CHAPTER VII
CHAPTER VII

CONVENIENT SYNTHESIS OF BIS(2,2'-BIPYRIDYL) COMPLEXES OF RUTHENIUM(III) AND TRIS(2,2'-BIPYRIDYL) OR (1,10-PHENANTHROLINE) COMPLEXES OF RUTHENIUM(II)

AND

NOVEL SYNTHESIS OF \( \text{L}_n \text{Ru}(1,10\text{-PHENANTHROLINE})_2 \text{Br}_2/X \) (X = Br, ClO\(_4\), BPh\(_4\))

The chemistry of diimine complexes of ruthenium(II) and ruthenium(III) is interesting because of their physical, chemical and structural properties. The attention of inorganic chemists during the past decade has been focussed on the chemistry of \( \text{L}_n \text{Ru}(\text{bipy})_3^{2+} \) and its derivatives due to a unique combination of chemical stability, redox properties, excited state reactivity, luminescence emission and excited state life time. In particular, the ruthenium(II) diimine complexes have played and are still playing a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, photo electrochemistry, chemi- and electrochemi- luminescence and electron and energy transfer.
As a result of which, such complexes are being considered as promising candidates for the role of ideal photocatalysts for the visible light photoinduced decomposition of water into dihydrogen and oxygen. The interest in evolving easy methods of synthesizing these compounds continues, besides studying their physical, chemical and photocatalytic behaviours in detail.

Synthesis of ruthenium(III) complexes containing (mono, bis or tris) 2,2'-bipyridyl or 1,10-phenanthroline is generally achieved by the oxidation of their ruthenium(II) analogues with (i) chlorine,2-5 (ii) a cerium(IV) compound,6-10 (iii) lead(IV) oxide11,12 or (iv) silver nitrate.6 Recently \[\text{KL-RuCl}_4\text{(bipy)}\] and \[\text{KL-RuCl}_3\text{(bipy)}\] were reported from \[\text{RuCl}_3\cdot\text{xH}_2\text{O}.\] The synthesis of \[\text{Ru(bipy)}\text{Cl}_2\text{Cl}\cdot\text{H}_2\text{O}\] was first described by Bailer et al.4 by the oxidation of \[\text{Ru(bipy)}\text{Cl}_2\text{Cl}\cdot\text{H}_2\text{O}\] with chlorine. Latter, Fergusson and Harris5 obtained this compound by the oxidation of \[\text{Ru(bipy)}\text{Cl}_2\text{Cl}\cdot\text{H}_2\text{O}\] with chlorine. Syntheses of \[\text{Ru(bipy)}\text{Cl}_2\text{Cl}\cdot\text{H}_2\text{O}\], described above, involve two steps, (i) preparation of a ruthenium(II) complex containing 2,2'-bipyridyl and (ii) its oxidation using chlorine. Recently Bottomley and Mukaida16 have reported a one pot synthesis of the ruthenium(III) complex described above. In this chapter, we describe a very simple method of synthesising
\[ \text{Ru(bipy)}_2\text{Cl}_2\text{Cl}_2\text{2H}_2\text{O}, \text{ by the metathesis of } \text{Me}_2\text{SO} \text{ groups in an easily synthesised ruthenium(III) compound, viz.} \]
\[ \text{fac- or mer- } \text{RuCl}_3(\text{Me}_2\text{SO})_3. \]

