Synthesis, characterization, electrochemistry, catalytic and biological activities of ruthenium(III) complexes containing dibasic tridentate Schiff bases

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The synthesis and characterisation of several ruthenium(III) Schiff base complexes of the type [RuX(L)(EPH)] (X = Cl or Br; E = P or As; L = dibasic anion of the Schiff bases derived by the condensation of thiosemicarbazide with acetoacetanilide, acetoacet-o-toluidide and o-chloro acetoacetanilide) are reported. IR, EPR, electronic spectra, electrochemistry and catalytic activity of the complexes are discussed. An octahedral structure has been tentatively assigned to all of the new complexes. The complexes have been subjected to antibacterial study.

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Mixed-ligand complexes of transition metals containing ligands with N, S and N, S, O donors are known to exhibit interesting stereochemical, electrochemical and electronic properties. Semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulfur donor ligands. Besides, thiosemicarbazones, in the last two decades, have emerged as an important class of sulfur ligands particularly for transition metal ions. The real impetus towards developing their coordination chemistry is their physicochemical properties and significant biological activities. The chemistry of ruthenium is currently receiving a lot of attention, primarily because of the fascinating electron-transfer and energy-transfer properties displayed by the complexes of this metal. 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. Moreover, tridentate Schiff base ligands have been successfully used in several catalytic asymmetric reactions.

In view of the growing interest in the biological and catalytic activities of ruthenium(III) complexes, we describe here the synthesis and characterisation of stable ruthenium(III) complexes of the type [RuX(L)(EPH)] (X = Cl or Br; L = dibasic tridentate Schiff base ligand; E = P or As).

**Materials and Methods**

All the reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to the standard procedures. RuCl₃·3H₂O was purchased from Loba Chemie and used without further purification. The analyses of carbon, hydrogen and nitrogen were performed in...
Ca rlo Eraba-1106 and Perkin-Elmer Model 240 CHN analyser at Central Drug Research Institute, Lucknow. IR spectra were recorded as KBr pellets in the 4000-5000 cm⁻¹ region using a Shimadzu FT-IR 8000 spectrophotometer. Electronic spectra were recorded in dichloromethane solution with a Hitachi Perkin-Elmer 20/200 spectrophotometer in the range 200-200 nm. EPR spectra of the powdered samples were recorded with Bruker Model ER-200-D spectrometer at X-band frequencies. Magnetic susceptibilities were recorded on EG and G-PARC vibrating sample magnetometer. Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and potentials were referenced to standard calomel electrode. Antibacterial studies were performed in the Department of Environmental Science, Bharathiar University, Coimbatore. Melting points were recorded with a Raaga heating table and are uncorrected.

The starting complexes [RuCl₃(PPh₃)₃]¹³, [RuCl₃(AsPh₃)₃]¹⁴, [RuBr₃(AsPh₃)₃]¹⁵, [RuBr₃(PPh₃)₂(MeOH)]¹⁶ and the ligands¹⁷ were prepared by reported methods. The procedure for antibacterial study was similar to that reported in our earlier paper¹⁸.

Preparation of the ruthenium(III) complexes

All the preparations were carried out under strictly anhydrous conditions. The Schiff bases (0.26-0.28 g, 0.01 mmol) were added to a solution of [RuX₃(EPh₃)₃] (0.99-1.13 g; 0.01 mmol) (E = P or As, X = Cl or Br) or [RuBr₃(PPh₃)₂(MeOH)] (0.98-1.12 g, 0.01 mmol) in 1:1 molar ratio in benzene (25 mL) and the mixture was refluxed for 6 h. The resulting dark coloured solution was concentrated to about 3 mL. The complexes were precipitated by the addition of a small quantity of petroleum ether (60-80°C). The complexes were then filtered, washed with petroleum ether and recrystallised from CH₂Cl₂/petroleum ether and dried under vacuum.

