NEW RUTHENIUM(III) COMPLEXES CONTAINING TETRADENTATE SCHIFF BASES AND THEIR ANTIBACTERIAL ACTIVITIES

In recent years there is a great deal of interest in the synthesis and characterisation of transition metal complexes containing Schiff bases as ligands, due to their importance as catalysts for many reactions\textsuperscript{1-4}. Although there is a wealth of information available on transition metal complexes of Schiff bases\textsuperscript{5}, it is largely confined to the first row metals, notably iron, cobalt and nickel\textsuperscript{6,7}. Relatively, little work has been done on the Schiff base complexes of ruthenium\textsuperscript{8-11}. Ruthenium(III) complexes showed a positive result on the antibacterial studies\textsuperscript{12}. In view of the growing interest in oxygenation and carboxylation with ruthenium(III) complexes as new catalysts, we describe in this chapter the synthesis and characterisation of stable ruthenium(III) Schiff base complexes.

The Schiff base ligands used in this study are of the following type.

\[ R = -\text{CH}_3 \text{ or } -\text{C}_6\text{H}_5; \quad R' = -\text{CH}_3 \text{ or } -\text{C}_6\text{H}_5; \quad W = -(\text{CH}_2)_4- \text{ or } -(\text{C}_6\text{H}_4)- \]
Experimental

All the reagents used were of Analar grade. Solvents were purified and dried according to standard procedure\textsuperscript{13}. RuCl\textsubscript{3}·3H\textsubscript{2}O was purchased from Loba Chemie Pvt. Ltd., Mumbai, India and was used without further purification. C, H and N analyses were performed at CDR1, Lucknow, India. Infrared spectra were recorded in KBr pellets in the 4000 – 600 nm\textsuperscript{-1} region using a Shimadzu FT-IR 8000 spectrophotometer. Electronic spectra were recorded in CH\textsubscript{2}Cl\textsubscript{2} solution with Hitachi Perkin – Elmer 20/200 spectrophotometer in the 800 – 200 nm range. EPR spectra of the powdered samples were recorded with a Bruker Model ER 200-D spectrometer at X-band frequencies. Cyclic voltammetric studies were carried out in MeCN using a glassy-carbon working electrode and potentials were referenced to a saturated calomel electrode. Magnetic susceptibilities were recorded on an EG and G-PARC vibrating sample magnetometer. Antibacterial studies were performed at Haffkine Institute for Training, Research and Testing, Mumbai, India. Melting points were recorded with a Boetius micro-heating table and are uncorrected.

The starting complexes [RuCl\textsubscript{3}(PPh\textsubscript{3})\textsubscript{3}]\textsuperscript{14}, [RuCl\textsubscript{3}(AsPh\textsubscript{3})\textsubscript{3}]\textsuperscript{15}, [RuBr\textsubscript{3}(AsPh\textsubscript{3})\textsubscript{3}]\textsuperscript{16}, [RuBr\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(MeOH)]\textsuperscript{17} and the Schiff bases\textsuperscript{18} were prepared according to literature methods.

Preparation of the new complexes

(i) Preparation of complexes of the type [RuCl(LL')(PPh\textsubscript{3})]

(\text{where, LL' = dianion of the tetradentate Schiff bases})

To a solution of [RuCl\textsubscript{3}(PPh\textsubscript{3})\textsubscript{3}] (0.099 g; 0.1 mmol) in benzene (20 cm\textsuperscript{3}), the appropriate Schiff bases (acactet, dbmtet and dbm-o-ph) (0.025 – 0.052 g; 0.1 mmol)
was added (molar ratio of ruthenium complex : Schiff base = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to ca. 3 cm$^3$. The product was separated by the addition of small quantity (5 cm$^3$) of petroleum ether (60-80°C). It was then filtered, washed with ethanol/petroleum ether, recrystallised from CHCl$_3$/petroleum ether (60 - 80°C) and dried under vacua.

Yield : 70 - 80%

(ii) Preparation of complexes of the type [RuCl(LL')(AsPh$_3$)]

(where, LL' = dianion of the Schiff base ligand)

To a solution of [RuCl$_3$(AsPh$_3$)$_3$] (0.113 g; 0.1 mmol) in benzene (20 cm$^3$), the appropriate Schiff bases (acacet, dbmtet and dbm-o-ph) (0.022 - 0.046 g, 0.1 mmol) was added (molar ratio of ruthenium complex : Schiff base = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to ca. 3 cm$^3$. The product was separated by the addition of small quantity (5 cm$^3$) of petroleum ether (60 - 80°C). It was then filtered, washed with ethanol/petroleum ether, recrystallised from CHCl$_3$/petroleum ether (60 - 80°C) and dried under vacua.

