An extensive amount of work has been done on metal β-diketonate complexes\(^1\), the chemistry of which is of importance due to their applications\(^2\text{-}^8\) in diverse fields. Though mixed ligand complexes of ruthenium(III) containing β-diketones and other related ligands have been reported\(^9\text{-}^{12}\), the study of the corresponding ruthenium(III) complexes containing α,β-unsaturated-β-ketoamine appears to have been a neglected one. In view of growing interest in the mixed ligand complexes as catalysts in oxygenation and carbonylation reactions\(^13\text{-}^{15}\), we report the synthesis and characterisation of some stable ruthenium(III) mixed ligand complexes of α,β-unsaturated-β-ketoamines in this chapter. Besides, it will be interesting to study the effect of electron donating groups present in the α,β-unsaturated-β-ketoamines on the antibacterial activities of new mixed ligand complexes.

The β-ketoamine ligands that have been used in this study are of the following type.

\[
\begin{align*}
R & \quad C=O \\
H_2C & \\
\quad C=NR'' \\
R' & \\
\end{align*}
\]

where,

\[
R = -CH_3; \quad R' = -C_6H_5; \quad R'' = -C_6H_5 \text{ or } 2-CH_3C_6H_4 \text{ or } 2-OCH_3C_6H_4
\]
Experimental

Commercially available RuCl₃·3H₂O was used without further purification. All the reagents used were chemically pure or analar grade. Solvents were purified and dried according to the standard procedures. Elemental analyses were performed at I.I.Sc., Bangalore, India. Infrared spectra were recorded in KBr pellets with a Shimadzu FT-IR 8200 spectrophotometer. Electronic spectra were recorded in dichloromethane with a Hitachi Perkin-Elemer 20/200 spectrophotometer. EPR spectra of the powdered samples were recorded on a Bruker ER-200D-SRC instrument in X-band frequencies at room temperature. DPPH was used as a field marker (g = 2.0036). Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and all the potentials were referenced to saturated calomel electrode (SCE). Melting points were recorded on a Mettler FP 51 instrument and are uncorrected.

The starting complexes [RuCl₃(PPh₃)₃]₁₇, [RuCl₃(AsPh₃)₃]₁₈, [RuBr₃(AsPh₃)₃]₁₉ and [RuBr₃(PPh₃)₂(MeOH)]²₀ and the various α,β-unsaturated-β-ketoamines²¹,²² were prepared according to the methods reported in the literature.

Preparation of the complexes

(i) Preparation of complexes of the type [RuCl₂(LL')(PPh₃)₂]

(where, LL' = α,β-unsaturated-β-ketoaminate)

To a solution of [RuCl₃(PPh₃)₂] (0.099 g; 0.1mmol) in benzene (25 cm³), the appropriate β-ketoamine (0.024-0.027 g; 0.1 mmol) was added (molar ratio of ruthenium complex : β-ketoamine = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to about 3 cm³ and the product was
separated by the addition of small quantity of petroleum ether (60-80°C). It was washed with ethanol and petroleum ether (60-80°C), recrystallised from CH₂Cl₂ / petroleum ether and dried under vacua. The purity of the complex was checked by t.l.c.

Yield : 67 – 77%

(ii) Preparation of complexes of the type [RuCl₂(LL')(AsPh₃)₂]
  (where, LL' = α,β-unsaturated-β-ketoaminate)

To a solution of [RuCl₃(AsPh₃)₃] (0.113 g; 0.1 mmol) in benzene (25 cm³), the appropriate β-ketoamine (0.021-0.023 g; 0.1 mmol) was added (molar ratio of ruthenium complex : β-ketoamine = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to about 3 cm³ and the product was separated by the addition of small quantity of petroleum ether (60-80°C). It was washed with ethanol and petroleum ether (60-80°C), recrystallised from CH₂Cl₂ / petroleum ether and dried under vacua. The purity of the complex was checked by t.l.c.

Yield : 65 – 70%

(iii) Preparation of complexes of the type [RuBr₂(LL')(AsPh₃)₂]
  (where, LL' = α,β-unsaturated-β-ketoaminate)

To a solution of [RuBr₃(AsPh₃)₃] (0.126 g; 0.1 mmol) in benzene (25 cm³), the appropriate β-ketoamine (0.019-0.020 g; 0.1 mmol) was added (molar ratio of ruthenium complex : β-ketoamine = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to about 3 cm³ and the product was separated by the addition of small quantity of petroleum ether (60-80°C). It was
washed with ethanol and petroleum ether (60-80°C), recrystallised from CH₂Cl₂ / petroleum ether and dried under vacua. The purity of the complex was checked by t.l.c.

