CHAPTER VII
RUTHENIUM(III) COMPLEXES OF 2,3-DIMETHYL-1-PHENYL-4-(2-HYDROXY-3-METHOXYPHENYLAZO) PYRAZOL-5-ONE

The growing interest of chemists in the study of Ru(III) complexes is due to their fascinating electron transfer and energy transfer properties (Venkatachalam and Ramesh, 2005; Chittilappilly and Mohammed, 2008). There has been considerable interest in ruthenium complexes now-a-days because of their redox stability, excited state life time and excited state reactivities (George and Harikumaran, 2004). Ruthenium offers a wide range of oxidation states and the reactivities of the ruthenium complexes depend on the stability and interconvertibility of these oxidation states, which, in turn, depends on the nature of the ligands bound to the metal. Complexation of ruthenium by ligands of different types has, thus been of particular interest (Balasubramanian et al., 2005). Change in coordination environment around ruthenium plays an important role in modulating the properties of the complexes. The presence of nitrogen and oxygen donor atoms turns the properties of the complexes to a great extent as effective and stereospecific catalysts for oxidation, reduction and hydrolysis (Harikumaran and Mariamma, 2007; Karvembu et al., 2003). These types of complexes are also reported to have carcinostatic, antitumour, antiviral and antibacterial activity (Viswanathamurthi and Natarajan, 1999). A survey of literature shows that very few Ru(III) complexes of azodyes derived from biologically active molecule 4-aminoantipyrine have been reported (Harikumaran and Prabhakaran, 2000).

The present study involves the preparation and characterization of Ru(III) complexes with methoxyphenolazoantipyrine on the basis of elemental
analyses, magnetic and molar conductance measurements, infrared, electronic and EPR data. Irradiation of one of the complexes, [Ru(MPAP)(PPh3)Cl3] was also incorporated.

EXPERIMENTAL

Details of the reagents used and method of preparation of the ligand MPAP are given in chapter III.

Synthesis of the complexes

The starting complex RuCl3(PPh3)3 was prepared by the reported procedure (Athappan et al., 2001).

The following method was adopted for the preparation of [Ru(MPAP)(PPh3)Cl3]. To a solution of [RuCl3(PPh3)3] (2 mmol) in 20 ml benzene, a methanolic solution of the ligand (2 mmol, 20 ml) was added. The contents were refluxed on a water bath for 5-6 h. The resulting solution was concentrated. On adding a small amount of petroleum ether, the solid separated was suction filtered washed with benzene and dried in vacuo over P4O10.

The following general method was adopted for the preparation of thiocyanate, nitrate, and perchlorate complexes. [RuCl3(PPh3)3] (2 mmol) in 20 ml benzene, containing 2 mmol of NH4NCS/2 mmol of LiNO3 / 1-2 drops of perchloric acid as the case may be, was added to a hot methanolic solution of the ligand (2 mmol, 20 ml). All complexes, except the thiocyanate complex, were precipitated on refluxing the solution for ~5-6 h. The thiocyanate complex was precipitated on stirring the solution at 40 °C for 20-25 min. The resulting solution was concentrated. On adding a small amount of petroleum ether, the solid separated was suction filtered washed with benzene and dried in vacuo.
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one

over P₄O₁₀.

**General properties**

All the chelates are deeply coloured, fairly stable at room temperature and possess good keeping qualities. They are non-hygroscopic solids and soluble in common organic solvents, like acetone, chloroform, methanol, acetonitrile, DMF and DMSO.

**Analysis and physico-chemical studies**

Elemental analyses and physical measurements were carried out as described in chapter III.

**RESULTS AND DISCUSSION**

The analytical data and physical properties of the ligand and their complexes are given in Table VII (1). The results show that the ligand coordinates to the metal ion in 1:1 ratio and suggest that the proposed formulae are $[\text{Ru(MPAP)(PPh}_3\text{Cl}_2\text{X]}$, where $X = \text{Cl, NCS, NO}_3$ or $\text{ClO}_4$.

**Electrical conductance**

The molar conductance values of $10^{-3}$ M solutions of the complexes in methanol and nitrobenzene are presented in Table VII (2). The complexes show molar conductance values in the range 3.2–5.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ in nitrobenzene and 16.2 – 19.9 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ in methanol. These values confirm the non electrolyte nature of the complexes.