Reports on the synthesis of ruthenium(III) complexes containing (mono or bis) 2,2'-bipyridyl or 1,10-phenanthroline and bromide ligands are very few. \[ \text{RuBr}_2(\text{py})_2(bipy)\text{ClO}_4 \text{ and RuBr}(\text{py})_3(bipy)\text{ClO}_4 \text{ were reported by the oxidation of their ruthenium(II) analogues with cerium(IV) ammonium sulphate.} ^2 \]
\[ \text{NH}_4\text{RuBr}_4(bipy)\text{ClO}_4 \text{ was reported by the metathesis and reduction of } \text{RuCl}_4(bipy)\text{ with HBr and NH}_4\text{Br.} ^2 \]
\[ \text{PhenH}_2\text{RuBr}_4(\text{phen})\text{ClO}_4\text{H}_2\text{O} \text{ was reported by the metathesis of K}_2\text{RuCl}_5(\text{H}_2\text{O})\text{ with HBr and NH}_4\text{Br in situ and reaction with 1,10-phenanthroline. In this chapter, we report the synthesis of a new ruthenium(III) complex, viz.} \]
\[ \text{Ru(phen)}_2\text{Br}_2\text{Br}, \text{ by a simple substitution of } \text{Me}_2\text{SO} \text{ with 1,10-phenanthroline in } \text{RuBr}_3(\text{Me}_2\text{SO})_3. \]

This is the first example of a bis(1,10-phenanthroline) ruthenium(III) complex containing bromide ligands. Chloro-analogue of this ruthenium(III) complex is known. \text{3}

Various methods have been described for the synthesis of ruthenium(II) complexes of the type, \[ \text{Ru(L-L)}_3\text{X}_2\\text{nH}_2\text{O} \]
\[ (\text{L-L} = \text{bipy or phen, } \text{X} = \text{Cl, Br, I, ClO}_4 \text{ etc).} ^\text{19} \]
Most of the methods make use of commercial RuCl$_3\cdot$XH$_2$O; a ruthenium(III) compound, \text{viz.} K$_2\text{RuCl}_5(\text{H}_2\text{O}).
viz. $K_2 \left[ \text{RuCl}_6 \right]_2$ or $K_4 \left[ \text{Ru}_2 \text{Cl}_{10} \right]$. In most cases, excess of the ligand acts as a reducing agent to give the ruthenium(II) compounds, $\left[ \text{Ru}(\text{L-L})_3 \right]_2 \text{X}_2 \cdot \text{nH}_2 \text{O}$. We report here a simple method of complete substitution of chloro and Me$_2$SO groups from fac or mer $\left[ \text{RuCl}_3 (\text{Me}_2\text{SO})_3 \right]$ by 2,2'-bipyridyl or 1,10-phenanthroline to give $\left[ \text{Ru}(\text{L-L})_3 \right]_2 \text{X}_2 \cdot \text{nH}_2 \text{O}$. Substitution reactions of $\left[ \text{RuCl}_2 (\text{Me}_2\text{SO})_4 \right]$ with 2,2'-bipyridyl or 1,10-phenanthroline were reported to give partially substituted products only.\(^{20}\)

**EXPERIMENTAL**

All the solvents were freshly distilled before use. fac and mer $\left[ \text{RuCl}_3 (\text{Me}_2\text{SO})_3 \right]$ and $\left[ \text{RuBr}_3 (\text{Me}_2\text{SO})_3 \right]$ were prepared as described in Chapter II and Chapter IV respectively. Analytical data and other physical measurements, viz. IR, $^1$HNMR, EPR, $\mu_{\text{eff}}$ were obtained as described in Chapters II and III. Analytical data and molar conductance data are reported in Table VII.1. Electronic absorption spectral data are given in Table VII.2.

**PREPARATIONS**

(a) $\left[ \text{Ru(bipy)}_2 \text{Cl}_2 \right] \text{Cl} \cdot 2 \text{H}_2 \text{O}$

To a solution of fac, or mer $\left[ \text{RuCl}_3 (\text{Me}_2\text{SO})_3 \right]$ (0.2g) in methanol (10 cm$^3$), 2,2'-bipyridyl (0.11g) (molar ratio,
1:1.5) was added and refluxed on a water-bath for 30 min. In case of \( \text{mer} \text{RuCl}_3\left(\text{Me}_2\text{SO}\right)_3 \), the product separated out on cooling, whereas in case of \( \text{fac} \text{RuCl}_3\left(\text{Me}_2\text{SO}\right)_3 \), diethyl ether was added to precipitate the orange coloured compound. It was centrifuged, washed with ether and dried in vacuo. Yield 0.18 g, (75%).