Yield: 68 - 72%

(iv) Preparation of complexes of the type [RuBr₂(LL')(PPh₃)₂]

(where, LL' = α,β-unsaturated-β-ketoaminate)

To a solution of [RuBr₃(PPh₃)₂(MeOH)] (0.090 g; 0.1 mmol) in benzene (25 cm³), the appropriate β-ketoamine (0.026-0.028 g; 0.1 mmol) was added (molar ratio of ruthenium complex : β-ketoamine = 1:1). The mixture was heated under reflux for 5 h. The resulting solution was concentrated to about 3 cm³ and the product was separated by the addition of small quantity of petroleum ether (60-80°C). It was washed with ethanol and petroleum ether (60-80°C), recrystallised from CH₂Cl₂ / petroleum ether and dried under vacua. The purity of the complex was checked by t.l.c.

Yield: 70 - 77%

Results and Discussion

All the new complexes have been obtained from the reactions of [RuX₃(EPh₃)₃] (where, X = Cl, E = P; X = Cl or Br, E = As) or [RuBr₃(PPh₃)₂(MeOH)] with various β-ketoamines. Analytical data (Table VI.1) are in good agreement with the general molecular formula and all the complexes are highly coloured and are quite stable in air and light.
Table VI.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>[RuCl₂(bzacani)(PPh₃)₂]</td>
<td>Brown</td>
<td>120</td>
<td>66.87(66.93)</td>
</tr>
<tr>
<td>[RuCl₂(bzacani)(AsPh₃)₂]</td>
<td>Brown</td>
<td>117</td>
<td>61.20(61.16)</td>
</tr>
<tr>
<td>[RuBr₂(bzacani)(AsPh₃)₂]</td>
<td>Black</td>
<td>122</td>
<td>56.30(56.35)</td>
</tr>
<tr>
<td>[RuBr₁₂(bzacani)(PPh₃)₂]</td>
<td>Black</td>
<td>119</td>
<td>61.30(61.21)</td>
</tr>
<tr>
<td>[RuCl₂(bzac-o-tol)(PPh₃)₂]</td>
<td>Black</td>
<td>109</td>
<td>67.29(67.20)</td>
</tr>
<tr>
<td>[RuCl₂(bzac-o-tol)(AsPh₃)₂]</td>
<td>Black</td>
<td>111</td>
<td>61.75(61.50)</td>
</tr>
<tr>
<td>[RuBr₂(bzac-o-tol)(AsPh₃)₂]</td>
<td>Brown</td>
<td>113</td>
<td>53.80(53.84)</td>
</tr>
<tr>
<td>[RuBr₂(bzac-o-tol)(PPh₃)₂]</td>
<td>black</td>
<td>107</td>
<td>61.50(61.54)</td>
</tr>
<tr>
<td>[RuCl₂(bzac-o-anz)(PPh₃)₂]</td>
<td>brown</td>
<td>114</td>
<td>66.15(66.09)</td>
</tr>
<tr>
<td>[RuCl₂(bzac-o-anz)(AsPh₃)₂]</td>
<td>brown</td>
<td>131</td>
<td>60.70(60.56)</td>
</tr>
<tr>
<td>[RuBr₂(bzac-o-anz)(AsPh₃)₂]</td>
<td>brown</td>
<td>136</td>
<td>56.00(55.92)</td>
</tr>
<tr>
<td>[RuBr₂(bzac-o-anz)(PPh₃)₂]</td>
<td>brown</td>
<td>127</td>
<td>59.50(59.47)</td>
</tr>
</tbody>
</table>
Where,

\[ X = \text{Cl or Br}; \ E = \text{P or As}; \ R = \text{-CH}_3; \ R' = \text{-C}_6\text{H}_5; \ R'' = \text{-C}_6\text{H}_5 \text{ or 2-CH}_3\text{C}_6\text{H}_4 \text{ or 2-OCH}_3\text{C}_6\text{H}_4 \]