**Magnetic susceptibilities**

The effective magnetic moments of ruthenium complexes are shown in
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one

Table VII (1)
Analytical data of MPAP and its complexes

<table>
<thead>
<tr>
<th>Ligand/Complex</th>
<th>colour</th>
<th>Found (calculated) %</th>
<th>μ\textsubscript{(eff)} (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ru</td>
<td>C</td>
</tr>
<tr>
<td>MPAP</td>
<td>Orange</td>
<td>-</td>
<td>63.1 (63.90)</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh\textsubscript{3})Cl\textsubscript{3}]</td>
<td>Dark Brown</td>
<td>12.68 (12.51)</td>
<td>53.41 (53.53)</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh\textsubscript{3})Cl\textsubscript{2}(NCS)]</td>
<td>Dark Brown</td>
<td>11.98 (12.17)</td>
<td>53.36 (53.47)</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh\textsubscript{3})Cl\textsubscript{2}(NO\textsubscript{3})]</td>
<td>Brown</td>
<td>12.46 (12.11)</td>
<td>51.46 (51.78)</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh\textsubscript{3})Cl\textsubscript{2}(ClO\textsubscript{4})]</td>
<td>Dark Brown</td>
<td>12.62 (11.59)</td>
<td>52.44 (52.87)</td>
</tr>
</tbody>
</table>
Table VII (1) at room temperature. The observed magnetic moment value, 1.94-1.98 B.M. is a little higher than expected for the spin only value of a single unpaired electron species (1.73 B. M), indicating a low spin $d^5$ state of the Ru(III) atom (Mahalingam et al., 2006; Li-Xia Bai et al., 2004).

Table VII (2)

Molar conductance data of ruthenium(III) complexes of MPAP

<table>
<thead>
<tr>
<th>Complex</th>
<th>Methanol</th>
<th>Nitrobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>*Conc.</td>
<td>**Conductance</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh$_3$)Cl$_3$]</td>
<td>0.97</td>
<td>16.7</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh$_3$)Cl$_2$NCS]</td>
<td>1.01</td>
<td>18.3</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh$_3$)Cl$_2$(NO$_3$)]</td>
<td>1.10</td>
<td>17.8</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh$_3$)Cl$_2$(ClO$_4$)]</td>
<td>1.03</td>
<td>19.9</td>
</tr>
</tbody>
</table>

$^*x10^{-3}M^*Ω^{-1}cm^2mol^{-1}$

$^1$H NMR spectrum

The $^1$H NMR spectrum (Mandlik et al., 2003) of the free ligand MPAP showed a sharp signal at $\delta$12.505 (phenolic OH). The spectrum displays three singlets, which correspond to methyl protons. The >C-CH$_3$ group of pyrazolone ring appears as a sharp singlet in the region $\delta$ 2.62 while the >N-CH$_3$ signal is observed as another singlet in the region $\delta$ 3.30 and –OCH$_3$ signal is observed at $\delta$ 3.819. The signal due to five aromatic protons of the antipyrene phenyl ring appear as multiplet between $\delta$ (7.29-7.44) and those due to the protons of phenyl rings are observed as multiplet between $\delta$ (6.67-6.78).
Infrared spectra

Important infrared spectral bands of the new azodye ligand and its mode of bonding to the metal ions are given in Table VII (3).

The spectrum of the ligand MPAP exhibits a broad medium band at 2925 cm\(^{-1}\), which is assigned to hydrogen bonded OH group (Sun et al., 2009; Sandbhor and Padhye, 2002). The broad bands assigned to H-bonded OH in the spectra of ligands are shifted to ~3400 cm\(^{-1}\) in all complexes, indicating the non participation of OH group in coordination. The ν\(_{C=O}\) phenolic band at 1282 cm\(^{-1}\) (Aswale et al., 2003) observed in the spectra of the free ligand occur at the same frequency supporting non participation of OH group in bonding. The >C=O stretching frequencies observed at 1634 cm\(^{-1}\) in the spectra of the ligand is shifted to lower frequency ~ 1600 cm\(^{-1}\) in the spectra of all complexes, providing evidence for the involvement of this group in complexation. The vibrational band assigned to the N=N group at 1465 cm\(^{-1}\) in the ligand spectrum shows downward shift by ~30 cm\(^{-1}\) in the spectra of all the complexes, confirming the coordination of one of the azo nitrogens with the metal ion (Mubarak et al.; 2007). Thus the ligand exhibit a neutral bidentate behaviour in all the complexes, coordinating through the C=O and –N=N-groups only. The bands due to coordinated PPh\(_3\) group usually observed in the range 1436-1430 cm\(^{-1}\) could not be located in the spectra of all the complexes due to its overlapping with the azo group vibrations (Harikumaran and Sheela, 2008). The other characteristic bands due to triphenyl phosphine ~1100 and 700 cm\(^{-1}\) are also present in the spectra of all the complexes (Karvembu and Natarajan, 2002). New bands, ~ 450 cm\(^{-1}\) and ~ 490 cm\(^{-1}\) in the metal complexes have been assigned to ν\(_{Ru-O}\) and ν\(_{Ru-N}\) modes respectively.
**Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one**