(b) \( \text{Ru(bipy)}_2\text{Cl}_2\text{ClO}_4 \)

To a solution of \( \text{Ru(bipy)}_2\text{Cl}_2\text{Cl}_2\text{H}_2\text{O} \) (0.2 g) in methanol (10 cm\(^3\)), a solution of \( \text{NH}_4\text{ClO}_4 \) (0.05 g) in methanol (5 cm\(^3\)) was added and the mixture was refluxed on a water-bath for 15 min, concentrated and cooled to room temperature. Brown crystalline compound separated out. It was centrifuged, washed with ether and dried in vacuo.

(c) \( \text{Ru(phen)}_2\text{Br}_2\text{Br} \)

To a solution of \( \text{RuBr}_3\left(\text{Me}_2\text{SO}\right)_3 \) (0.2 g), in toluene (10 cm\(^3\)), 1,10-phenanthroline (0.1 g) (molar ratio 1:1.5) was added and warmed on a water-bath for 10 min. A compound separated, which was centrifuged, washed with ethanol and then with ether and dried in vacuo. Yield 0.16 g, (66%).

(d) \( \text{Ru(phen)}_2\text{Br}_2\text{X} \), \( \text{X} = \text{ClO}_4, \text{BPh}_4 \)

\( \text{Ru(phen)}_2\text{Br}_2\text{Br} \) (0.2 g), was dissolved in methanol (20 cm\(^3\)) and a methanolic solution of \( \text{NH}_4\text{ClO}_4 \) or \( \text{NaBPh}_4 \)
(molar ratio of the complex : X = 1:1.5) was added to it. In case of NaBPh₄ an orange compound separated on mixing at room temperature, whereas in case of NH₄ClO₄, refluxing of the mixture for 30 min and cooling to room temperature yielded a brown crystalline compound. The compounds were centrifuged, washed with ether and dried in vacuo.

\[
\text{(e)} \quad \text{Ru(bipy)}_3\text{Cl}_2\text{H}_2\text{O}
\]

To a solution of fac or mer \[\text{RuCl}_3(\text{Me}_2\text{SO})_3\] (0.2g) in ethanol (20 cm³), 2,2'-bipyridyl (0.22g) (molar ratio 1:3) was added and refluxed the mixture for 2 h, when a dark orange solution was obtained. The solution was concentrated to ~5 cm³, cooled to room temperature and diethyl ether was added to precipitate the compound. The compound was centrifuged, washed with ether and dried in vacuo. Yield 0.2g, (65%).

\[
\text{(f)} \quad \text{Ru(bipy)}_3\text{Br}_2
\]

\[\text{RuBr}_3(\text{Me}_2\text{SO})_3\] (0.2g) was dissolved in ethanol (20 cm³) and a solution of 2,2'-bipyridyl (0.2g) (molar ratio ~1:4) in ethanol was added to it. The mixture was refluxed for 2 h when an orange coloured solution was obtained. The solution was concentrated, cooled, and diethyl ether was added to precipitate a yellow orange compound. It was centrifuged, washed with ether and dried in vacuo. Yield 0.18g, (~72%).
To the orange coloured solution obtained in reaction (e) or in reaction (f) above, an ethanolic solution of NH$_4$ClO$_4$ or NaBPh$_4$ (molar ratio of the complex : X = 1:3) was added. In case of NaBPh$_4$, the mixture on stirring at room temperature for 5 min. yielded an orange coloured compound, whereas in case of NH$_4$ClO$_4$, refluxing of the mixture for 15 min and cooling to room temperature yielded the red crystalline compound. The compounds were separated as in (e) above.

(fac or mer) $\text{RuCl}_3(\text{Me}_2\text{SO})_3$ (0.2g) was dissolved in ethanol (5 cm$^3$) and 1,10-phenanthroline (0.28g) (molar ratio 1:3) was added to the solution. To the above reaction mixture, toluene (10 cm$^3$) was added and heated on a water-bath for 2 h. The solution was concentrated (~ 5 cm$^3$) and an ethanolic solution of NH$_4$ClO$_4$ or NaBPh$_4$ (molar ratio of the complex : X = 1:3) was added. Complexes separated in similar way as in reaction (g) above.