**Infrared spectra**

The infrared spectra of free β-ketoamines were compared with those of the new complexes in order to determine the mode of coordination of the ligands. In the IR spectra of the β-ketoamines\textsuperscript{21} the \( \nu_{C=O} \) absorption was found in the region 1640-1620 cm\(^{-1}\). In the complexes, this band was shifted towards the lower region (1600-1590 cm\(^{-1}\)) indicating the coordination of the ligand through the oxygen atom\textsuperscript{22}. The bands appeared in the region 1580-1560 cm\(^{-1}\) (Table VI.2)
<table>
<thead>
<tr>
<th>Complex</th>
<th>ν&lt;sub&gt;C=O&lt;/sub&gt;</th>
<th>ν&lt;sub&gt;C=O&lt;/sub&gt; + C=C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt; (bzaacami)(PPh&lt;sub&gt;3&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1570</td>
<td>1590</td>
<td>350, 360, 490</td>
<td>2&lt;sup&gt;T&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; → 2&lt;sup&gt;A&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; charge transfer</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt; (bzaacami)(AsPhP&lt;sub&gt;3&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1600</td>
<td>1590</td>
<td>350, 360, 490</td>
<td>2&lt;sup&gt;T&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; → 2&lt;sup&gt;A&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; charge transfer</td>
</tr>
<tr>
<td>[RuB&lt;sub&gt;2&lt;/sub&gt;(bzaacami)(PPh&lt;sub&gt;3&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1570</td>
<td>1570</td>
<td>360, 510, 505</td>
<td>2&lt;sup&gt;T&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; → 2&lt;sup&gt;A&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; charge transfer</td>
</tr>
<tr>
<td>[RuCl&lt;sub&gt;2&lt;/sub&gt; (bzaac-o-tol)(AsPhP&lt;sub&gt;3&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1570</td>
<td>1570</td>
<td>345, 510, 350</td>
<td>2&lt;sup&gt;T&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; → 2&lt;sup&gt;A&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; charge transfer</td>
</tr>
<tr>
<td>[RuB&lt;sub&gt;2&lt;/sub&gt;(bzaac-o-tol)(AsPhP&lt;sub&gt;3&lt;/sub&gt;)]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1570</td>
<td>1570</td>
<td>350, 360, 490</td>
<td>2&lt;sup&gt;T&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; → 2&lt;sup&gt;A&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; charge transfer</td>
</tr>
<tr>
<td>RuB&lt;sub&gt;2&lt;/sub&gt;(bzaac-o-tol)(PPh&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>1600</td>
<td>1570</td>
<td>350, 360, 490, 415, 355</td>
<td>2&lt;sup&gt;T&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; → 2&lt;sup&gt;A&lt;/sup&gt;&lt;sub&gt;2g&lt;/sub&gt; charge transfer</td>
</tr>
</tbody>
</table>

contd...
<table>
<thead>
<tr>
<th>Complex</th>
<th>$2T_{2g} \rightarrow 2A_{2g}$</th>
<th>$3T_{2g} \rightarrow 2A_{2g}$</th>
<th>charge transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuBr(bzac-o-anz)(AsPh$_3$)$_2$</td>
<td>500</td>
<td>575</td>
<td>360 charge transfer</td>
</tr>
<tr>
<td>RuCl(bzac-o-anz)(AsPh$_3$)$_2$</td>
<td>360</td>
<td>350</td>
<td>360...</td>
</tr>
</tbody>
</table>
have been assigned to the mixed modes of vibration arising from $\nu_{C=N}$ and $\nu_{C=C}$ vibrations\textsuperscript{23}. This clearly indicates that the nitrogen atom of $\beta$-ketoamine is the second donor atom. The $\nu_{\text{Ru-Cl}}$ or $\nu_{\text{Ru-Br}}$ lies around 325 cm$^{-1}$ in all the complexes. All the other characteristic bands due to triphenylphosphine/arsine and $\beta$-ketoamines were also present in the expected region.

**Electronic spectra**

The ground state of ruthenium(III) 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 $t_{2g}^4 e_g^1$ configuration\textsuperscript{24}. In most of the ruthenium(III) complexes, the electronic spectra showed only charge transfer bands\textsuperscript{25}. Since in a d$^5$ system, and especially in ruthenium(III) which has relatively high oxidising properties, the charge transfer bands of the type $L_{\text{xy}} \rightarrow t_{2g}$ are prominent in the low energy region, which obscure the weaker bands due to d-d transition. It therefore, becomes difficult to assign conclusively the bands of ruthenium(III) complexes which appear in the visible region. The electronic spectra of all the $\beta$-ketoaminate complexes in dichloromethane showed two to three bands in the region 575-345 nm (Table VI.2). The bands appearing around 575-490 nm is assigned to ligand field transition $^2T_{2g} \rightarrow ^2A_{2g}$\textsuperscript{26}. Other absorptions which appear around 425-345 nm can be assigned to charge transfer bands of the type $L_{\text{xy}} \rightarrow t_{2g}$. In general, the electronic spectra of all the complexes are characteristic of an octahedral environment around ruthenium(III) ion.