### Table VII (3)

**IR spectral data of MPAP and its ruthenium(III) complexes**

<table>
<thead>
<tr>
<th>MPAP</th>
<th>[Ru(MPAP)(PPh₂)Cl₃]</th>
<th>[Ru(MPAP)(PPh₂)Cl₂(NCS)]</th>
<th>[Ru(MPAP)(PPh₂)Cl₂(NO₃)]</th>
<th>[Ru(MPAP)(PPh₂)Cl₂(ClO₄)]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3435 mb</td>
<td>3440 mb</td>
<td>3433 mb</td>
<td>3432 mb</td>
<td>ν₀-O-H (Phenolic)</td>
</tr>
<tr>
<td>2925 bm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>ν₀-O-H (H-bonded)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2054 vs</td>
<td>-</td>
<td>-</td>
<td>ν₁-C=N (thiocyanate)</td>
</tr>
<tr>
<td>1634 vs</td>
<td>1585 s</td>
<td>1591 s</td>
<td>1603 s</td>
<td>1583 s</td>
<td>ν₁-O=O (pyrazolone)</td>
</tr>
<tr>
<td>1465 s</td>
<td>1434 s</td>
<td>1433s</td>
<td>1436 s</td>
<td>1435 s</td>
<td>ν₂=N=N (azomethine)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1385 s</td>
<td>-</td>
<td>ν₁(NO₂) (coordinated)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1114 s</td>
<td>ν₄(NO₂) (coordinated)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1076 m</td>
<td>-</td>
<td>ν₂(NO₂) (coordinated)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1034 m</td>
<td>-</td>
<td>ν₃(NO₂) (coordinated)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>744m</td>
<td>-</td>
<td>ν₁(C=S (thio))</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>634m</td>
<td>ν₃(ClO₄) (coordinated)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>612 m</td>
<td>ν₅(ClO₄) (coordinated)</td>
</tr>
<tr>
<td>-</td>
<td>482bm</td>
<td>484bm</td>
<td>488bm</td>
<td>490bm</td>
<td>ν₁(Ru-N)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>474 m</td>
<td>-</td>
<td>-</td>
<td>δ₁(NCS) (thiocyanate)</td>
</tr>
<tr>
<td>-</td>
<td>448 w</td>
<td>440 w</td>
<td>450 w</td>
<td>440 w</td>
<td>ν₁(Ru-O)</td>
</tr>
</tbody>
</table>

vs-very strong; br-strong branched; s-strong ; mb- medium broad; m-medium; w-weak
In the IR spectra of nitrate complex of MPAP the three additional bands 1495 cm\(^{-1}\), 1385 cm\(^{-1}\) and 1023 cm\(^{-1}\) which are not present in the spectra of the ligands, are attributed to \(v_4\), \(v_1\) and \(v_2\) modes of the coordinated nitrate ion. Since the difference between \(v_4\) and \(v_1\) is 110 cm\(^{-1}\), it is suggested that the nitrate ion is coordinated monodentately to the metal ion.

The thiocyanate complexes show very strong band at 2054 cm (\(v_{C-N}\)), medium intensity bands at 744 cm\(^{-1}\) (\(v_{C-S}\)) and 474 cm\(^{-1}\) (\(\delta \text{NCS}\)) confirming N-coordinated nature of the thiocyanate group. Two split bands observed 1114 cm\(^{-1}\) and 1076 cm\(^{-1}\) assigned to \(v_4\) and \(v_1\) and another set of split bands, 634 cm\(^{-1}\) and 612 cm\(^{-1}\), assigned to \(v_3\) and \(v_5\) vibrations are characteristic of monodentately coordinated perchlorate group (Sali and Harikumaran, 2007).