Yield : 65 - 70%

(iii) Preparation of complexes of the type [RuBr(LL')(AsPh$_3$)]

(where, LL' = dianion of the Schiff base ligand).

To a solution of [RuBr$_3$(AsPh$_3$)$_3$] (0.126 g; 0.1mmol) in benzene (20 cm$^3$), the appropriate Schiff bases (acacet, dbmtet and dbm-o-ph) (0.020 - 0.040 g; 0.1 mmol) was added (molar ratio of ruthenium complex : Schiff base = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to
ca. 3 cm$^3$. The product was separated by the addition of a small quantity (5 cm$^3$) of petroleum ether (60 – 80°C). It was then filtered, washed with ethanol/petroleum ether, recrystallised from CHCl$_3$/petroleum ether (60 – 80°C) and dried under vacua.

Yield: 67 – 75%

(iv) Preparation of complexes of the type [RuBr(LL')(PPh$_3$)]

( where, LL' = dianion of the Schiff base ligand).

To a solution of [RuBr$_3$(PPh$_3$)$_2$(MeOH)] (0.090 g; 0.1mmol) in benzene (20 cm$^3$), the appropriate Schiff bases (acactet, dbmtet and dbm-o-ph) (0.028 – 0.051 g; 0.1 mmol) was added (molar ratio of ruthenium complex : Schiff base = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to ca. 3 cm$^3$. The product was separated by the addition of a small quantity (5 cm$^3$) of petroleum ether (60 – 80°C). It was then filtered, washed with ethanol/petroleum ether, recrystallised from CHCl$_3$/petroleum ether (60 – 80°C) and dried under vacua.

Yield: 70 – 75%

Results and Discussion

The dibasic tetradeionate Schiff base ligands react with [RuCl$_3$(PPh$_3$)$_3$], [RuCl$_3$(AsPh$_3$)$_3$], [RuBr$_3$(AsPh$_3$)$_3$] and [RuBr$_3$(PPh$_3$)$_2$(MeOH)] in a 1:1 molar ratio to give hexa coordinated ruthenium(III) Schiff base complexes of the type [RuX(LL')(EPh$_3$)] as shown in the following equation.
The analytical data obtained for the new complexes (Table II.1) are in good agreement with the formula proposed.
### Table II.1 Analytical data of ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Melting point °C</th>
<th>Elemental analysis Found (Calcd.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>[RuCl(acactet)(PPh₃)]</td>
<td>green</td>
<td>146</td>
<td>58.90(59.10)</td>
</tr>
<tr>
<td>[RuCl(acactet)(AsPh₃)]</td>
<td>green</td>
<td>132</td>
<td>55.30(55.30)</td>
</tr>
<tr>
<td>[RuBr(acactet)(AsPh₃)]</td>
<td>brown</td>
<td>119</td>
<td>52.00(52.00)</td>
</tr>
<tr>
<td>[RuBr(acactet)(PPh₃)]</td>
<td>black</td>
<td>124</td>
<td>55.20(55.30)</td>
</tr>
<tr>
<td>[RuCl(dbmtet)(PPh₃)]</td>
<td>brown</td>
<td>126</td>
<td>68.80(69.40)</td>
</tr>
<tr>
<td>[RuCl(dbmtet)(AsPh₃)]</td>
<td>brown</td>
<td>109</td>
<td>66.40(66.30)</td>
</tr>
<tr>
<td>[RuBr(dbmtet)(AsPh₃)]</td>
<td>brown</td>
<td>117</td>
<td>63.40(63.30)</td>
</tr>
<tr>
<td>[RuBr(dbmtet)(PPh₃)]</td>
<td>brown</td>
<td>122</td>
<td>66.30(66.20)</td>
</tr>
<tr>
<td>[RuCl(dbm-ο-ph)(PPh₃)]</td>
<td>brown</td>
<td>150</td>
<td>69.90(70.60)</td>
</tr>
<tr>
<td>[RuCl(dbm-ο-ph)(AsPh₃)]</td>
<td>brown</td>
<td>137</td>
<td>67.30(67.40)</td>
</tr>
<tr>
<td>[RuBr(dbm-ο-ph)(AsPh₃)]</td>
<td>brown</td>
<td>140</td>
<td>63.80(64.50)</td>
</tr>
<tr>
<td>[RuBr(dbm-ο-ph)(PPh₃)]</td>
<td>brown</td>
<td>121</td>
<td>67.40(67.40)</td>
</tr>
</tbody>
</table>
Infrared spectra