RESULTS AND DISCUSSION

Synthesis of ruthenium(III) complexes containing 2,2'-bipyridyl or 1,10-phenanthroline were generally reported by the oxidation of their ruthenium(II) analogues. Only, in
case of mono diimine complexes, direct reactions of commercial 
RuCl₃·xH₂O with the diimines were reported. ¹³⁻¹⁵ We have been 
able to achieve the synthesis of bis diimine ruthenium(III) 
complexes using easily synthesizable compounds, viz. fac or 
mer [RuCl₃(Me₂SO)₃] and [RuBr₃(Me₂SO)₃]. Reaction between 
the Me₂SO complexes and the diimines resulted under suitable 
condition, complete substitution of Me₂SO and resulted in the 
formation of [Ru(bipy)₂Cl₂]Cl·2H₂O and [Ru(phen)₂Br₂]Br 
respectively.

[Ru(bipy)₂Cl₂]Cl·2H₂O, synthesised by the substitution 
of Me₂SO molecules from fac or mer [RuCl₃(Me₂SO)₃], were 
characterised by the elemental analysis (Table VII.1) and 
various physical methods. Similarly, [Ru(bipy)₂Cl₂]ClO₄, 
synthesised by the metathesis of the chloro-compound, was 
also characterised. The electronic absorption spectra of these 
compounds in acetonitrile were similar to the ones reported 
earlier. ⁴⁻⁶,¹⁶ The IR spectrum showed complete substitution of 
Me₂SO groups. All characteristic IR bands due to bipyridyl were 
observed. Far IR spectra showed two bands at 340 and 320 cm⁻¹ 
which may be due to ν Ru-Cl, similar to those reported earlier. ⁴ 
Presence of two bands due to ν Ru-Cl conforms to the cis 
geometry of the complex in solid state. ⁴ In case of 
[Ru(bipy)₂Cl₂]ClO₄, a very strong band at 1090 cm⁻¹ was also 
observed, which is characteristic of the ClO₄⁻ group present in 
the ionic fashion. ²¹ An EPR spectrum of [Ru(bipy)₂Cl₂]Cl·2H₂O
Table VII.1 Analytical and Physical data of Ruthenium(III) and Ruthenium(II) Complexes containing 2,2'-Bipyridyl or 1,10-Phenanthroline

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>$\Lambda_M$ in $\Omega^{-1}$cm$^2$mol$^{-1}$ in CH$_3$CN</th>
<th>Analytical data$^a$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\text{Ru(bipy)}_2\text{Cl}_2\right]$</td>
<td>Orange</td>
<td>120</td>
<td>C: 43.1(43.2) H: 3.8(3.6) N: 9.9 (10.1)</td>
</tr>
<tr>
<td>$\left[\text{Ru(bipy)}_2\text{Cl}_2\text{ClO}_4\right]$</td>
<td>Brown</td>
<td>130</td>
<td>C: 41.0(41.1) H: 2.9(2.7) N: 9.4 (9.6)</td>
</tr>
<tr>
<td>$\left[\text{Ru(phen)}_2\text{Br}_2\text{Br}\right]$</td>
<td>Brown</td>
<td>118</td>
<td>C: 41.0(41.1) H: 2.6(2.3) N: 7.7 (8.0)</td>
</tr>
<tr>
<td>$\left[\text{Ru(phen)}_2\text{Br}_2\text{ClO}_4\right]$</td>
<td>Reddish brown</td>
<td>120</td>
<td>C: 39.6(39.9) H: 2.0(2.2) N: 7.6 (7.8)</td>
</tr>
<tr>
<td>$\left[\text{Ru(phen)}_2\text{Br}_2\text{BPh}_4\right]$</td>
<td>Orange</td>
<td>120</td>
<td>C: 61.0(61.2) H: 3.6(3.8) N: 5.6 (5.9)</td>
</tr>
<tr>
<td>$\left[\text{Ru(bipy)}_3\text{Cl}_2\text{H}_2\text{O}\right]$</td>
<td>Orange</td>
<td>220</td>
<td>C: 54.3(54.7) H: 3.6(3.9) N: 12.5 (12.3)</td>
</tr>
<tr>
<td>$\left[\text{Ru(bipy)}_3\text{Br}_2\text{Br}_2\text{H}_2\text{O}\right]$</td>
<td>Yellow orange</td>
<td>260</td>
<td>C: 42.4(42.6) H: 3.8(3.3) N: 9.7 (9.9)</td>
</tr>
<tr>
<td>$\left[\text{Ru(bipy)}_3\text{ClO}_4\right]_2\text{H}_2\text{O}$</td>
<td>Red</td>
<td>230</td>
<td>C: 45.9(45.8) H: 3.2(3.3) N: 10.6(10.7)</td>
</tr>
</tbody>
</table>

