CHAPTER VI
CHAPTER VI

CATIONIC AND ANIONIC COMPLEXES OF RUTHENIUM(III):

\[
\begin{align*}
\text{Me}_4\text{N} & \quad [\text{RuCl}_4(\text{Me}_2\text{SO})_2]^+ \\
\text{Et}_4\text{N} & \quad [\text{RuBr}_4(\text{Me}_2\text{SO})_2]^+
\end{align*}
\]

Hexakis-dimethylsulphoxide ruthenium(II) cation is reported in the literature by different groups of workers,\textsuperscript{1-3} and has been characterized using various physical methods including X-ray crystallography.\textsuperscript{3} The cation is found to have three \text{Me}_2\text{SO} molecules coordinated to ruthenium(II) via the oxygen atoms and the rest three \text{Me}_2\text{SO} molecules, via the sulphur atoms to give the facial isomer of irregular octahedral geometry.\textsuperscript{3}

Synthesis of \( [\text{Ru}(\text{Me}_2\text{SO})_6]^{2+} \) has been achieved either from \( [\text{cis-RuCl}_2(\text{Me}_2\text{SO})_4]^+ \) or from \( [\text{Ru(cod)(Me}_2\text{SO})_4]^{2+} \). Similar cation of ruthenium(III), \textit{viz.} \( [\text{Ru}(\text{Me}_2\text{SO})_6]^{3+} \) has been reported by Bora and Singh.\textsuperscript{4,5} However, these are not well characterised and our attempts to repeat the preparation according to Bora and Singh were unsuccessful. The compounds reported by Bora and Singh are \( [\text{Ru(Me}_2\text{SO})_6]^{2+} \) (X = Cl, Br, or ClO\textsubscript{4}).

The synthesis reported by them make use of RuCl\textsubscript{3} or RuBr\textsubscript{3}. In this chapter, we report the synthesis and characterization of \( [\text{Ru}(\text{Me}_2\text{SO})_6]^{2+} \) (X = ClO\textsubscript{4} or BPh\textsubscript{4}) using \textit{fac} or \textit{mer}

\[
\begin{align*}
[\text{RuCl}_3(\text{Me}_2\text{SO})_3]^+ & \quad \text{or} \quad [\text{Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4]^+
\end{align*}
\]
complex cation has been characterized using various physical methods and seems to have a structure similar to that of its ruthenium(II) analogue.

The reports on the synthesis and characterization of ruthenium(II) and ruthenium(III) complex anions containing halide and \( \text{Me}_2\text{SO} \) ligands are very scarce. Such compound reported for ruthenium(II) is \( \text{[NMe}_2\text{H}_2\text{]RuCl}_3(\text{Me}_2\text{SO})_3^- \)\(^6\). X-ray crystallographic studies and other physical measurements reveal that the complex ion has a facial structure and has all S-bonded \( \text{Me}_2\text{SO} \) groups.\(^6\) The compounds reported for ruthenium(III), \textit{viz.} \( \text{M}[\text{RuCl}_4(\text{Me}_2\text{SO})_2^- \) (where \( \text{M} = \text{Na, NBu}_4 \)), are very poorly characterised \(^4\) and their syntheses are not reproducible. In this chapter, synthesis and characterization of some ruthenium(III) anions, \textit{viz.} \( \text{[RuX}_4(\text{Me}_2\text{SO})_2^- \) are described. Use of fac or \( \text{mer} \) \( \text{[RuCl}_3(\text{Me}_2\text{SO})_3^- \) or \( \text{[Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4^- \) or \( \text{[RuBr}_3(\text{Me}_2\text{SO})_3^- \) has been made to synthesize them.

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**EXPERIMENTAL**

All the solvents were freshly distilled before use. fac and \( \text{mer} \) \( \text{[RuCl}_3(\text{Me}_2\text{SO})_3^- \), \( \text{[Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4^- \) and \( \text{[RuBr}_3(\text{Me}_2\text{SO})_3^- \) were prepared as described in Chapters II and IV. Analytical data and all physical measurements were obtained as described in Chapters II and III. Analytical data, molar conductance values
and magnetic moment of the complexes are presented in Table VI.1. Important IR and electronic absorption bands are given in Table VI.2.