Results and Discussion

The ligands used in this work were synthesized by the condensation of thiosemicarbazide with the appropriate substituted acetooacetanilide in 1:1 molar ratio. These ligands react with [RuCl₃(PPh₃)₃], [RuCl₃(AsPh₃)₃], [RuBr₃(AsPh₃)₃] or [RuBr₃(PPh₃)₂(MeOH)] in 1:1 molar ratio to give hexa-coordinated ruthenium(III) complexes of the type [RuX₂(L)(EPh₃)₂] (X = Cl or Br; L = dibasic tridentate Schiff base ligand; E = P or As). All of the complexes are reddish brown coloured and quite stable in air and light. The analytical data given in Table 1 for the complexes are in good agreement with the formula proposed.

IR spectra of the free ligands, when compared with that of the new complexes confirm the coordination of thiosemicarbazones to the ruthenium metal. IR spectra of the free ligands display two bands around 3450 and 3300 cm⁻¹ due to νas and νsym of terminal NH₂ group.¹⁹ These bands remain unaltered in the corresponding metal complexes indicating the non-involvement of this group on complexation. The absorption due to νC=S of the free ligand appearing in the 1620 cm⁻¹ region undergoes a negative shift by 5-25 cm⁻¹ in the spectra of the complexes indicating the coordination of azomethine nitrogen to the metal.¹ The bands of strong intensities in the spectra of the ligand around 1650 cm⁻¹ are due to νC=O. In the spectra of complexes, this band is absent and a new band is observed around 1620 cm⁻¹, which can be attributed to the enolisation and subsequent coordination through the deprotonated oxygen atom of the –CH₂-C=O group.²⁰ The band due to νC=S appears around 830 cm⁻¹ in the free ligands, disappears on complexation and a new band appears around 720-750 cm⁻¹. These observations may be attributed to thioenolisation of the -NH–C=O group and subsequent coordination through the deprotonated sulphur.²¹ In addition, the other characteristic bands due to triphenylphosphine and triphenyarsine were also present in the expected regions.²² From the IR spectral data, it is inferred that the thiosemicarbazones are potentially dibasic tridentate ligands and the coordination sites are the β-nitrogen and thiolato sulphur and oxygen after deprotonation. The possibility of α-nitrogen coordination is ruled out because of considerable strain.²³

The electronic spectra of all the complexes in CH₂Cl₂ showed two bands in the region 275-207 nm (Table 1). The ground state of ruthenium(III) (t₁g⁵ configuration) is T₂g and the first excited doublet levels in the order of increasing energy are 3A₂g and 3T₁g which arise from the t₁g⁵ e² configuration. In most of the ruthenium(III) complexes, the electronic spectra show only charge transfer bands.²⁴ It has been observed that charge transfer bands of the type L²⁵ → T₂g are prominent in the low energy region, which obscure the weaker d-d transition. Hence, it becomes difficult to assign conclusively the bands of
Complexes have been measured at room temperature exchange, which may broaden the lines, or to the using an almost perfect octahedral environment around the orbitals. The nature and pattern of EPR spectra suggest an almost perfect octahedral environment around the ruthenium(III) ion in the complexes.

The magnetic moments for ruthenium(III) complexes have been measured at room temperature using a vibrating sample magnetometer and diamagnetic corrections have been applied. The values obtained were from 1.92-2.00 BM indicating the presence of one unpaired electron, suggesting a low spin $t_{2g}$ configuration for the ruthenium(III) ion in an octahedral environment in all of these complexes.

Cyclic voltammetric studies were performed for some of the complexes in acetonitrile solution at a glassy-carbon working electrode. The oxidations and reductions of some complexes are achieved by well-defined waves with $E_1$ values in the range from 0.69 to 1.50 V (oxidation) and from 0.499 to 1.1 V (reduction) against saturated calomel electrode (Table 2). The redox processes observed for these complexes are metal-centered only. Most of the complexes showed reversible couples with peak-to-peak separation values ($\Delta E_p$) ranging from 0-300 mV indicating a single step one-electron transfer process.$^{128}$

