CHAPTER IV

New series of Ru(III) Schiff base complexes of N,O- donors:

Synthesis, spectral, electrochemical, antibacterial and
DNA binding properties

Abstract

A series of new ruthenium(III) complexes of the type \([\text{Ru(Cl)}_2(\text{DMAPIMP-X})(\text{EPh}_3)_2]\); DMAPIMP={2-[(4-N,N’-dimethylaminophenylimino)-methyl]-4-X-Phenol}; \(X = \text{Cl, Br or I; E = P or As}\) have been synthesized by reacting \([\text{Ru(Cl)}_3(\text{EPh}_3)_3]\) (Where \(E = \text{P or As}\)) with bidentate Schiff base ligand DMAPIMP in 1:1 molar ratio. The complexes have been characterized by spectral (UV-Vis, IR and ESR), magnetic and cyclic voltammetric studies. All complexes show strong metal to ligand charge transfer (MLCT) transition in the visible region. The coordination of imine nitrogen and phenolic oxygen of ligands to ruthenium metal was confirmed with the change in the IR stretching frequency values. The three line e.s.r spectrum of Ru\(^{\text{III}}\) complexes with \(g_x \neq g_y \neq g_z\) indicates magnetic anisotropy and an asymmetry in the electronic environment around the Ru atom. Based on the above datas, tetragonally distorted octahedral structure has been confirmed for the new complexes. Cyclic voltammogram of the complexes in nitrogen atmosphere show an irreversible Ru\(^{\text{III}}/\text{Ru}^{\text{II}}\) reduction couple. The oxidation potential observed in the range \(-0.567\) to \(-0.667\) V and reduction around \(-1.076\) to \(-1.296\) V \textit{versus Ag/AgCl} electrode. The peak-to-peak separation value (\(\Delta\text{Ep}\)) fell in the range 505 to 650 mV suggesting that the irreversible metal centered electron transfer
process. The representative Schiff bases and their complexes were tested in vitro to their antibacterial activity against Gram-Positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Proteus mirabilis*. Further more, the DNA binding experiment of the complex [Ru(Cl)$_2$(DMAPIMP-Br)(AsPh$_3$)$_2$] (5) was carried out by UV-Vis absorption spectral titration and the binding constant $K_b = 2.9 \pm 0.4 \times 10^4$ M$^{-1}$ have been found.

**Introduction**

Molecules containing donor-acceptors such as Schiff bases are the subjects of current interest. Due to the increasing potential as versatile catalysts for organic synthesis and polymer chemistry, in particular polymeric ultraviolet stabilizers, as laser dyes and as molecular switches in logic or memory circuits. Ru-complexes witnessed a spectacular development during the last decade [1-10]. Several families of ruthenium compounds have been prepared and extensively used in a variety of chemical transformations such as hydrogenation [11], hydration [12], oxidation [5], epoxidation [13], isomerization [14], decarbonylation [15], cyclopropanation [16], olefin metathesis [17], Diels-Alder reaction [18], Kharasch addition [19], enol-ester synthesis [19], atom transfer radical polymerization [20] and other related catalytic processes [21]. To achieve an appropriate balance between the electronic and steric environment around the metal and in order to control their activity, stability and chemoselectivity, many of these novel ruthenium complexes have been endowed with specific ligands (eg. hydride, halide, hydra, carboxylate, phosphine, amine, oxygen or nitrogen chelating groups, Schiff bases, arenes, carbenes, etc.) [22-27]. Some of the novel ruthenium complexes are chiral [28] or immobilized on solid supports [29]. As result of their particular structure, these
ruthenium complexes display an enhanced activity and selectivity in a multitude of organic transformations [30]. Significantly, some of the above ligands impart to the catalyst a good tolerance towards organic functionalities, air and moisture, in this way widening the area of their application [31,32]. For several reasons, Schiff bases have been found to be among the most convenient and attractive ligands for ruthenium complexes. First, steric and electronic effects around the ‘Ru’ core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor known to stabilize the higher oxidation state of the ruthenium atom whereas the imine nitrogen is a softer donor and, accordingly, will stabilize the lower oxidation state of the ruthenium. Thirdly, Schiff bases are currently prepared in high yield through one-step procedures via condensation of common aldehydes with amines, in practically quantitative yields [33]. Taking into account the highly desirable attributes of this type of ligands, vast families of bidentate, tridentate and tetradeinate Schiff base-ligated ruthenium complexes, of wide applicability as catalysts in numerous organic reactions, have been designed and prepared. Some of them, e.g. tetradeinate Ru–salen [34] and Ru–porphyrin [35,36] complexes, boost good to excellent activity and remarkably high dia- and enantioselectivity in catalyzing a variety of organic processes. The so-called “dangling-ligands”, particularly those of salicylaldiminato-type, have been recently introduced in arene, alkylidene, vinylidene and diene ruthenium complexes [37,38]. In association with other commonly used ligands like chloride, phosphine, imidazol-2-
ylidene, cyclodienes, they provided a novel class of ruthenium catalysts of versatile application and utility in organic synthesis and polymer chemistry.