PREPARATIONS

(a) \[ \text{Ru(Me}_2\text{SO)}_6\text{ClO}_4\] (b) \[ \text{Ru(Me}_2\text{SO)}_6\text{BPh}_4\]

To a solution/suspension of \[ \text{Ru}_2\text{Cl}_6\text{ClO}_4\] or fac or mer \[ \text{RuCl}_3\text{ClO}_4\] (0.5g) in ethanol (30 cm\(^3\)), a solution of \text{AgClO}_4 in ethanol (10 cm\(^3\)) (molar ratio 1:4) was added. The mixture was stirred at room temperature for 10-12 h and then refluxed on a water-bath for 1 h. The solution was cooled to room temperature and centrifuged out the precipitated AgCl. To the light violet mother liquor, dimethylsulphoxide (1 cm\(^3\)) was added and stirred at room temperature for 2-3 h. The solution was concentrated on a water-bath to a small volume (~2 cm\(^3\)). It was cooled in ice and methanol was added to precipitate the violet compound. The compound was recrystallized from acetone and dried in vacuo. Yield 0.82g (~75%). It was analysed for \[ \text{Ru(Me}_2\text{SO)}_6\text{ClO}_4\].

\[ \text{Ru(} \text{Me}_2\text{SO)}_6\text{ClO}_4\] (0.2g), was dissolved in acetone (10 cm\(^3\)) and a solution of \text{NaBPh}_4 (0.25g) in acetone (10 cm\(^3\)) was added to it. The reaction mixture was stirred at room
temperature for 1 h, when the colour changed from violet to green. The green solution was concentrated at room temperature, to small volume (~2 cm$^3$). Methanol was added to precipitate the light green compound. The compound was centrifuged, washed with little acetone and dried in vacuo. It was analysed for $\text{Ru}(\text{Me}_2\text{SO})_6\text{BPh}_4$.  

(c) $\text{Me}_4\text{N} \text{RuCl}_4(\text{Me}_2\text{SO})_2$  

$\text{Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4$, or fac or mer $\text{RuCl}_3(\text{Me}_2\text{SO})_3$ (0.5 g) was dissolved in methanol (20 cm$^3$). A solution of tetramethylammonium chloride (0.2 g) in methanol (5 cm$^3$) was added to it and the reaction mixture was refluxed on a water bath for 1 h. After concentrating and cooling the solution to room temperature, orange crystals separated out. The compound was centrifuged, washed with diethyl ether and dried in vacuo. Yield 0.4 g (~75%). It was analysed for $\text{Me}_4\text{N} \text{RuCl}_4(\text{Me}_2\text{SO})_2$.  

(d) $\text{Et}_4\text{N} \text{RuBr}_4(\text{Me}_2\text{SO})_2$  

$\text{RuBr}_3(\text{Me}_2\text{SO})_3$ (0.3 g) was dissolved in methanol (20 cm$^3$) and a solution of tetraethylammonium bromide (0.15 g) in methanol (10 cm$^3$) was added to it. The reaction mixture was refluxed for 10 min, concentrated and cooled to room temperature. Violet crystals separated out which were centrifuged, washed with methanol and dried in vacuo. Yield 0.3 g (~80%). It was analysed for $\text{Et}_4\text{N} \text{RuBr}_4(\text{Me}_2\text{SO})_2$. 
RESULTS AND DISCUSSION

\[ \text{Ru}(\text{Me}_2\text{SO})_6\text{X}_3 \ (X = \text{Cl}, \text{Br} \text{ or ClO}_4) \] were reported by Bora and Singh,\(^4\) \(5\) \(\text{Ru}(\text{Me}_2\text{SO})_6\text{X}_3 \ (X = \text{Cl} \text{ or Br}) \) were synthesized by them using \(\text{RuCl}_3\cdot\text{XH}_2\text{O} \) or \(\text{RuBr}_3\cdot\text{XH}_2\text{O} \). However, our attempts to synthesize these compounds according to Bora and Singh were unsuccessful. \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_3 \) was reported by the metathesis of \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_3 \) with silver perchlorate.\(^4\)

We have synthesized \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_3 \) by the reaction of \(\text{Ru}_2\text{Cl}_6(\text{Me}_2\text{SO})_4 \) or \(\text{RuCl}_3(\text{Me}_2\text{SO})_3 \) with silver perchlorate in presence of excess dimethylsulphoxide. A metathetic reaction of \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_3 \) with NaBPh\(_4\) resulted in \(\text{Ru}(\text{Me}_2\text{SO})_6\text{BPh}_4 \).