Table 1 — Analytical, spectral and catalytic data of the ruthenium(III) complexes

| Complex | M.Pt. (°C) | Yield (%) | Found (Calcld.) | $\nu_{\text{C-S}}$ (cm$^{-1}$) | $\nu_{\text{C-N}}$ (cm$^{-1}$) | $\nu_{\text{N-H}}$ (cm$^{-1}$) | $\lambda_{\text{max}}$ (nm) | $\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) | Yield (%) | Turn-over$^b$
|-----------|------------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------|-----------------
| [RuBr(AAT)(PPh$_3$)$_3$] (1) | 178 | 75 | 59.01 | 4.33 | 5.9 | 692 | 1596 | 3100 | 246.1 | 17550 | 34 | 85
| C$_2$H$_2$N$_2$O$_2$Ru$_2$P$_2$Br | (58.29) | (4.31) | (5.81) | 207 | 19026 |
| [RuBr(AAT)(PPh$_3$)$_3$] (2) | 190 | 80 | 60.05 | 4.47 | 5.83 | 692 | 1598 | 3119 | 246.1 | 17550 | 37 | 87
| C$_2$H$_2$N$_2$O$_2$Ru$_2$P$_2$Br | (59.92) | (4.51) | (5.81) | 207 | 19026 |
| [RuBr(AAT)(PPh$_3$)$_3$] (3) | 182 | 64 | 58.19 | 4.32 | 5.92 | 692 | 1591 | 3120 | 275.2 | 16427 | 41 | 95
| C$_2$H$_2$N$_2$O$_2$Ru$_2$P$_2$BrCl | (58.30) | (4.30) | (5.90) | 239 | 17800 |
| [RuCl(AAT)(PPh$_3$)$_3$] (4) | 168 | 72 | 59.08 | 4.54 | 6.21 | 692 | 1596 | 3178 | 275.2 | 16427 | 30 | 84
| C$_2$H$_2$N$_2$O$_2$Ru$_2$Cl | (59.27) | (4.53) | (6.21) | 239 | 17800 |
| [RuCl(AAT)(PPh$_3$)$_3$] (5) | 167 | 65 | 62.50 | 4.69 | 6.11 | 692 | 1596 | 3120 | 243.1 | 17557 | 32 | 80
| C$_2$H$_2$N$_2$O$_2$Ru$_2$Cl | (62.73) | (4.63) | (6.10) | 207 | 19026 |
| [RuCl(AAT)(PPh$_3$)$_3$] (6) | 169 | 76 | 60.09 | 4.42 | 5.81 | 692 | 1594 | 3120 | 243.1 | 17557 | 33 | 91
| C$_2$H$_2$N$_2$O$_2$Ru$_2$Cl | (59.32) | (4.41) | (5.79) | 207 | 19026 |
| [RuCl(AAT)(AsPh$_3$)$_3$] (7) | 172 | 74 | 57.17 | 4.14 | 5.9 | 692 | 1593 | 3127 | 246.1 | 17500 | 24 | 65
| C$_2$H$_2$N$_2$O$_2$Ru$_2$AsCl | (56.24) | (4.10) | (5.9) | 207 | 19026 |
| [RuCl(AAT)(AsPh$_3$)$_3$] (8) | 182 | 79 | 57.40 | 4.68 | 5.83 | 692 | 1597 | 3120 | 243.1 | 17557 | 30 | 84
| C$_2$H$_2$N$_2$O$_2$Ru$_2$AsCl | (52.14) | (4.72) | (5.94) | 207 | 19026 |
| [RuCl(AAT)(AsPh$_3$)$_3$] (9) | 186 | 67 | 55.60 | 4.13 | 5.85 | 692 | 1595 | 3120 | 243.1 | 17557 | 34 | 94
| C$_2$H$_2$N$_2$O$_2$Ru$_2$AsCl | (54.93) | (4.10) | (5.82) | 207 | 19026 |
| [RuBr(AAT)(AsPh$_3$)$_3$] (10) | 179 | 79 | 54.59 | 3.96 | 5.90 | 692 | 1596 | 3120 | 275.2 | 16427 | 30 | 77
| C$_2$H$_2$N$_2$O$_2$Ru$_2$AsBr | (54.97) | (3.93) | (5.89) | 246 | 17550 |
| RuBr(AAT)(AsPh$_3$)$_3$ (11) | 186 | 80 | 54.97 | 4.10 | 5.83 | 692 | 1591 | 3118 | 225.1 | 18410 | 24 | 65
| C$_2$H$_2$N$_2$O$_2$Ru$_2$AsBr | (54.90) | (4.09) | (5.82) | 207 | 19026 |
| [RuBr(AAT)(AsPh$_3$)$_3$] (12) | 190 | 82 | 54.56 | 4.11 | 5.82 | 692 | 1598 | 3117 | 227.1 | 18400 | 33 | 82
| C$_2$H$_2$N$_2$O$_2$Ru$_2$AsBrCl | (54.53) | (4.10) | (5.81) | 207 | 19026 |