The infrared spectra of the free Schiff bases were compared with that of the ruthenium complexes in order to elucidate the binding mode of the Schiff base ligands to ruthenium metal in the complexes. The important infrared frequencies for all the ruthenium(III) Schiff base complexes are given in Table II.2. A strong band is observed around 1600 – 1580 cm\(^{-1}\) in the free Schiff base ligands, which is characteristic of \(\nu_{C=O}\). In the complexes, the absorption due to \(\nu_{C=O}\) were observed at lower frequencies indicating coordination has been taking place through oxygen atom of the Schiff base ligand. However, the same \(\nu_{C=O}\) absorption for the complexes derived from electron donating group containing Schiff bases was observed slightly higher than that of the other complexes. The bands in the region around 1590 – 1550 cm\(^{-1}\) have been assigned to the mixed mode of vibration arising from the \(\nu_{C=N}\) and \(\nu_{C=C}\) vibrations\(^{19}\). This is indicative of the coordination of the Schiff base nitrogen atom to the metal atom. In addition to the above, other characteristic bands due to triphenylphosphine and triphenylarsine were also present in the spectra of the complexes.

Electronic spectra

Electronic spectra of all the complexes in dichloromethane showed two to four bands in the 560 – 240 nm region (Table II.2). The ground state of ruthenium(III) (\(t_{2g}^5\) configuration) is \(^2T_{2g}\) and the first excited doublet levels in the order of increasing energy are \(^2A_{2g}\) and \(^2T_{1g}\) which arise from the \(t_{2g}^4\ \text{e}_g^1\) configuration. In most of the ruthenium(III) complexes, the electronic spectra showed only charge transfer bands\(^{20}\). Those at around 550 – 400 nm have been assigned to the \(^2T_{2g} \rightarrow ^2A_{2g}\) transition, in conformity with assignments made for
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{C=O}$</th>
<th>$\nu_{C=N} + \nu_{C=C}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl(acac)(PPh₃)]</td>
<td>1630</td>
<td>1590</td>
<td>301, 241, 500</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuCl(acac)(AsPh₃)]</td>
<td>1610</td>
<td>1580</td>
<td>390, 487, 559</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuBr(acac)(AsPh₃)]</td>
<td>1590</td>
<td>1570</td>
<td>350</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuBr(acac)(PPh₃)]</td>
<td>1600</td>
<td>1570</td>
<td>345, 400</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuCl(dbmt)(PPh₃)]</td>
<td>1580</td>
<td>1570</td>
<td>358, 400, 500</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuCl(dbmt)(AsPh₃)]</td>
<td>1590</td>
<td>1580</td>
<td>317, 350, 400, 495</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuBr(dbmt)(AsPh₃)]</td>
<td>1600</td>
<td>1580</td>
<td>325, 370</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuBr(dbmt)(PPh₃)]</td>
<td>1580</td>
<td>1550</td>
<td>350, 400, 515</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuCl(dbm-o-ph)(PPh₃)]</td>
<td>1600</td>
<td>1570</td>
<td>340, 410</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuCl(dbm-o-ph)(PPh₃)]</td>
<td>1590</td>
<td>1580</td>
<td>375, 420, 499</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuBr(dbm-o-ph)(PPh₃)]</td>
<td>1600</td>
<td>1580</td>
<td>400, 525</td>
<td>charge transfer</td>
</tr>
<tr>
<td>[RuBr(dbm-o-ph)(PPh₃)]</td>
<td>1590</td>
<td>1570</td>
<td>350, 400</td>
<td>charge transfer</td>
</tr>
</tbody>
</table>

$a = \text{cm}^{-1}; \ b = \text{nm}$
similar octahedral ruthenium(III) complexes\textsuperscript{10,21}. The other bands in the region 400 - 240 nm have been assigned to charge transfer transitions.