The compositions of \(\text{Ru}(\text{Me}_2\text{SO})_6\text{X}_3 \ (X = \text{ClO}_4 \text{ or BPh}_4) \) were confirmed with the help of analytical data (Table VI,1). The molar conductance values for these complexes in acetonitrile was about 350 \(\Omega^{-1}\) cm\(^2\) mol\(^{-1}\) which is nearly the expected value for a 1:3 electrolyte.\(^7\) The IR spectra of these complexes are similar to those of the reported ruthenium(II) complexes, \(\text{viz.} \)

\[ \text{Ru}(\text{Me}_2\text{SO})_6\text{X}_2 \ (X = \text{BF}_4 \text{ or BPh}_4) \].\(^2\)\(^3\) The IR spectrum of \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_3 \) (Fig VI,1a) was superimposable with that of \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_2 \), prepared according to Evans et al.\(^1\)

The IR spectrum of the compound \(\text{Ru}(\text{Me}_2\text{SO})_6\text{Cl}_3 \), showed strong absorption at 1140, 1120 and 1090 cm\(^{-1}\) in the region 1150 - 1050 cm\(^{-1}\). These bands may be due to \(\text{SO}^+ \) of S-bonded
Table VI.1 Analytical and Physical data of some Cationic and Anionic Complexes of Ruthenium(III)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>M.P. °C</th>
<th>Analysisa(%)</th>
<th>Conductance Ω⁻¹ cm² mol⁻¹ in CH₃CN</th>
<th>M eff at RT in BM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Ru(Me₂SO)₆⁻/(ClO₄)₃</td>
<td>Violet</td>
<td>120</td>
<td>16.2 (16.2)</td>
<td>4.2 (4.2)</td>
<td>350</td>
</tr>
<tr>
<td>L-Ru(Me₂SO)₆⁻/(BPh₄)₃</td>
<td>Light green</td>
<td>170</td>
<td>65.2 (65.8)</td>
<td>6.0 (6.3)</td>
<td>340</td>
</tr>
<tr>
<td>Me₄N L-RuCl₄(Me₂SO)₂⁻</td>
<td>Orange yellow</td>
<td>260(d)</td>
<td>20.1 (20.3)</td>
<td>5.3 (5.1)</td>
<td>2.7 (2.9)</td>
</tr>
<tr>
<td>Et₄N L-RuBr₄(Me₂SO)₂⁻</td>
<td>Violet</td>
<td>205-208</td>
<td>20.8 (20.4)</td>
<td>4.9 (4.5)</td>
<td>1.8 (2.0)</td>
</tr>
</tbody>
</table>

a, Calculated values are in parentheses
b, in methanol
d, decomposes
Table VI.2 Important IR and electronic absorption bands of cationic and anionic complexes of Ruthenium(III)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>IR bands in cm$^{-1}$</th>
<th>Electronic absorption bands $\lambda_{\text{max}}$ in nm ($\epsilon$) in CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\text{Ru(Me}_2\text{SO)}_6\right]^{\text{7}(\text{ClO}_4})_3$</td>
<td>1140s, 1120s, 1090s, 925m, 480m-w, 429m-w</td>
<td>575 (320)</td>
</tr>
<tr>
<td>$\left[\text{Ru(Me}_2\text{SO)}_6\right]^{\text{7}(\text{BPh}_4})_3$</td>
<td>1570m, 1470m, 1120s, 920s, 700s, 480m-w, 430m</td>
<td>-</td>
</tr>
<tr>
<td>Me$_4$N $\left[\text{RuCl}_4\right]^{\text{7}(\text{Me}_2\text{SO})}_2$</td>
<td>1120s, 955m-w, 415m, 345s, 330s, 265m, 225m</td>
<td>475 (350)</td>
</tr>
<tr>
<td>Et$_4$N $\left[\text{RuBr}_4\right]^{\text{7}(\text{Me}_2\text{SO})}_2$</td>
<td>1080w, 1060w, 1030m-s, 997m-s, 977m-s, 290m, 235m, 208m, 195m</td>
<td>535 (1260)</td>
</tr>
<tr>
<td></td>
<td>s, strong;</td>
<td>m, medium; w, weak;</td>
</tr>
<tr>
<td></td>
<td>sh, shoulder</td>
<td></td>
</tr>
</tbody>
</table>
Fig. VI.1 INFRARED SPECTRUM OF