Table VII.1 continued
Table VII.1 continued

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>$\Lambda_M$ in $\Omega$ cm$^{-1}$</th>
<th>$\Lambda_M$ in CH$_3$CN</th>
<th>Analytical data$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\text{Ru(bipy)}_3\right]^+\left(\text{BPh}<em>4\right)</em>{2}\text{H}_2\text{O}$</td>
<td>Orange</td>
<td>220</td>
<td>76.0 (76.3)</td>
<td>5.6 (5.5)</td>
</tr>
<tr>
<td>$\left[\text{Ru(phen)}_3\right]^+\left(\text{ClO}<em>4\right)</em>{2}\cdot\text{2H}_2\text{O}$</td>
<td>Brown</td>
<td>210</td>
<td>46.2 (46.4)</td>
<td>3.0 (3.0)</td>
</tr>
<tr>
<td>$\left[\text{Ru(phen)}_3\right]^+\left(\text{BPh}<em>4\right)</em>{2}\cdot\text{6H}_2\text{O}$</td>
<td>Yellow orange</td>
<td>220</td>
<td>72.3 (72.6)</td>
<td>5.1 (5.4)</td>
</tr>
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</table>

$^a$: Calculated values are in parentheses
Table VII.2 Electronic Absorption Spectral Data of the Complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\lambda_{\text{max}}$ nm ( $\epsilon$ ) in CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{[Ru(bipy)$_2$Cl$_2$Cl].2H$_2$O}$</td>
<td>420sh; 380 (6.3 x 10$^3$); 310sh 295 (2.4 x 10$^4$)</td>
</tr>
<tr>
<td>2. $\text{[Ru(bipy)$_2$Cl$_2$ClO$_4$}$</td>
<td>425sh; 382 (6.5 x 10$^3$); 310sh 295 (2.7 x 10$^4$)</td>
</tr>
<tr>
<td>3. $\text{[Ru(phen)$_2$Br$_2$Br}$</td>
<td>560 (1.36 x 10$^3$); 490 (4.30 x 10$^3$); 395 (3.25 x 10$^3$); 360 (2.93 x 10$^3$); 292sh; 267 (4.2 x 10$^4$)</td>
</tr>
<tr>
<td>4. $\text{[Ru(bipy)$_3$Cl$_2$.2H$_2$O}$</td>
<td>450 (1.15 x 10$^4$); 420sh; 390sh 350sh; 288 (6.76 x 10$^4$); 254sh; 242 (2.07 x 10$^4$)</td>
</tr>
<tr>
<td>5. $\text{[Ru(bipy)$_3$ClO$_4$.2H$_2$O}$</td>
<td>450 (1.12 x 10$^4$); 430sh; 392sh; 325sh; 284 (7.5 x 10$^4$); 255sh 240sh</td>
</tr>
<tr>
<td>6. $\text{[Ru(bipy)$_3$Br$_4$.2H$_2$O}$</td>
<td>450 (1.32 x 10$^4$); 430sh; 395sh; 323sh; 286 (7.8 x 10$^4$); 255sh 240sh</td>
</tr>
<tr>
<td>7. $\text{[Ru(phen)$_3$Br$_4$.2H$_2$O}$</td>
<td>442 (1.64 x 10$^4$); 418 (1.62 x 10$^4$); 315sh; 285sh; 262 (10.2 x 10$^4$)</td>
</tr>
</tbody>
</table>
in powder form at room temperature showed only one broad signal around $g = 2.15$. However, a frozen solution EPR spectrum in chloroform at liquid nitrogen temperature (Fig. VII.1) gave two $g$ values, $g_1 = 2.62$ and $g_2 = 2.43$. If one assumes a trans structure in solution, distortion from cubic geometry is expected along the Cl - Ru - Cl axis. Hence two $g$ values are expected.