**Cyclic voltammetric studies**

Cyclic voltammetric studies were carried out for some of the ruthenium(III) $\beta$-ketoaminate complexes in acetonitrile solution at a glassy-carbon working electrode. The cyclic voltammetric data are given in Table VI.3 and the representative cyclic voltammograms are displayed (Fig. VI.1). The cyclic
Table VI.3 Cyclic Voltammetric data of ruthenium(III) complexes*

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru$^{IV}$ - Ru$^{III}$</th>
<th>Ru$^{III}$ - Ru$^{II}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pc}$(V)</td>
<td>$E_{pa}$(V)</td>
</tr>
<tr>
<td>$[\text{RuCl}_2(\text{bzacani})(\text{PPh}_3)_2]$</td>
<td>0.71</td>
<td>0.62</td>
</tr>
<tr>
<td>$[\text{RuCl}_2(\text{bzacani})(\text{AsPh}_3)_2]$</td>
<td>0.66</td>
<td>0.60</td>
</tr>
<tr>
<td>$[\text{RuBr}_2(\text{bzacani})(\text{AsPh}_3)_2]$</td>
<td>0.78</td>
<td>0.70</td>
</tr>
<tr>
<td>$[\text{RuBr}_2(\text{bzacani})(\text{PPh}_3)_2]$</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{RuCl}_2(\text{bzac-o-tol})(\text{PPh}_3)_2]$</td>
<td>0.69</td>
<td>0.61</td>
</tr>
<tr>
<td>$[\text{RuBr}_2(\text{bzac-o-tol})(\text{AsPh}_3)_2]$</td>
<td>0.78</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{RuBr}_2(\text{bzac-o-tol})(\text{PPh}_3)_2]$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{RuCl}_2(\text{bzac-o-anz})(\text{AsPh}_3)_2]$</td>
<td>0.70</td>
<td>0.62</td>
</tr>
<tr>
<td>$[\text{RuBr}_2(\text{bzac-o-anz})(\text{AsPh}_3)_2]$</td>
<td>0.78</td>
<td>0.70</td>
</tr>
<tr>
<td>$[\text{RuBr}_2(\text{bzac-o-anz})(\text{PPh}_3)_2]$</td>
<td>0.77</td>
<td>0.69</td>
</tr>
</tbody>
</table>

*supporting electrolyte: [NBu$_4$]ClO$_4$ (0.05M); concentration of the complex: 0.001M; scan rate: 100 mVs$^{-1}$; all the potentials are referenced to saturated calomel electrode; $E_f = 0.5 (E_{pa} + E_{pc})$, where, $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials respectively.
Fig. VI.1(i) Cyclic voltammogram

$[\text{RuCl}_2\text{(bzac-ani)(PPh}_3)_2]\$

$[\text{RuCl}_2\text{(bzac-ani)(AsPh}_3)_2]\$

$V_{vs\ SCE}$
Fig. VI.1 (ii) Cyclic voltammogram
Fig. VI.1 (iii) Cyclic voltammogram
Fig. VI.1 (iv) Cyclic voltammogram

\[
\left[ \text{RuCl}_2(\text{bzac-o-anz})(\text{AsPh}_3)_2 \right]
\]

\[
\left[ \text{RuBr}_2(\text{bzac-o-anz})(\text{AsPh}_3)_2 \right]
\]

V vs SCE
Fig. VI. 1(v) Cyclic voltammogram
voltammograms of the complexes showed well defined waves in the range from 0.63 V to 0.74 V (oxidation) and from -0.37 V to -0.77 V (reduction) against saturated calomel electrode. The oxidation and reduction waves are due to the metal centered Ru(III) → Ru(IV) and Ru(III) → Ru(II) processes respectively. Most of the complexes showed reversible redox couples with peak-to-peak separation values (ΔE_p) ranging from 60 to 100 mV, indicating a single step one electron transfer. The complexes namely, [RuBr₂(bzacani)(PPh₃)₂], [RuBr₂(bzac-o-tol)(AsPh₃)₂] and [RuBr₂(bzac-o-tol)(PPh₃)₂] showed only reduction potential and the complexes [RuCl₂(bzac-o-tol)(PPh₃)₂] and [RuBr₂(bzac-o-anz)(PPh₃)₂] showed only oxidation potential. The reason for the irreversibility may be due to short lived oxidation state of the metal or due to oxidative degradation of the ligand.