(a) $[\text{Ru(Me}_2\text{SO}_4](\text{ClO}_4)_3$

(b) $[\text{Ru(Me}_2\text{SO}_4](\text{BPh}_4)_3$
Me$_2$SO and due to ionic ClO$_4^-$. The IR spectrum of 
$\text{Ru(Me}_2\text{SO)}_6\text{ClO}_4\text{)}_3$ (Fig VI.1b) showed only one absorption in 
that region at 1120 cm$^{-1}$ which can unambiguously be assigned to 
$\nu$ of S-bonded Me$_2$SO groups. Thus, for $\text{Ru(Me}_2\text{SO)}_6\text{ClO}_4\text{)}_3$, 
the absorption at 1120 cm$^{-1}$ can be assigned to $\nu$ of S-bonded 
Me$_2$SO and the absorption at 1140 and 1090 cm$^{-1}$ to ionic perchlorate. 
Further one band at 925 cm$^{-1}$ of medium intensity was observed 
for $\text{Ru(Me}_2\text{SO)}_6\text{X}_3$ ($X=\text{ClO}_4$ or BPh$_4$), which could be assigned 
to $\nu$ of the O-bonded Me$_2$SO groups. The positions of IR bands 
due to $\nu$ (S-bonded) and $\nu$ (O-bonded) observed for 
$\text{Ru(Me}_2\text{SO)}_6\text{X}_3$ are same as reported for the ruthenium(II) 
analogues, viz $\text{Ru(Me}_2\text{SO)}_6\text{X}_2$ ($X=\text{BPh}_4$ or BF$_4$). In the 
far IR region, bands of weak to medium intensity were observed 
at 480 and 429 cm$^{-1}$ which may be assigned to $\nu$ Ru-O and $\nu$ Ru-S 
respectively. Besides the bands described above IR spectrum 
of $\text{Ru(Me}_2\text{SO)}_6\text{ClO}_4\text{)}_3$, showed bands at 1570, 1470, and 700 cm$^{-1}$ 
also, which are characteristic of the presence of BPh$_4^-$ anion. An X-ray crystal study of BF$_4^-$ salt of $\text{Ru(Me}_2\text{SO)}_6^{2+}$ revealed 
that the ruthenium(II) was coordinated to three Me$_2$SO molecules, 
via the oxygen atom and to the rest three Me$_2$SO molecules, via 
the sulphur atom, to give the facial isomer having C$_{3v}$ symmetry.
As the IR spectrum of $\text{Ru(Me}_2\text{SO)}_6^{3+}$ is superimposable to that 
of $\text{Ru(Me}_2\text{SO)}_6^{2+}$, we also propose a structure for the 
ruthenium(III) cationic complex, same as for the ruthenium(II) 
cationic complex. EPR spectral observation (discussed later) also 
support the same.
The magnetic moment value observed at room temperature for 
\[ \text{LRu(Me}_2\text{SO)}_6\text{ClO}_4)_3 \] was 1.9 B.M., characteristic of a low-spin 
d^5, ruthenium(III) system. The EPR spectrum of 
\[ \text{LRu(Me}_2\text{SO)}_6\text{ClO}_4)_3 \] in powder form at room temperature, (Fig VI.2) showed two signals 
at g = 2.31 and 1.88. If one presumes, three S-bonded Me_2SO and 
three O-bonded Me_2SO groups bonded to the metal to give a facial 
isomer (vide supra) a C_{3v} symmetry is expected. For such 
ruthenium(III) compounds having facial geometry, generally a two 
line spectrum is observed.\textsuperscript{11,12} The electronic absorption spectrum 
of 
\[ \text{LRu(Me}_2\text{SO)}_6\text{ClO}_4)_3 \] in acetonitrile in the visible region 
showed a broad band at 575 nm having molar extinction coefficient 
(\( \epsilon \)), 320. Absorption in ruthenium(III) system with \( \epsilon = 10^2 \) could 
normally be assigned due to spin allowed d-d transition.\textsuperscript{13} Thus 
575 nm band may be assigned to one of the d-d transition, \textit{viz}.
\[ 2T_2 \rightarrow \frac{2}{3}A_2, \frac{2}{3}T_1 \text{ or } 2T_2. \] Thus, with the help of the above 
studies, a facial structure with three S-bonded and three 
O-bonded Me_2SO groups, for 
\[ \text{LRu(Me}_2\text{SO)}_6\text{Cl}_3^3 \] is proposed.