Cyclic voltammetric studies

In an electrochemical redox experiment, electrons were usually transferred heterogeneously between the electrode surface and the dissolved electroactive substance. In the case of the ruthenium complexes, the two types of processes can be stated as,

\[
\text{RuL} + e^- \rightarrow \boxed{\text{Ru}} \quad \text{L} \quad \rightarrow \quad (1)
\]

\[
\text{RuL} + e^- \rightarrow \text{Ru} \quad \boxed{\text{L}} \quad \rightarrow \quad (2)
\]

where L is a general ligand. In each equation, the box schematically represents the primary nature of the redox orbital, i.e., the orbital occupied by the transferred electron. The orbital is essentially metal in character in equation (1) and ligand in character in equation (2). The oxidation state of the metal changes in equation (1) while that of the ligand changes in equation (2). We have studied cyclic voltammetry for all the ruthenium(III) complexes presented in this thesis by the consideration of metal centred redox reactions only. Ruthenium exhibit all oxidation states\textsuperscript{22} in the range \(-2\) to \(+8\) with the exception of \(-1\). In terms of the number of known compounds and the amount of available chemistry, a three tier classification can be made: uncommon, common and very common. These classifications were displayed in the following table. The two very common oxidation states belong to the medium level while the high and very low \((-2\) oxidation states are common.
Classification of oxidation states of ruthenium

A. degree of oxidation

(a) high \[+5, +6, +7, +8\]
(b) medium \[+2, +3, +4\]
(c) low \[-2, 0, +1\]

B. occurrence

(a) uncommon \[+2, +5, +6, +7, +8\]
(b) common \[0, +1, +4\]
(c) very common \[+2, +3\]

The purpose of the electrochemical experiments was to investigate the suitability of the present ligand system in achieving higher oxidation states of metal. As the ligands used in this work are not reversibly reduced or oxidised within the potential limit employed, we believe that the redox processes observed for the complexes were expected for low-spin six-coordinate ruthenium(III) complexes, since the electrons can be added or removed from t_{2g} orbitals. These orbitals were sterically more accessible than the e_{g} orbitals and electron changes that takes place within the t_{2g} set requires less reorganisation energy than changes that takes place within e_{g} orbitals. In general, the charge transfer process for the Ru^{III} – Ru^{II} state is not as rapid as in the case for Ru^{IV} – Ru^{III} couple.\(^{11}\)

Cyclic voltammetric studies were performed for some of the complexes in acetonitrile solution at a glassy-carbon working electrode. The redox potentials of the complexes characterised by well-defined waves in the range from 0.63 V to 0.72 V (Ru^{IV} – Ru^{III}) (oxidation) and from -0.85 V to -0.88 V (Ru^{III} – Ru^{II}) (reduction) versus a saturated calomel electrode. The cyclic voltammetric data are
Table III.3 Cyclic voltammetric data for ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru$^V$ - Ru$^III$</th>
<th>Ru$^III$ - Ru$^II$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pa}$ (V)</td>
<td>$E_{pc}$ (V)</td>
</tr>
<tr>
<td>[RuCl(acac)(PPh$_3$)]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[RuBr(acac)(AsPh$_3$)]</td>
<td>0.77</td>
<td>0.68</td>
</tr>
<tr>
<td>[RuCl(dbmt)(PPh$_3$)]</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>[RuCl(dbmt)(AsPh$_3$)]</td>
<td>0.67</td>
<td>0.59</td>
</tr>
<tr>
<td>[RuCl(dbm-o-ph)(PPh$_3$)]</td>
<td>0.70</td>
<td>0.60</td>
</tr>
<tr>
<td>[RuBr(dbm-o-ph)(AsPh$_3$)]</td>
<td>0.70</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*supporting electrolyte: 0.05 M [Et$_4$N]ClO$_4$; concentration of the complex: 0.001M; scan rate: 50 mVs$^{-1}$; all the potentials are referenced to Ag/AgCl; $E_c$: 0.5 ($E_{pa} + E_{pc}$), where $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials respectively.
Fig. 11.1 (i) Cyclic voltammograms

abbreviations:
- [RuCl(PPH₃)(acac-tet)]
- [RuBr(AsPh₃)(acac-tet)]
- [RuCl(PPh₃)(dbmtet)]

V vs SCE

Fig. 11.1 (i) Cyclic voltammograms
Fig. II.1(ii) Cyclic voltammograms

[V vs SCE]

[\text{RuCl(AsPh}_3\text{)(dbmtet)}]

[\text{RuCl(PPh}_3\text{)(dbm-o-ph)}]