A number of metal chelates have been used as probes of DNA structures in solution as agents for mediation of duplex DNA and as chemotherapeutic agents [39].

A large number of Schiff bases and their complexes are significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties [41,42].

**Scope of the present work**

Schiff base complexes of transition metals [42] having O and N donor atoms have shown an exponential increase as inorganic catalysts for various organic transformations. Among the second row transition metal ions, ruthenium mediated oxidations are finding application due to the unique properties of this extremely versatile transition metal, whose oxidation state can vary from -2 to +8 [43,44]. The transition metal phosphine/arsine complexes, especially ruthenium complexes, find application in classical catalytic processes such as hydrogenation, isomerisation, decarbonylation, reductive elimination, oxidative addition and in making C-C bonds [45-49]. Unquestionably, transition metal based catalytic systems have established themselves as the most employed ‘work-horses’ in modern oxidation chemistry for preparative purposes. Studies pertaining the metal ion-DNA intercalation have been utilized for developing novel chemotherapeutic agents, footprinting agents and for gene manipulation in biotechnology and medicine. In addition, new kind of chemotherapeutic
Schiff bases are now attracting the attention of biochemists [50]. Earlier work reported that some drugs showed increased activity when administered as metal complexes rather than as organic compounds and their intercalations with DNA have been reported [51]. Chen et al [52] have proposed that intercalation, hydrogen bonding and p–p interactions are some of the features implicated in the mode of action of ruthenium complexes as antitumour and antimetastatic agents and some compounds are in advance stages of preclinical studies. Although the mechanism of the action of antitumour-active ruthenium compounds is not fully understood yet, it is thought that, similar to platinum drugs [53], the chloride complexes can hydrolyze in vivo, allowing the Ru to bind to the nucleobases of the DNA [54].

The crucial role of Schiff bases in the biological function of bacteriorhodopsin has also been proven [55]. The retinal chromophore is bound covalently to the protein via a protonated Schiff base [56].

In view of recent interest in the energetic of metal ligand binding in metal chelates involving N, O donor ligands [57-60] we started to study the course of the reaction of Schiff base 2-[(4-N,N’-dimethylaminophenylimino)methyl]-4-X-Phenol with Ru(III), and the products were characterized. The antibacterial screening of these complexes and the free ligands against the bacterial species *Staphylococcus aureus* and *Proteus mirabilis* as well as DNA binding properties have been reported.
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(III) complexes have been described in Chapter III (Scheme 3.1).

Synthesis of starting complexes

Starting complexes for the synthesis of the ruthenium(III) complexes were prepared by the following reported procedure [61].

Synthesis of [RuCl$_3$(EPh$_3$)$_3$] (E = P or As)

Solutions of commercial RuCl$_3$.3H$_2$O (1.0 mmol) in ethanol (20 ml) and con. HCl (50 ml) were added quickly and successively to a boiling solution of triphenylphosphine or triphenylarsine (6.0 mmol) in ethanol (50 ml). The resultant solution was heated under reflux for 10 minutes and allowed to cool to room temperature. The reddish brown solid that obtained was filtered and washed with ether and dried \textit{in vacuo}.