EPR spectra

The EPR spectra of powdered samples were recorded at X-band frequencies at room temperature. Most of the complexes exhibit only one signal with 'g' values between 2.34 -2.46 (Fig. VI.2), indicating a high symmetry around the ruthenium ion. Such isotropic lines are usually the result of either intermolecular spin exchange which can broaden the lines or occupancy of the unpaired electron in a degenerate orbital. Overall, the position of the lines and the nature of the EPR spectra are characteristic of ruthenium(III) octahedral complexes.

Antibacterial activity studies

The antibacterial activity of the ligand and their ruthenium(III) complexes have been screened against *E. coli* and *A. hydrophila* by agar well diffusion method using nutrient agar medium with an incubation period of 24 - 48h at 35°C. The test solutions were prepared in DMF. It has been
\[ \text{Fig. VI. 2(i) EPR spectra} \]
Fig. VI.2(ii) EPR spectra
Fig. VI.2 (iii) EPR spectra

$[\text{RuCl}_2(\text{bzac-o-tol})(\text{AsPh}_3)_2]$,

$[\text{RuBr}_2(\text{bzac-o-tol})(\text{PPh}_3)_2]$
Fig. VI.2(iv) EPR spectra
Fig. VI.2 (v) EPR spectra
observed from the results (Table VI.4), that the ruthenium chelates have a higher activity than their parent free ligands which could be explained by Tweedy’s chelation theory\textsuperscript{35}. According to the theory, 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. Furthermore, the mode of action of the compounds may involve the formation of hydrogen bond through the azomethine (\(>\text{C}=\text{N}\)) group with the active centres of cell constituents resulting in the interference with normal cell process\textsuperscript{36}. The complexes containing electron donating group (-OCH\(_3\)) showed more activity than the other complexes. The toxicity of the complexes increases with increase in the concentration of the test solution.

Based on the elemental analyses, spectral (IR, electronic and EPR) and electrochemical data, the following octahedral structure has been tentatively proposed for all the new ruthenium(III) complexes.

\[
\begin{align*}
\text{X} = \text{Cl or Br; } E = \text{P or As; } R'' &= -\text{C}_6\text{H}_5 \text{ or 2-CH}_3\text{C}_6\text{H}_4 \text{ or 2-OCH}_3\text{C}_6\text{H}_4
\end{align*}
\]

where,

\[
\begin{align*}
\text{X} &= \text{Cl or Br; } E = \text{P or As; } R'' = -\text{C}_6\text{H}_5 \text{ or 2-CH}_3\text{C}_6\text{H}_4 \text{ or 2-OCH}_3\text{C}_6\text{H}_4
\end{align*}
\]
Table VI.4 Antibacterial activity data of ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diameter of inhibition Zone (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1% 2% 1% 2%</td>
</tr>
<tr>
<td>(bzacani)</td>
<td>10 12 8 11</td>
</tr>
<tr>
<td>[RuCl₂(bzacani)(AsPh₃)₂]</td>
<td>13 14 15 17</td>
</tr>
<tr>
<td>[[RuBr₂(bzacani)(PPh₃)₂]</td>
<td>15 17 18 19</td>
</tr>
<tr>
<td>(bzac-o-tol)</td>
<td>12 15 16 18</td>
</tr>
<tr>
<td>[RuCl₂(bzac-o-tol)(PPh₃)₂]</td>
<td>15 18 18 20</td>
</tr>
<tr>
<td>[RuBr₂(bzac-o-tol)(PPh₃)₂]</td>
<td>17 20 22 23</td>
</tr>
<tr>
<td>(bzac-o-anz)</td>
<td>15 17 20 21</td>
</tr>
<tr>
<td>[RuCl₂(bzac-o-anz)(AsPh₃)₂]</td>
<td>18 24 23 25</td>
</tr>
<tr>
<td>[RuBr₂(bzac-o-anz)(PPh₃)₂]</td>
<td>26 28 29 32</td>
</tr>
</tbody>
</table>

1% and 2% indicate 1 gm and 2 gms of the compound in 100 cm³ of test solution.
References