Electronic spectra

The electronic spectral bands of the ligands and the complexes in methanol are given in Table VII (4) with their tentative assignments. The electronic spectrum of the ligand shows intense bands at 235 nm and a band of less intensity at 344 nm due to \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions respectively. These bands suffer marginal shifts on complexation. The electronic spectra of the complexes showed a red shift to \(~280\) nm and \(~360\) nm. The electronic spectra of Ru(III) complexes in methanol show two to three bands in the region 530-280 nm. The ground state of Ru(III) (\(t^{5}_{2g}\) configuration) is \(^2T_{2g}\) while the first excited doublet levels in the order of increasing energy are \(^2A_{2g}\) and \(^2T_{1g}\) which arise from the \(t^{4}_{2g}\ e^{1}_{g}\) configuration (Ballhausen, 1962). In most of the Ru(III) complexes, the electronic spectra show only charge transfer bands (Lever, 1984). Since in a d\(^5\) system, and especially in ruthenium(III) that has relatively high oxidising properties, the charge transfer bands of the type \(L_{\alpha\beta} \rightarrow t_{2g}\) are prominent in the low energy region obscuring the weaker bands.
due to d–d transition. Therefore, it becomes difficult to assign conclusively the bands of ruthenium(III) complexes appearing in the visible region. Hence, all the bands that appear in this region have been assigned to charge transfer transitions, which are in conformity with the assignments made for similar ruthenium(III) complexes (Thangadurai and Natarajan, 2001; Jayabalakrishnan et al., 2002; Priyarega et al., 2011).

Table VII (4)

Electronic spectral bands of MPAP and its ruthenium(III) complexes

<table>
<thead>
<tr>
<th>MPAP ($\lambda_{\text{max}}$/nm)</th>
<th>[Ru(MPAP)(PPh$_3$)$<em>3$Cl] ($\lambda</em>{\text{max}}$/nm)</th>
<th>[Ru(MPAP)(PPh$_3$)$_2$Cl$<em>2$(NCS)] ($\lambda</em>{\text{max}}$/nm)</th>
<th>[Ru(MPAP)(PPh$_3$)$_2$Cl$_2$(NO$<em>3$)] ($\lambda</em>{\text{max}}$/nm)</th>
<th>[Ru(MPAP)(PPh$_3$)$_3$Cl$_3$(ClO$<em>4$)] ($\lambda</em>{\text{max}}$/nm)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>235</td>
<td>279</td>
<td>275</td>
<td>290</td>
<td>274</td>
<td>$\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td>344</td>
<td>360</td>
<td>352</td>
<td>362</td>
<td>354</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
<tr>
<td>-</td>
<td>520</td>
<td>534</td>
<td>528</td>
<td>532</td>
<td>charge transfer</td>
</tr>
</tbody>
</table>

EPR spectra

The nature and extend of the subtle distortions of grossly octahedral environment of low spin d$^5$ ions can be studied by EPR spectra. X-band EPR spectrum Fig. VII (1) of complex [Ru(MPAP)(PPh$_3$)$_3$Cl] was recorded in the polycrystalline form at liquid nitrogen temperature. The complex exhibits three lines with different ‘g’ values ($g_x = 2.28$, $g_y = 2.0027$, $g_z = 1.96$) ($g_x \neq g_y \neq g_z$) indicating the presence of magnetic anisotropy. The average g value was found to be ~2.09. These values are in the range that are obtained for similar other Ru(III) complexes. Three g values observed for the complex indicates rhombohedral distortion of octahedral geometry (Ghosh et al., 1993; Chittilappilly and Yusuff, 2003).
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one

Fig. VII (1)

EPR spectrum of [Ru(MPAP)(PPh₃)Cl₃]

FAB mass spectra

The FAB mass spectra of MPAP and one of its complexes, [Ru(MPAP)(PPh₃)Cl₃] were recorded and their stoichiometric compositions were compared. The molecular ion peak for the ligand shows peak at 339.77 m/z (C₁₈H₁₈N₄O₃), corresponding to 338.36, where as its complex shows the molecular ion peak at 808.08, [Ru(C₁₈H₁₈N₄O₃)(PPh₃)Cl₃], which shows the stoichiometry of the complex as [Ru(MPAP)(PPh₃)Cl₃]. The peaks at m/z = 772.63 [M–Cl]⁺ and 701.73 [M–Cl–Cl]⁺ and 439.43 [M–Cl–Cl–Cl–PPh₃]⁺ in the complex suggests the presence of three chloride ions and one PPh₃ in the complex (Sharma et al., 2006.; Harikumaran and Thankamani, 2010).