Synthesis of Schiff base Ruthenium(III) complexes (Scheme 4.1)

A solution of [Ru(Cl)$_3$(PPh$_3$)$_3$] (0.1 mmol, 99.342 mg) or [Ru(Cl)$_3$(AsPh$_3$)$_3$] (0.1 mmol, 112.542 mg) in C$_6$H$_6$ (20 cm$^3$) and a solution of the appropriate Schiff base (0.1 mmol, 27.4-36.6 mg) in CHCl$_3$ (10 cm$^3$) was added, colour change was noticed on
the addition of the ligand due to the formation of complexes. The contents were refluxed for 4-5h. The resulting solution was concentrated to small volume (3 cm$^3$) on a rotary evaporator and the product was separated by the addition of small amount of pet-ether (60-80°C). The compound that separated was filtered, washed with benzene followed by ether, dried *in vacuo* over anhydrous CaCl$_2$, then recrystallised from 1:2 (v:v) chloroform-pet ether (60-80°C) mixture.
Scheme 4.1 Synthesis of Schiff base Ruthenium(III) complexes.
Antibacterial Screening

The *in vitro* antibacterial screening effects of the investigated compounds were tested against the bacteria *Staphylococcus aureus* and *Proteus mirabilis* by well diffusion method and followed the procedure described in chapter III.

Results and discussion

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

Electronic spectra

The electronic absorption spectral bands of the complexes (Fig 4.1-4.4) were recorded over the range 200-800 nm in MeCN together with tentative assignments [62] (Table 4.1) are discussed in detail.

The low spin paramagnetic ruthenium(III), a d$^5$ system with $^2$T$_{2g}$ as the ground term and the first excited doublet levels in the order of increasing energy are $^2$A$_{2g}$ and $^2$T$_{1g}$, which arise from $^4$T$_{2g}$ $\rightarrow$ $^1$E$_g$ configuration.

All complexes exhibit three bands in the range 203-630 nm. The band between 616-630 nm is assigned to the d-d transition [63,64] ($^2$T$_{2g}$ $\rightarrow$ $^2$A$_{2g}$) [30]. The spectral profiles below 400 nm are very similar and are ligand centered transitions. These bands have been designated as $\pi$-$\pi$ * and n-$\pi$ * transitions of non-bonding electrons present on the imine group in the Schiff base complexes [65,66].
Thus the band positions of electronic spectra of all the complexes are characteristic and similar of those observed for other octahedral ruthenium(III) complexes.

**FT-IR spectra**

The IR spectra (Table 4.2) of the free Schiff bases (Fig 3.9&3.10) were compared with their respective ruthenium complexes (Fig 4.5-4.6) in order to determine the coordination mode of the ligands [67]. The free ligands show a broad band of medium intensity observed at ca. 3430-3464 cm\(^{-1}\) is assigned to \(\nu_{(O-H)}\) of the phenolic group. In complexes the two intense bands centered at ca.1605-1619 cm\(^{-1}\) and 1355-1467 cm\(^{-1}\) assigned to \(\nu_{(C=N)}\) and \(\nu_{(C-O)}\) respectively [68]. The bands observed in the region 407-474 cm\(^{-1}\) has been assigned to \(\nu_{(Ru-O)}\) and \(\nu_{(Ru-N)}\) [63]. The disappearance of \(\nu_{(O-H)}\), the downward shift of \(\nu_{(C-O)}\) and the lower frequency of \(\nu_{(C=N)}\) [69] on complexation proves the bonding of ligands through imine nitrogen [66] and deprotonated phenolic oxygen [70,71]. Also the characteristic bands due to triphenylphosphine/arsine were observed in the expected regions [5].

**ESR Spectra**

The solid state e.s.r spectrum of ruthenium(III) complexes recorded at liquid nitrogen temperature (77 K) shows a simple three line spectra indicating magnetic anisotropy [5,72] in these systems and the complexes are in a low spin octahedral geometry. The average ‘g’ values \((g_x, g_y, g_z)\) with \(g_x \neq g_y \neq g_z\) lie in the 2.219-2.226 BM
range (Table 4.3) and these values fit very well with the values obtained for other similar octahedral ruthenium (III) complexes [73-75].

**Magnetic properties**

The effective magnetic moments $\mu_{\text{eff}}$ (Table 4.3) lie in the range 1.916-1.923 also suggesting that these complexes are one electron paramagnetic low spin $^5t_{2g}$ ($s =1/2$) configuration of the ruthenium(III) ion in an octahedral environment which is similar to reported O,N – coordinated Ru(III) complexes [65].