$^a$ Yield of benzaldehyde based on substrate
$^b$ Moles of product per mole of catalyst
Table 2—Cyclic voltammetric data for ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ru&lt;sup&gt;V&lt;/sup&gt; - Ra&lt;sup&gt;III&lt;/sup&gt;</th>
<th>Ra&lt;sup&gt;III&lt;/sup&gt; - Ru&lt;sup&gt;II&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pa}$ (V)</td>
<td>$E_{pc}$ (V)</td>
</tr>
<tr>
<td>(3)</td>
<td>0.666</td>
<td>0.791</td>
</tr>
<tr>
<td>(4)</td>
<td>0.523</td>
<td>0.952</td>
</tr>
<tr>
<td>(6)</td>
<td>0.856</td>
<td>1.142</td>
</tr>
<tr>
<td>(9)</td>
<td>0.850</td>
<td>0.950</td>
</tr>
<tr>
<td>(10)</td>
<td>0.666</td>
<td>0.749</td>
</tr>
</tbody>
</table>

Supporting electrolyte: [NBu<sub>4</sub>][ClO<sub>4</sub>] (0.05 M); concentration of the complexes: 0.01 M; scan rate: 50 mVs<sup>-1</sup>; all the potentials are referenced to silver-silver chloride electrode [$E_r = 0.5 (E_{pa}+E_{pc})$ where, $E_{pa}$ and $E_{pc}$ are the anodic and cathodic potentials, respectively].

Table 3—Antibacterial activity of ligands and ruthenium(III) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Escherichia coli</th>
<th>Aeromonas hydrophila</th>
<th>Salmonella typhi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter of inhibition zone (mm)</td>
<td>0.25%</td>
<td>0.5%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;AAT</td>
<td></td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>(1)</td>
<td>9</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>(10)</td>
<td>10</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;ATT</td>
<td></td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>(4)</td>
<td>10</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>(7)</td>
<td>12</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;CAT</td>
<td></td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>(6)</td>
<td>13</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>(3)</td>
<td>14</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Streptomycin</td>
<td>22</td>
<td>23</td>
<td>28</td>
</tr>
</tbody>
</table>

Fig. 1—Proposed structure of the ruthenium complexes

The oxidation of benzyl alcohol was carried out with ruthenium complexes as catalyst in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant in chloroform. Benzaldehyde was formed from benzylalcohol after 3 h stirring at room temperature. The products formed were quantified as their 2,4-dinitrophenylhydrazone derivatives. In no case, there was any detectable oxidation of alcohols in the presence of N-methylmorpholine-N-oxide alone and without ruthenium complexes. All of the synthesised ruthenium complexes were found to catalyze the oxidation of alcohols to aldehyde but the yield and turnovers were found to vary with different catalysts. The yields and turnovers in the present study are comparable to those reported for the oxidation of alcohols by similar ruthenium(III) complexes<sup>29,30</sup>. It has also been found that triphenylphosphine complexes possess higher catalytic activity than the triphenylarsine complexes<sup>31</sup>. This may be due to the higher donor ability of the arsine ligand compared to the phosphine ligand.

Thus, based on the analytical, spectral (IR, electronic and EPR) and electrochemical data, the following octahedral structure (Fig. 1) has been proposed for all new ruthenium(III) complexes.

The ligands and their complexes have been tested for in vitro growth inhibitory activity against E. coli, Aeromonas hydrophila and Salmonella typhi by using the disc diffusion method<sup>44</sup>. From the results (Table 3), it is concluded that all of the complexes...
exhibit moderate activity against all species of bacteria used in this study. The complexes are more toxic than their parent ligand. The toxicity increases with increase in concentration of the test solution containing new complexes.

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References