Irradiation studies

Colour, thermal behavior, X-ray diffraction and surface morphology of the complex [Ru(MPAP)(PPh₃)Cl₃] were studied before and after gamma irradiation.
Colour

No colour change occurred upon irradiation, indicating the absence of colour centers in the sample.

Non-isothermal decomposition

Thermal analysis plays an important role in the study of the structure and stability of dyes. The resistance to heat at elevated temperatures is one of the main properties required for dyes used in high temperature processes such as dyeing, printing and photocopying and in high technology areas such as lasers and electro-optical devices. Because of the good thermal stability of azo compounds, one of the most important applications of azo compounds is in optical data storage. Therefore the thermal behavior of one of the complexes [Ru(MPAP)(PPh₃)Cl₃], as a representative, was investigated (before and after gamma irradiation) by TGA and DTG techniques by heating in nitrogen atmosphere at a rate of 10 °C per min. Thermal curves were redrawn as percentage mass vs temperature curves to a convenient scale and presented in the fig. VII (2). Thermal analytical results are given in the Table VII (5).
Ruthenium(III) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one

Fig. VII (2)

TG and DTG curves of unirradiated and irradiated [Ru(MPAP)(PPh₃)Cl₃]

Table VII (5)

Thermal analytical results of the [Ru(MPAP)(PPh₃)Cl₃] before and after irradiation

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Stages of decomposition</th>
<th>Decomposition temp (°C)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Unirradiated</td>
<td>I</td>
<td>193 312 233</td>
<td>41.63</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Irradiated to 800 kGy</td>
<td>I</td>
<td>174 271 213</td>
<td>38.61</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Unirradiated</td>
<td>II</td>
<td>431 519 475</td>
<td>27.09</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Irradiated to 800 kGy</td>
<td>II</td>
<td>419 490 456</td>
<td>29.78</td>
</tr>
</tbody>
</table>
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo) pyrazol-5-one

Thermograms of unirradiated and irradiated samples are essentially similar in each case. Thermal decomposition of unirradiated and irradiated samples of [Ru(MPAP)(PPh₃)Cl₃] proceeds in two stages. Percentage mass loss during the first stage in each case suggests the departure of the ligand part of the complex and the second stage accounts for the oxidative decomposition of the remaining part of the complex to give Ru₂O₃ as the ultimate residue. Thermograms of unirradiated and irradiated samples are essentially of the same pattern. It is evident that decomposition is relatively faster in the irradiated sample but does not alter the reaction interval significantly. It can be noted that irradiation results in lowering of reactivity parameters. The enhanced reactivity of irradiated sample has been ascribed to lattice defects as well as products of chemical damage. Systems in which thermal decomposition are accompanied by melting; the lattice defects introduced by irradiation do not have any significant role. Thus the enhancement is due to damage fragments only.

Kinetic parameters viz. activation energy E, frequency factor Z and entropy of activation ΔS were evaluated by the integral method following Coats-Redfern equation. The results along with correlation coefficient (r) are presented in Table VII (6). The Coats-Redfern plots of the two stages of decomposition are presented in Fig. VII (3). The activation energy values calculated for both unirradiated and irradiated complex suggest that the irradiation enhances the decomposition in all stages. The enhancement of decomposition may be due to the catalyzing effect of the fragments such as Cl, liberated during radiolysis (Nair and James, 1985).
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo) pyrazol-5-one

Fig. VII 3a. Coats-Redfern plot for stages I&II decompositions of unirradiated [Ru(MPAP)(PPh₃)Cl₃]

Fig. VII 3b. Coats-Redfern plot for stage I decomposition [Ru(MPAP)(PPh₃)Cl₃] irradiated to 800 KGy

Fig. VII (3)
Coats-Redfern plot for the decomposition of [Ru(MPAP)(PPh₃)Cl₃]
Table VII (6)