The complex ion 
\[ \text{LRuCl}_4\text{(Me}_2\text{SO)}_2^- \] was reported by Bora 
and Singh from 
\[ \text{LRu(Me}_2\text{SO)}_6\text{Cl}_3 \text{.} \] As described earlier, synthesis 
of 
\[ \text{LRu(Me}_2\text{SO)}_6\text{Cl}_3 \] according to Bora and Singh was not reproducible, hence the synthesis of 
\[ \text{LRuCl}_4\text{(Me}_2\text{SO)}_2^- \] could not be 
reproduced. We have achieved the synthesis of \( \text{Me}_4\text{N } \text{LRuCl}_4\text{(Me}_2\text{SO)}_2^- \), 
using \[ \text{LRuCl}_3\text{(Me}_2\text{SO)}_3^- \text{, fac or mer } \text{LRuCl}_3\text{(Me}_2\text{SO)}_3^- \]. 
\( \text{Et}_4\text{N } \text{LRuCl}_3\text{(Me}_2\text{SO)}_3^- \) has been synthesized using 
\[ \text{LRuBr}_3\text{(Me}_2\text{SO)}_3^- \].
Fig. VI.2 E P R SPECTRUM OF \([\text{Ru}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3\) AT R T.
The compositions of $\text{Me}_4\text{N} \left[ \text{RuCl}_4 (\text{Me}_2\text{SO})_2 \right]^-$ and $\text{Et}_4\text{N} \left[ \text{RuBr}_4 (\text{Me}_2\text{SO})_2 \right]^-$ were confirmed with the help of analytical data (Table VI.1). The molar conductance values for the compounds in acetonitrile were about 120 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ which is characteristic of their 1:1 electrolytic behaviour.

The IR spectra of $\text{Me}_4\text{N} \left[ \text{RuCl}_4 (\text{Me}_2\text{SO})_2 \right]^-$ (Fig VI.3) obtained from $\left[ \text{Ru}_2\text{Cl}_6 (\text{Me}_2\text{SO})_4 \right]^-$ or fac or mer $\left[ \text{RuCl}_3 (\text{Me}_2\text{SO})_3 \right]^-$ were superimposable, which means the mode of coordination of Me$_2$SO to ruthenium in $\left[ \text{RuCl}_4 (\text{Me}_2\text{SO})_2 \right]^-$ is independent of the starting compounds (having either completely S-bonded Me$_2$SO molecules or both S and O-bonded Me$_2$SO molecules). The complex anion has only S-bonded Me$_2$SO groups, evident from the presence of a strong band at 1120 cm$^{-1}$ due to $\nu_{\text{SO}}$ (S-bonded Me$_2$SO). A band of medium to weak intensity was observed at 955 cm$^{-1}$ which is due to the presence of $\text{Me}_4\text{N}^+$ cation. The possibility of the presence of this band due to $\nu_{\text{SO}}$ of O-bonded Me$_2$SO cannot be ruled out. However, looking at its intensity (medium to weak) and comparing with that of 1120 cm$^{-1}$ band, it seems unlikely that the band is due to $\nu_{\text{SO}}$ of O-bonded Me$_2$SO. Further, an absorption at 415 cm$^{-1}$ could be assigned due to $\nu_{\text{Ru-S}}$.\textsuperscript{9,10} Four bands at 345(s), 330(s), 265(m) and 225(m)cm$^{-1}$ were observed in the region 350 - 200 cm$^{-1}$. If one presumes a
trans geometry for the complex leading to \( D_{4h} \) symmetry, according to group theory, only one absorption band due to \( \nu_{\text{Ru-Cl}} \) is expected, whereas for a \textit{cis} complex four \( \nu_{\text{Ru-Cl}} \) are expected. Thus the four absorptions in the region 350 - 200 cm\(^{-1}\) may be assigned due to \( \nu_{\text{Ru-Cl}} \) of the \textit{cis} \( \sqrt[4]{\text{RuCl}_4 (\text{Me}_2 \text{SO})_2} \)\( \sqrt[4]{-} \), similar to four \( \nu_{\text{Pt-Cl}} \) at 353, 344, 330 and 206 cm\(^{-1}\) for \( \textit{cis} \sqrt[4]{\text{PtCl}_4 (\text{NH}_3)_2} \).\(^{14} \) Hence a \textit{cis} geometry for \( \sqrt[4]{\text{RuCl}_4 (\text{Me}_2 \text{SO})_2} \)\( \sqrt[4]{-} \) is proposed.