**Cyclic Voltammetry**

The redox properties of the mixed ligand complexes of ruthenium in MeCN were studied by cyclic voltammetry under nitrogen atmosphere and the relevant electrochemical data are given in Table 4.4. All Ru(III) complexes (Fig 4.7-4.10) exhibit redox peak ($E_{1/2}$ values) in the range – 0.826 to – 0.971 V has been assigned to metal based reduction [Ru(III)/Ru(II)] with peak-to-peak separation value ($\Delta E_p$) ranging from 505 to 650 mV suggesting that an irreversible one electron transfer process. The presence of such redox waves seems to be typical for ruthenium salicyliminato complexes [65,68&76]. The Schiff bases, when co-ordinated through N and O, stabilise ruthenium(III) rather than ruthenium(II). That is, the hard oxygen atom stabilises the higher oxidation state of ruthenium and lower valencies are stabilised by $\pi$-acid ligands like triphenyl phosphine and triphenyl arsine.
Antibacterial investigation

The Schiff base ligands and ruthenium(III) complexes were screened \textit{in vitro} for their microbial activity against two pathogenic bacterial species \textit{S. aureus} and \textit{P. mirabilis} using the well diffusion method (Fig 4.11 & 4.12). The test solutions were prepared in MeCN and the results are summarized in Table 4.5. 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). These compounds were found to exhibit moderate activity against both the organisms. The complexes are more active than their parent ligands, which is consistent with earlier reports [68,77&78]. Such an increased activity for the metal chelates as compared to the free ligands can be explained on the basis of Tweedy’s chelation theory [79]. The activity increases with increase in concentration of test solution containing the new complexes. The different compounds exhibit microbial activity with small variations against the bacterial species and this difference in activity could be attributed to the impermeability of the cell of the microbes or differences in the ribosomes of the microbial cells [80]. Although the complexes are active, they did not reach the effectiveness of the conventional bactericide ampicillin.

DNA binding Experiment

Electronic absorption spectroscopy is one of the most useful experimental techniques for probing metal ion-DNA interactions. The electronic spectra of Ru(III)
complex \([\text{Ru(Cl)}_2(\text{DMAPIMP-Br})(\text{AsPh}_3)_2]\) (5) was monitored in both the presence and absence of Herring sperm DNA. The ultraviolet band centered at 262 nm arises from interligand \(\pi-\pi^*\) transition is prominent than the charge transfer band. The binding constant for the interaction of complex (5) with DNA was obtained from absorption titration data. A fixed concentration (5\(\mu\text{M}\)) of the complex (5) was titrated with increasing amounts of HS DNA over a range of 0 — 60 \(\mu\text{M}\). The binding constant was determined using

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

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 coefficient for the complex in the fully bound form respectively.

A plot (Fig 4.13) of \(\frac{[\text{DNA}]}{(\varepsilon_A - \varepsilon_f)}\) Vs [DNA] gives \(K_b\) as the ratio of the slope to intercept and found to be \(2.3 \pm 0.4 \times 10^4 \text{ M}^{-1}\) which is lesser than the typical intercators reported in the literature [81]. Generally, it has been shown that the intercalator will show bathochromic shift and hypochromism. In the present case, with the addition of DNA, hyperchromism accompanied by moderate red shift of 3 nm in the absorbtivity of interligand bands were observed. Such a small change in \(\lambda_{\text{max}}\) is more in keeping with groove binding, leading to small perturbations [82,83].
References


[51] B.K. Kepler, *Metal Complexes in Cancer Chemotherapy*, VCH, Weinheim,


Figure 4.1 Electronic spectra of $[\text{Ru (Cl)}_2 (\text{DMAIIMP-Cl}) (\text{PPh}_3)_2]$
Figure 4.2 Electronic spectra of \([\text{Ru} \ (\text{Cl})_2 \ (\text{DMAPIMP-Br}) \ (\text{PPh}_3)_2]\)

Figure 4.3 Electronic spectra of \([\text{Ru} \ (\text{Cl})_2 \ (\text{DMAPIMP-I}) \ (\text{PPh}_3)_2]\)
Figure 4.4 Electronic spectra of $[\text{Ru}(\text{Cl})_2(\text{DMAPIMP-Br})(\text{AsPh}_3)_2]$.