Kinetic parameters for the thermal decomposition of [RuCl₃(PPh₃)(MPAP)] before and after irradiation

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stage</th>
<th>E (kJmol⁻¹)</th>
<th>A (S⁻¹)</th>
<th>ΔS (kJ mol⁻¹)</th>
<th>Correlation coefficient(r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Unirradiated</td>
<td>I</td>
<td>160.41</td>
<td>2.21×10¹⁴</td>
<td>31.74</td>
<td>0.9940</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Irradiated to 800 kGy</td>
<td>I</td>
<td>138.97</td>
<td>6.25×10¹²</td>
<td>2.85</td>
<td>0.9917</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Unirradiated</td>
<td>II</td>
<td>401.81</td>
<td>1.13×10²²</td>
<td>249.95</td>
<td>0.9963</td>
</tr>
<tr>
<td>[Ru(MPAP)(PPh₃)Cl₃] Irradiated to 800 kGy</td>
<td>II</td>
<td>285.50</td>
<td>2.59×10¹⁸</td>
<td>104.05</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

Surface morphology and X-ray diffraction studies

The SEM micrographs of the ligand and complex [Ru(MPAP)(PPh₃)Cl₃] are shown in Fig. VII(4). The SEM image of the ligand is shown in Fig. VII (4a). The SEM images reveal an amorphous nature for the ligand. However, after complex formation, a drastic change in morphology can be observed. The SEM images of the Ru(III) complex before irradiation (Fig. VII(4b) and VII(4c)) distinctly reveal the presence of porous structure for the complex, the pore size being in the nanometer range. The formation of inter-aggregated voids is closely related to the solution conditions, which may have significant effects on the surface physical chemistry of the synthesised complexes. The Ru(III) complex was γ irradiated and the SEM micrographs of the irradiated samples are shown in Fig. VII(4d) and VII(4e). As evident from the SEM images, the porous nature of the complexes has been lost on irradiation. The induced changes in the surface characteristics of solids due to γ-irradiation could be attributed to splitting of their crystallites (EI-Shobaky et al., 2002), desorption.
of chemisorbed oxygen, removal of surface hydroxyl groups, pore wall erosion and progressive blocking of pores as bulk expansion took place. Irradiation changed the surface morphology as is evident from SEM images. Changes in the scanning electron micrographs indicate that the applied dose can cause changes in the surface morphology of crystals.

X-ray powder photograph obtained for the complex [Ru(MPAP)(PPh₃)Cl₃] recorded only very few reflections and hence could not be indexed. This may be an indication of the amorphous nature of the complex.
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one

Fig 4a. Ligand (MPAP)

Fig 4b, Fig 4c [Ru(MPAP)(PPh₃)Cl₃] unirradiated

Fig 4d, Fig 4e [Ru(MPAP)(PPh₃)Cl₃] irradiated to 800KgY

Fig. VII (4)

SEM micrographs of [Ru(MPAP)(PPh₃)Cl₃]: unirradiated and irradiated
Antimicrobial studies

The in vitro biological screening effects of the investigated ligand and complexes were tested against Mycobacterium tuberculosis H37Rv, E. coli and Lactobacillus leichmannii by the Resazurin assay method at concentrations 1, 10 and 100 µg/mL. All the synthesized complexes exhibited activity at 100 µg/ml against M. tuberculosis H37Rv are given in Fig. VII (5) and active against E. coli at 100, 10, and 1 µg /ml are given in Fig. VII (6). The complexes were not active against Lactobacillus leichmannii.

Fig. VII (5)
Anti tubercular activity of MPAP (C9) and [Ru(MPAP)(PPh₃)Cl₃](C10) against M. tuberculosis

Fig. VII(6)
Antibacterial activity of MPAP(L) and [Ru(MPAP)(PPh₃)Cl₃](C) against E. coli
Coordination number and geometry

The ligands are coordinated to the metal ion in a neutral bidentate fashion. The anions are unidentatively coordinated. The IR and electronic spectra are in favor of hexa coordinate octahedral geometry for the complexes. EPR spectrum suggests that the complex is monomeric in nature.

Based on the above observations, the suggested structure of ruthenium(III) complex is given in Fig. VII (7).