The IR spectrum of \( \text{Et}_4 \text{N} \sqrt[4]{\text{RuBr}_4 (\text{Me}_2 \text{SO})_2} \) (Fig VI.4), showed two weak bands at 1080 and 1060 cm\(^{-1}\) and three bands of medium to strong intensity at 1030, 997 and 977 cm\(^{-1}\) in the region 1100 - 900 cm\(^{-1}\). The bands at 1080 and 1060 cm\(^{-1}\) are present in \( \text{Et}_4 \text{NBr} \). A band at 1030 cm\(^{-1}\) could be due to \( \nu_{\text{R-(CH}_3)} \) of \( \text{Me}_2 \text{SO} \). The bands at 997 and 977 cm\(^{-1}\) may be assigned due to \( \nu_{\text{SO}} \) of O-bonded \( \text{Me}_2 \text{SO} \) molecules. Thus in \( \sqrt[4]{\text{RuBr}_4 (\text{Me}_2 \text{SO})_2} \), the mode of coordination of \( \text{Me}_2 \text{SO} \) to ruthenium most probably remains O-bonded, same as that of the starting compound, \textit{viz.} \( \sqrt[4]{\text{RuBr}_3 (\text{Me}_2 \text{SO})_3} \). The spectrum in the region 350 - 180 cm\(^{-1}\) showed medium intensity bands at 290, 235, 208 and 195 cm\(^{-1}\). These bands may be assigned due to \( \nu_{\text{Ru-Br}} \). Presence of four bands due to \( \nu_{\text{Ru-Br}} \) is indicative of a \textit{cis} geometry, for \( \sqrt[4]{\text{RuBr}_4 (\text{Me}_2 \text{SO})_2} \), similar to \( \sqrt[4]{\text{RuCl}_4 (\text{Me}_2 \text{SO})_2} \) (vide supra).
The magnetic moment values, $\mu_{\text{eff}}$, for the two anionic complexes are 1.8 and 1.9 BM, thereby confirming that the complexes contain low-spin, $d^5$ ruthenium(III). The EPR spectrum of $\text{Et}_4\text{N}[\mathrm{RuBr}_4(\text{Me}_2\text{SO})_2]$ in powder form at room temperature showed a broad signal at $g = 2.17$. However, for a cis geometry of the complex (vide supra) one expects $g_x \neq g_y \neq g_z$ and hence three $g$ values are expected. The presence of one broad signal at $g = 2.17$ means that the symmetry around ruthenium(III) is close to cubic which is possible if one assumes that the O-bonded Me$_2$SO groups and the bromides have similar ligand field. Similar observations were made for $\mathrm{RuBr}_3(\text{Me}_2\text{SO})_3$ (discussed in Chapter IV).

The electronic absorption spectrum of $\mathrm{L-RuCl}_4(\text{Me}_2\text{SO})_2$ in CH$_3$CN (Fig. VI.5a) showed one band of low intensity at 475 nm ($\varepsilon = 350$) and two bands of higher intensities, viz. at 405 nm ($\varepsilon = 4520$) and at 292 nm ($\varepsilon = 1220$). The band at 475 nm may be assigned due to one of the d-d transition of the type $^2T_2 \rightarrow ^2A_2$, $^2T_1$ or $^2T_2$. Other bands may be mostly due to charge-transfer type of transitions from ligand to the metal. The electronic absorption spectrum of $\mathrm{L-RuBr}_4(\text{Me}_2\text{SO})_2$ in methanol (Fig. VI.5b) showed bands at 535 nm ($\varepsilon = 1260$), 490 nm ($\varepsilon = 1180$), 440 nm ($\varepsilon = 1880$) and a shoulder at 385 nm. Since all these bands have $\varepsilon$ values around $10^3$, these may be assigned to charge transfer type of transition from ligand to the metal as in the case of its chloro-analogue.
Fig VI.5. ELECTRONIC SPECTRA OF (a) $\text{Me}_4\text{N}[\text{RuCl}_4(\text{Me}_2\text{SO})_2]$ in CH$_3$CN
(b) $\text{Et}_4\text{N}[\text{RuBr}_4(\text{Me}_2\text{SO})_2]$ in CH$_3$OH
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