Figure 4.5 FT-IR spectra $[\text{Ru}(\text{Cl})_2(\text{PDMAAS-Br})(\text{AsPh}_3)_2]$. 
Figure 4.6 FT-IR spectra [Ru(Cl)$_2$(PDMAAS-I)(AsPh)$_3$)$_2$

Figure 4.7 Cyclic Voltammogram [Ru(Cl)$_2$(PDMAAS-Cl)(PPh)$_3$)$_2$]
Figure 4.8 Cyclic Voltammogram \([\text{Ru(Cl)}_2(\text{PDMAAS-Br})(\text{PPh}_3)_2]\)

Figure 4.9 Cyclic Voltammogram \([\text{Ru(Cl)}_2(\text{PDMAAS-Br})(\text{AsPh}_3)_2]\)
Figure 4.10 Cyclic Voltammogram \([\text{Ru(Cl)}_2(\text{PDMAAS-I})(\text{AsPh}_3)_2]\)
Figure 4.11 Zone of inhibition of \([\text{Ru(Cl)}_2(\text{DMAPIMP-Cl})(\text{PPh}_3)_2]\) against \textit{Staphylococcus aureus}

Figure 4.12 Zone of inhibition of \([\text{Ru(Cl)}_2(\text{DMAPIMP-I})(\text{AsPh}_3)_2]\) against \textit{Proteus mirabilis}
Figure 4.13 Plot of [DNA]/(ε_a − ε_f) vs [DNA] for the absorption spectral titration of DNA (10, 20, 30, 40, 50 & 60 µM) with [Ru(Cl)₂(DMAPIMP–Br)(AsPh₃)]₂ (5 µM)
Table 4.1 Electronic spectral data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)  $[\text{Ru (Cl)}_2 (\text{DMAPIMP-Cl}) (\text{PPh}_3)_2]$</td>
<td>$212^a, 369^b, 630^c$</td>
</tr>
<tr>
<td>(2)  $[\text{Ru (Cl)}_2 (\text{DMAPIMP-Br}) (\text{PPh}_3)_2]$</td>
<td>$213^a, 374^b, 621^c$</td>
</tr>
<tr>
<td>(3)  $[\text{Ru (Cl)}_2 (\text{DMAPIMP-I}) (\text{PPh}_3)_2]$</td>
<td>$203^a, 369^b, 618^c$</td>
</tr>
<tr>
<td>(4)  $[\text{Ru (Cl)}_2 (\text{DMAPIMP-Cl}) (\text{AsPh}_3)_2]$</td>
<td>$214^a, 400^b, 616^c$</td>
</tr>
<tr>
<td>(5)  $[\text{Ru (Cl)}_2 (\text{DMAPIMP-Br}) (\text{AsPh}_3)_2]$</td>
<td>$223^a, 365^b, 619^c$</td>
</tr>
<tr>
<td>(6)  $[\text{Ru (Cl)}_2 (\text{DMAPIMP-I}) (\text{AsPh}_3)_2]$</td>
<td>$211^a, 355^b, 618^c$</td>
</tr>
</tbody>
</table>