[\text{RuBr(AsPh}_3\text{)(dbm-o-ph)}]
given in Table II.3 and the representative cyclic voltammograms are displayed in Fig. II.1. The redox processes observed for these complexes are metal centered only. Most of the complexes show reversible oxidation [ruthenium(IV) – ruthenium(III) couple] with peak to peak separation (ΔE_p) ranging from 80 – 100 mV, suggestive of a single step one electron transfer process^{11,23-25}. Some of the complexes, namely [RuBr(acacet)(AsPh3)], [RuCl(dbmoph)(PPh3)] and [RuBr(dbmoph)(AsPh3)] undergo both oxidation and reduction although the ruthenium(III) complex, [RuCl(dbmtet)(AsPh3)] show only an oxidation process. The [RuCl(dbmtet)(PPh3)] complex show no reversible oxidation, only irreversible process. The cyclic voltammogram run for [RuCl(dbmtet)(PPh3)] from 0.5 V to –1.2 V showed the first reductive process to be quasi reversible as ip_a/ip_c < 1. Complexes of the type [RuCl(acacet)(PPh3)] show only a reduction process. The reason for the irreversibility for these complexes may be due to short lived oxidised state of the metal ion^{26} or due to oxidative degradation of the ligands^{27}. The irreversibility observed in reduction of some of the complexes indicate that the charge transfer process for Ru^{III} – Ru^{II} is not rapid compared to Ru^{IV} – Ru^{III}. The cyclic voltammogram for complex [RuCl(dbmtet)(PPh3)] run at 50 mVs^{-1}, 100 mVs^{-1}, 150 mVs^{-1} and 200 mVs^{-1} scan speeds showed no change in the redox potentials. Moreover, the ratio ip/sr (sr = scan rate) was constant and the ratio of anodic to cathodic current (ip_c/ip_a) was approximately same, until the peak separation being independent of the scan rate. This indicates that the electron transfer is reversible, or approaches reversibility, and that mass transfer is limited. There is not much variation in the redox potentials due to the replacement of triphenylarsine by triphenylphosphine or triphenylphosphine by triphenylarsine. Hence, it has been observed from the electrochemical data that the present ligand system is ideally suited for stabilising the higher oxidation state of the ruthenium ion.
Magnetic moment studies

The magnetic susceptibility measurements have been carried out for few samples and the values lie between from 1.70 to 1.90 BM indicating +3 oxidation state for ruthenium in all these complexes.\(^{27}\)

EPR spectra

The nature and extent of the subtle distortions of grossly octahedral environment of low spin d\(^5\) – ions can be studied by EPR spectra. A general distortion of the octahedron is expressed as the sum of axial and rhombic distortion. The axial distortion which can be tetragonal (or trigonal) splits one electron into ‘b’ and ‘e’ representations (small letters are used for one electron representation and capital letters for state representation). The rhombic components splits ‘e’ further into two non-degenerate orbitals. The axial splitting parameter (\(\Delta\)) is defined to be positive when ‘b’ lies above ‘e’ as in Fig. A. In the d\(^5\) system the spin-orbit coupling parameter (\(\lambda\)) is positive.

In a tetragonal system with Z as the tetragonal axis, d\(_{xy}\) lies above d\(_{xz}\) and d\(_{yz}\) when, \(\Delta\) is positive and d\(_{yz}\) lies above d\(_{xz}\) when, the added rhombic splitting V is positive. In a trigonal system (Z is the trigonal axis here) \(\Delta\) is positive when, d\(_z^2\) lies high.

The ground state of ruthenium(III) is \(^2T_{2g}\) in the strong cubic field. It is split into two states by a tetragonal field, a doubly degenerate \(^2B_2\) state and a four fold degenerate \(^2E\) state. These have a total energy separation of \(\delta\), which is defined as the tetragonal field strength. First order spin-orbit coupling within these states further splits the \(^2E\) states into two doubly degenerate spin states.
As a result of these interactions and the interactions in the magnetic field, it can be shown in a octahedral field with tetragonal distortion, \( g_x = g_y \neq g_z \) and one should, thus, expect two values for ‘g’ \(^{29}\). A mathematical expression to calculate the values of \( g_1 \) and \( g_{11} \) for low spin \( d^5 \) system having octahedral symmetry with tetragonal distortion has been given \(^{30}\). The presence of three ‘g’ values suggests the octahedral geometry with rhombic distortion in which case \( g_x \neq g_y \neq g_z \)^{29}. 