![Proposed 2D structures of [Ru(MPAP)(PPh₃)Cl₂X]](image)

Proposed 2D structures of [Ru(MPAP)(PPh₃)Cl₂X]

(X=Cl, NCS, NO₃ or ClO₄)
3D molecular modeling

The molecular modeling was constructed using modeling and analysis software (Chem Bio Office Ultra, 2008). The possible 3D structure of the complex [Ru(MPAP)(PPh3)Cl3] was optimized by molecular mechanics calculations, MM2 giving the lowest energy CHEM 3D models. Proposed 3D structures of the complexes are given in Fig VII (8). The selected bond lengths and bond angles are given in Table VII (7).

**Fig. VII (8)**

Proposed 3D structure of [Ru(MPAP)(PPh3)Cl3]
Ruthenium(iii) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one

Table VII (7)

Selected bond lengths and angles of \([\text{Ru(MPAP)(PPh}_3\text{)Cl}_3]\)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bond length, Å</th>
<th>Atoms</th>
<th>Bond angle, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(13)-Cl(17)</td>
<td>2.2494</td>
<td>Cl(17)-Ru(13)-P(16)</td>
<td>93.7078</td>
</tr>
<tr>
<td>Ru(13)-P(16)</td>
<td>2.3558</td>
<td>Cl(17)-Ru(13)-Cl(15)</td>
<td>86.0651</td>
</tr>
<tr>
<td>Ru(13)-Cl(15)</td>
<td>2.2497</td>
<td>Cl(17)-Ru(13)-Cl(14)</td>
<td>94.4813</td>
</tr>
<tr>
<td>Ru(13)-Cl(14)</td>
<td>2.2500</td>
<td>Cl(17)-Ru(13)-O(9)</td>
<td>85.9067</td>
</tr>
<tr>
<td>O(9)-Ru(13)</td>
<td>1.8826</td>
<td>Cl(17)-Ru(13)-N(6)</td>
<td>147.1799</td>
</tr>
<tr>
<td>N(6)-Ru(13)</td>
<td>1.9632</td>
<td>P(16)-Ru(13)-Cl(15)</td>
<td>97.0134</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(16)-Ru(13)-Cl(14)</td>
<td>90.7873</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(16)-Ru(13)-O(9)</td>
<td>170.4607</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(16)-Ru(13)-N(6)</td>
<td>119.0811</td>
</tr>
<tr>
<td>Cl(15)-Ru(13)</td>
<td>172.1323</td>
<td>Cl(15)-Ru(13)-O(9)</td>
<td>92.4716</td>
</tr>
<tr>
<td>Cl(15)-Ru(13)</td>
<td>88.3561</td>
<td>Cl(15)-Ru(13)-N(6)</td>
<td>79.7490</td>
</tr>
<tr>
<td>Cl(14)-Ru(13)</td>
<td>86.9495</td>
<td>Cl(14)-Ru(13)-O(9)</td>
<td>62.0367</td>
</tr>
<tr>
<td>O(9)-Ru(13)</td>
<td></td>
<td>Cl(14)-Ru(13)-N(6)</td>
<td></td>
</tr>
</tbody>
</table>

SUMMARY

Four new ruthenium(III) complexes were synthesized using MPAP as the ligand and Cl\(^-\), NCS\(^-\), NO\(_3^-\) or ClO\(_4^-\) as counter ions. They were characterized by elemental analysis, conductance and magnetic measurements, IR, NMR, UV-Vis, EPR and FAB mass spectral studies. The analytical data, physical measurements and spectral studies suggests that the general formulae are \([\text{Ru(MPAP)(PPh}_3\text{)Cl}_2\text{X}]\), where X =Cl, NCS, NO\(_3^-\) or ClO\(_4^-\). IR spectral
studies revealed the bidentate chelating behavior of the ligand and monodentate coordination of the anions in these complexes. Conductance data reveals the non electrolytic nature of the complexes. Electronic and ESR spectral data suggests an octahedral environment around the central metal ion. Irradiation studies reveal that irradiation enhanced thermal decomposition, lowering thermal and kinetic parameters. The unit cell parameters changed upon irradiation. The irradiated sample showed lesser degree of crystallinity as evidenced by peaks of lower intensity in XRD and SEM micrographs. Antimicrobial studies reveal that the complexes exhibited significant activity against *E.*coli. The ligand was inactive against all applied pathogenic bacteria.