>(\Delta E_p)</td>
<td>(E_{1/2})</td>
</tr>
<tr>
<td>[Ru (Phen)(_2) (2H-2H-FPIMP)]ClO(_4) 2H(_2)O</td>
<td>352</td>
<td>284</td>
<td>-566</td>
<td>192</td>
<td>-684</td>
</tr>
<tr>
<td>[Ru (Phen)(_2) (2Cl-4Cl-FPIMP)]ClO(_4) 2H(_2)O</td>
<td>404</td>
<td>14</td>
<td>-555</td>
<td>212</td>
<td>-670</td>
</tr>
<tr>
<td>[Ru (Phen)(_2) (2Br-4Cl-FPIMP)]ClO(_4) 2H(_2)O</td>
<td>308</td>
<td>309</td>
<td>-547</td>
<td>219</td>
<td>-219</td>
</tr>
<tr>
<td>[Ru (Phen) (DPPZ) (2Cl-4Cl-FPIMP)]ClO(_4) 2H(_2)O</td>
<td>148</td>
<td>268</td>
<td>-503</td>
<td>203</td>
<td>-203</td>
</tr>
<tr>
<td><a href="ClO(_4)">Ru (Phen) (DPPZ) (2Cl-4Cl-FPIMP)</a>(_2) 2H(_2)O</td>
<td>316</td>
<td>315</td>
<td>–</td>
<td>308</td>
<td>-696</td>
</tr>
<tr>
<td>[Ru (Phen) (DPPZ) (2Br-4Cl-FPIMP)]ClO(_4) 2H(_2)O</td>
<td>252</td>
<td>308</td>
<td>-530</td>
<td>220</td>
<td>-648</td>
</tr>
<tr>
<td><a href="ClO(_4)">Ru (Phen) (DPPZ) (2Br-4Cl-FPIMP)</a>(_2) 2H(_2)O</td>
<td>274</td>
<td>389</td>
<td>–</td>
<td>306</td>
<td>-683</td>
</tr>
</tbody>
</table>

*Solvent – Dimethyl sulphoxide ; supporting electrolyte – [Bu\(_4\)N]ClO\(_4\) (TBAP) 0.1M ; reference electrode – SCE ; \(E_{1/2} = 0.5(E_{pa} + E_{pc})\) where \(E_{pa}\) and \(E_{pc}\) are anodic and cathodic peak potential respectively ; \(\Delta E_p = E_{pa} - E_{pc}\) ; scan rate = 100 mVs\(^{-1}\).*