* In acetonitrile

$^a\pi–\pi^*\text{ transition}$

$^b\text{n–}\pi^*\text{ transition}$

$^c\text{d–d transition}$
Table 4.2 FT-IR spectral data (cm\(^{-1}\)) of the ligands and Ru\(^{III}\) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{(C=N)})</th>
<th>(\nu_{(C-O)})</th>
<th>(\nu_{(O-H)})</th>
<th>(\nu_{(Ru-O)})</th>
<th>(\nu_{(Ru-N)})</th>
<th>Bands for PPh(_3)/AsPh(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMAPIMP-Cl</td>
<td>1619</td>
<td>1369</td>
<td>3464</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DMAPIMP-Br</td>
<td>1619</td>
<td>1370</td>
<td>3454</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DMAPIMP-I</td>
<td>1619</td>
<td>1355</td>
<td>3430</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td><a href="DMAPIMP-Cl">Ru(Cl)(_2)</a>(PPh(_3))(_2)]</td>
<td>1611</td>
<td>1386</td>
<td>–</td>
<td>423</td>
<td>472</td>
<td>1428,1021,692</td>
</tr>
<tr>
<td><a href="DMAPIMP-Br">Ru(Cl)(_2)</a>(PPh(_3))(_2)]</td>
<td>1611</td>
<td>1361</td>
<td>–</td>
<td>425</td>
<td>469</td>
<td>1434,1078,695</td>
</tr>
<tr>
<td><a href="DMAPIMP-I">Ru(Cl)(_2)</a>(PPh(_3))(_2)]</td>
<td>1611</td>
<td>1394</td>
<td>–</td>
<td>425</td>
<td>467</td>
<td>1434,1077,694</td>
</tr>
<tr>
<td><a href="DMAPIMP-Cl">Ru(Cl)(_2)</a>(AsPh(_3))(_2)]</td>
<td>1611</td>
<td>1440</td>
<td>–</td>
<td>411</td>
<td>453</td>
<td>1433,1071,697</td>
</tr>
<tr>
<td><a href="DMAPIMP-Br">Ru(Cl)(_2)</a>(AsPh(_3))(_2)]</td>
<td>1611</td>
<td>1453</td>
<td>–</td>
<td>424</td>
<td>457</td>
<td>1435,1067,692</td>
</tr>
<tr>
<td><a href="DMAPIMP-I">Ru(Cl)(_2)</a>(AsPh(_3))(_2)]</td>
<td>1611</td>
<td>1440</td>
<td>–</td>
<td>407</td>
<td>474</td>
<td>1434,1077,694</td>
</tr>
</tbody>
</table>
Table 4.3 ESR spectral and magnetic moment data of Ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$&lt;g&gt;^*$</th>
<th>$\mu_{\text{eff}}^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-Cl)(AsPh$_3$)$_2$]</td>
<td>2.415</td>
<td>2.243</td>
<td>1.979</td>
<td>2.219</td>
<td>1.916</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-Br)(AsPh$_3$)$_2$]</td>
<td>2.385</td>
<td>2.248</td>
<td>2.030</td>
<td>2.226</td>
<td>1.923</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-I)(AsPh$_3$)$_2$]</td>
<td>2.335</td>
<td>2.354</td>
<td>2.146</td>
<td>2.280</td>
<td>1.973</td>
</tr>
</tbody>
</table>

$<g>^* = \left[ \frac{1}{3}g_x^2 + \frac{1}{3}g_y^2 + \frac{1}{3}g_z^2 \right]^{1/2}$

$\mu_{\text{eff}}^{**} = g_{av} \sqrt{s (s + 1)}$
Table 4.4 Electrochemical redox data of Ruthenium(III) complexes *

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru$^{II}$/Ru$^{III}$ (mV)</th>
<th>Potential (V)</th>
<th>Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E$_{pa}$</td>
<td>E$_{pc}$</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-Cl)(PPh$_3$)$_2$]</td>
<td>-0.591</td>
<td>-1.147</td>
<td>0.556</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-Br)(PPh$_3$)$_2$]</td>
<td>-0.667</td>
<td>-1.183</td>
<td>0.516</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-I)(PPh$_3$)$_2$]</td>
<td>-0.576</td>
<td>-1.076</td>
<td>0.505</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-Cl)(AsPh$_3$)$_2$]</td>
<td>-0.567</td>
<td>-1.122</td>
<td>0.555</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-Br)(AsPh$_3$)$_2$]</td>
<td>-0.646</td>
<td>-1.296</td>
<td>0.650</td>
</tr>
<tr>
<td>[Ru(Cl)$_2$(DMAPIMP-I)(AsPh$_3$)$_2$]</td>
<td>-0.596</td>
<td>-1.288</td>
<td>0.619</td>
</tr>
</tbody>
</table>

*Solvent – acetonitrile ; 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$^{-1}$
Table 4.5 Antibacterial activity data of Schiff base ligands and Ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Staphylococcus aureus</th>
<th></th>
<th>Proteus mirabilis</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15%</td>
<td>0.2%</td>
<td>0.25%</td>
<td>0.15%</td>
<td>0.2%</td>
</tr>
<tr>
<td>DMAPIMP-Cl</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DMAPIMP-Br</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>DMAPIMP-I</td>
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<tr>
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<td>10</td>
<td>12</td>
<td>13</td>
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<tr>
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<td>10</td>
<td>13</td>
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</tr>
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<td>[Ru(Cl)_2(DMAPIMP-Cl)(AsPh_3)_2]</td>
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<td>12</td>
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<tr>
<td>Control ( Acetonitrile )</td>
<td>—</td>
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</tr>
<tr>
<td>Standard ( Ampicillin )</td>
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Symbol “—” denotes no activity.