A reaction of $[\text{RuBr}_3(\text{Me}_2\text{SO})_3]$ with 1,10-phenanthroline yielded a brown compound of the composition, $[\text{Ru}(\text{phen})_2\text{Br}_2]$. Reactions of $[\text{Ru}(\text{phen})_2\text{Br}_2]$ with $\text{NH}_4\text{ClO}_4$ or $\text{NaBP}_4 \text{H}_4$ in methanolic solution yielded $[\text{Ru}(\text{phen})_2\text{Br}_2\text{X}_2]$ (X = $\text{ClO}_4$, $\text{BPh}_4$). All these compounds, viz. $[\text{Ru}(\text{phen})_2\text{Br}_2\text{X}_2]$ (X = Br, $\text{ClO}_4$ or $\text{BPh}_4$) showed molar conductance value in acetonitrile in the range 100 - 110 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, confirming that these are 1:1 electrolytes. The IR spectra of these compounds showed the presence of all the bands due to 1,10-phenanthroline and absence of any $\text{Me}_2\text{SO}$ groups present. In case of complexes containing $\text{ClO}_4^-$ and $\text{BPh}_4^-$ anions, IR absorptions at 1085 and 1580 cm$^{-1}$ respectively were also observed which are characteristic of the ionic nature of the respective anionic groups.$^{21,22}$

The magnetic moment ($\mu_{\text{eff}}$) values at room temperature for $[\text{Ru}(\text{phen})_2\text{Br}_2]$ and $[\text{Ru}(\text{phen})_2\text{Br}_2\text{ClO}_4]$ were 2.2 B.M and 1.8 B.M respectively, which is characteristic of a low-spin $d^5$, ruthenium(III) complex. A room temperature EPR spectrum of $[\text{Ru}(\text{phen})_2\text{Br}_2]$ showed a broad signal at $g = 2.18$ which
Fig VII.1 EPR SPECTRUM OF FROZEN SOLUTION OF 
\([\text{Ru(bipy)}_2\text{Cl}_2]\text{Cl}_2\text{H}_2\text{O IN CHCl}_3\) AT 77°K
further confirms the low-spin d$^5$ configuration for this complex. The electronic spectrum of the complex (Fig VII.2) in CH$_3$CN showed absorption at 560, 490, 395 and 360 nm in the visible region. These absorptions having $\epsilon$ of the order of $10^3$ are mostly of the charge transfer type. These bands may be assigned to the charge-transfer from Br$^-$ to the empty orbital on the metal viz. ($e_g^*$). Similar observations were reported for $\mathcal{L}^2\text{Ru(bipy)}_2\text{Cl}_2\mathcal{L}\cdot2\text{H}_2\text{O}$.$^5$ Electronic absorptions in the UV-region were observed at 292 and 265 nm with $\epsilon$ of the order of $10^4$. These bands may be assigned to $\Pi - \Pi^*$ type of transitions in 1,10-phenanthroline.$^5, 23$