The EPR spectra of the some of new ruthenium(III) complexes have been recorded at X-band frequencies. All the complexes exhibit three lines with different ‘g’ values indicating the presence of magnetic anisotropy in these complexes. The average ‘g’ values lie in the 2.08 – 2.20 range (Table II.4) and the representative spectra are displayed in Fig. II.2. These values are in the range
Table II.4 EPR spectral data for ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$g^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl(acactet)(PPh₃)]</td>
<td>2.26</td>
<td>2.19</td>
<td>2.05</td>
<td>2.17</td>
</tr>
<tr>
<td>[RuCl(acactet)(AsPh₃)]</td>
<td>2.29</td>
<td>2.21</td>
<td>2.08</td>
<td>2.20</td>
</tr>
<tr>
<td>[RuBr(acactet)(AsPh₃)]</td>
<td>2.25</td>
<td>2.18</td>
<td>2.05</td>
<td>2.16</td>
</tr>
<tr>
<td>[RuCl(dbmtet)(PPh₃)]</td>
<td>2.27</td>
<td>2.10</td>
<td>2.05</td>
<td>2.14</td>
</tr>
<tr>
<td>[RuCl(dbmtet)(AsPh₃)]</td>
<td>2.27</td>
<td>2.17</td>
<td>2.05</td>
<td>2.17</td>
</tr>
<tr>
<td>[RuBr(dbm-o-ph)(AsPh₃)]</td>
<td>2.15</td>
<td>2.09</td>
<td>2.02</td>
<td>2.08</td>
</tr>
</tbody>
</table>

$g^* = \left[ \frac{1}{3} (g_x)^2 + \frac{1}{3} (g_y)^2 + \frac{1}{3} (g_z)^2 \right]^{1/2}$
Fig. II.2 (i) EPR spectra

\[ [\text{RuCl} (\text{PPh}_3)(\text{acactet})] \]

\[ [\text{RuCl} (\text{AsPh}_3)(\text{acactet})] \]

Magnetic field (Gauss)
Fig. II.2 (ii) EPR spectra
Fig. II.2 (iii) EPR spectra
that are obtained for similar other ruthenium(III) complexes\textsuperscript{21,31,32}. The presence of three ‘g’ values indicates the presence of a rhombic distortion in these complexes.

**Antibacterial activity**

The antibacterial activity of the ligand and the complex was studied by agar-well diffusion method\textsuperscript{33}. Nine days old cultures of *Salmonella aureus* and *Salmonella typhi* were used as test organisms. DMSO was used as solvent for these studies. The ruthenium(III) complexes show a fair degree of activity against both the bacterial species (Table II.5). However, the ligands show a minimal inhibitory effect compared to the complexes. The toxicity increases with increase in the concentration of the complexes. Ruthenium chelates are generally found to be more active than the free ligands. This can be attributed to the Tweedy’s chelation theory\textsuperscript{34}, according to which the chelation reduces the polarity of the central metal atom mainly because of partial sharing of its positive charge with the ligand. Consequently, this favours the permeation of the complexes through the lipid layer of cell membrane. The ruthenium complexes showed a higher inhibitory action\textsuperscript{35} when compared to standard bactericide (*Streptomycin sulfate*). The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells\textsuperscript{36}.

Based on the analytical, spectroscopic data (IR, electronic and EPR), magnetic measurements and electrochemistry, the following octahedral structure has been tentatively proposed for all these new complexes.
Table II.5  Antibacterial activity data of ruthenium(III) complex

<table>
<thead>
<tr>
<th>Compound</th>
<th>Minimum inhibitory concentration against</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( S. aureus )</td>
</tr>
<tr>
<td>Stereptomycin sulfate</td>
<td>active at 450 ( \mu g/cm^3 )</td>
</tr>
<tr>
<td>(standard bacteriocide)</td>
<td></td>
</tr>
<tr>
<td>(acactet)</td>
<td>not active at 200 ( \mu g/cm^3 )</td>
</tr>
<tr>
<td>[RuCl(acactet)(PPh₃)]</td>
<td>active at 200 ( \mu g/cm^3 )</td>
</tr>
</tbody>
</table>
where,

\[ X = \text{Cl or Br}; \ E = \text{P or As}; \ W = -(\text{CH}_2)_n \text{- or -(C}_6\text{H}_4)\text{-}; \]
\[ R = -\text{CH}_3 \text{ or -C}_6\text{H}_5; \ R' = -\text{CH}_3 \text{ or -C}_6\text{H}_5 \]
References

34. B.G. Tweedy, Phptopathology, 55, 910 (1964).