$\mathcal{L}^2\text{Ru(bipy)}_3\text{Cl}_2$ and $\mathcal{L}^2\text{Ru(L-L)}_3\mathcal{L}^2\text{X}_2\cdot\text{nH}_2\text{O}$ ($X = \text{ClO}_4^-$, BPh$_4^-$, L-L = bipy or phen) were obtained by the reaction of fac or mer $\mathcal{L}^2\text{RuCl}_3(\text{Me}_2\text{SO})_3$ with excess of the diimines and metathesis of the chloro analogue (obtained in situ), with ClO$_4^-$ or BPh$_4^-$ respectively. $\mathcal{L}^2\text{Ru(bipy)}_3\text{Br}_2\cdot2\text{H}_2\text{O}$ was obtained by the reaction of $\mathcal{L}^2\text{RuBr}_3(\text{Me}_2\text{SO})_3$ with excess of 2,2'-bipyridyl. These complexes are diamagnetic in nature, thereby confirming that ruthenium is present in 2+ oxidation state. The reduction of ruthenium(III) in $\mathcal{L}^2\text{RuX}_3(\text{Me}_2\text{SO})_3$ ($X = \text{Cl}$ or Br) to ruthenium(II) in these compounds is achieved by the diimines, which act both as the ligand and the reducing agents, in these reactions. In fact, most of the methods of preparation of these complexes make use of the reaction of ruthenium(III) or ruthenium(IV) compounds with the diimines.$^{19} \mathcal{L}^2\text{Ru(bipy)}_3\mathcal{L}^2\text{X}_2\cdot\text{H}_2\text{O}$ ($X = \text{ClO}_4^-$,
Fig VII.2 ELECTRONIC SPECTRUM OF $\left[\text{Ru(phen)}_2\text{Br}_2\right]\text{Br}^-$ IN CH$_3$CN
or BPh₄) obtained either from fac or mer \( [\text{RuCl}_3(\text{Me}_2\text{SO})_3] \) or from \( [\text{RuBr}_3(\text{Me}_2\text{SO})_3] \) are same as evidenced from the overlapping IR and \(^1\text{H} \) NMR spectra.

The characterization of these complexes was made with the help of analytical data (Table VII.1) and various physical methods. The UV-visible spectra of these complexes were superimposable with those of the reported ones earlier\(^{23-25}\) (Table VII.2). The IR spectra of all these complexes did not show absorption bands due to Me₂SO groups. All IR absorption bands due to 2,2'-bipyridyl or 1,10-phenanthroline were present. The IR spectra of these complexes in the region 350-200 cm\(^{-1}\) showed no absorption bands, thereby confirming the absence of any covalently bonded terminal chloro groups. Presence of ionic ClO₄⁻ groups was confirmed by the appearance of a strong and broad band at 1085 cm\(^{-1}\).\(^{21}\) Presence of BPh₄⁻ groups in the complexes was confirmed by the appearance of bands at 1575 and 1480 cm\(^{-1}\).\(^{22}\)

The \(^1\text{H} \) NMR spectra of \( [\text{Ru(bipy)}_3X_2] (X = \text{Cl, ClO}_4) \) in (CD₃)₂SO showed a doublet at δ 8.9, a triplet at δ 8.2, and a quintet at δ 7.7. The signals were same as reported for \( [\text{Ru(bipy)}_3]^{2+} \) systems.\(^{26}\) The \(^1\text{H} \) NMR spectrum of the compound \( [\text{Ru(bipy)}_3(BPh}_4)_2 \cdot \text{H}_2\text{O} \) showed all the signals as mentioned above and more signals in the region δ 6.7 to δ 7.3 which could be assigned due to the phenyl protons of BPh₄⁻ groups.
The $^1$H NMR spectrum of $\text{Ru(phen)}_3\text{ClO}_4$ showed signals in the region $\delta 7.3 - 8.6$. The signals are similar to the ones reported earlier. $^{27}$
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24. R.J. Staniewicz and D.G. Hendrick, 

25. R.J. Staniewicz, R.F. Sympson and D.G. Hendrick, 