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# Synthesis, characterization, catalytic and antimicrobial studies of ruthenium(III) complexes

**Research Article**

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**Abstract:** Ru(III) complexes of the type [RuXB(L)2] have been prepared by the reaction of 3,4-dihydropyrimidin-2(1H)-ones/thiones ($HL^1$- $HL^4$) with the precursors of the type [$RuX_3B_3$] where X=Cl or Br; B=$PPh_3$ or $AsPh_3$ and L is the deprotonated ligand. The synthesized complexes were characterized by physico-chemical methods, electrochemical and magnetic moment data. The catalytic efficiency of the complexes were examined in the oxidation of alcohols and antimicrobial studies were also carried out.

**Keywords:** *Ruthenium(III) • NMO • Antimicrobial activity • EPR • Cyclic voltammetry*



## 1. Introduction

Catalysis has played an important role in the development of the chemical industry, including new technologies and solving environmental problems. Homogeneous catalysis by metal complexes have some unique features including high activity and selectivity under milder operating conditions, which has led to major breakthroughs in the reactions of carbonylation, hydroformylation, oxidation, hydrogenation, oligomerization and metathesis [1]. Oxidation is one of the most fundamental reactions in organic synthesis. Owing to the current needs to develop forward-looking technology that is environmentally friendly with negligible formation of inorganic salts and efficient highly selective formation of products, many aspects must be considered in the search for new catalytic oxidation reactions [2]. Though many catalytic systems have been reported for the oxidation of alcohols, most of them have limitations. Chromium based oxidations are effective, but they have serious drawbacks in terms of green chemistry and environmental impact. They generate stoichiometric amounts of heavy-metal waste and Cr(VI) is a proven carcinogen [3]. Despite its usefulness as an effective oxidant, practical applications of iodosylbenzene as an oxidant are hampered by its low solubility in non-reactive media, as well as the low thermal stability and the explosive properties upon moderate heating [4]. Ionic liquids are excellent cleaner solvents, but suffer from the drawback of reduced activity due to the residual chloride ion [5] and are an ineffective oxidate of aliphatic alcohols [6]. Ruthenium and its chloro complexes, particularly in the +3 oxidation state, have evinced a great deal of interest in recent years because of their use in homogeneous catalysis [7]. Ruthenium catalyst is also known to be sufficiently selective to avoid over oxidation of aldehydes to acids and are tolerant towards many functional groups that may be present in an alcohol-containing molecule. Catalytic oxidation with molecular

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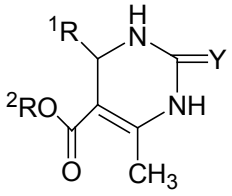
oxygen is particularly attractive from an economical and environmental point of view [8].

Over the past decade, dihydropyrimidin-2(1H)-ones and their derivatives have attracted considerable attention in organic and medicinal chemistry as the dihydropyrimidine (or Scaffold), and displays a fascinating array of pharmacological and therapeutic properties. Several alkaloids that contain the dihydropyrimidine core have been isolated from marine sources, and also exhibit interesting biological properties [9]. The dihydropyrimidinone ring system is contained within a number of pharmacologically active agents, for example, calcium channel blockers; antiviral, antitumor and anti-inflammatory drugs and they have been subject of extensive investigations [10]. The coordination chemistry of the pyrimidine thiolates is of great interest due to the versatility in their coordinated forms, the variety of bonding and their relevance to biological systems. There are two donor atoms in these types of ligands, soft donor 'S' and hard donor 'N' which enable these ligands to coordinate to both hard and soft metals [11].

In this paper, as a part of continuation of our work [12], we report the synthesis, structural characterization and electrochemical properties of a series of ruthenium(III)-3,4-dihydropyrimidin-2(1H)-one/thione complexes. In relevance to the application of the prepared complexes, we have examined the catalytic efficiency of these systems in the oxidation of alcohols in the presence of N-methylmorpholine-N-oxide (NMO)/molecular oxygen as oxidant and the inhibition activity of the complexes against the growth of the bacteria, Escherichia Coli and Bacillus Subtilis. Ligands used in this study have structure presented on Fig. 1.




| Ligand | $R^1$ | $R^2$ | Y |
|---|---|---|---|
| $HL^1$ | 4-($OCH_3$)-$C_6H_4$ | $C_2H_5$ | O |
| $HL^2$ | 4-($OCH_3$)-$C_6H_4$ | $C_2H_5$ | S |
| $HL^3$ | 4-($OCH_3$)-$C_6H_4$ | $CH_3$ | O |
| $HL^4$ | 4-($OCH_3$)-$C_6H_4$ | $CH_3$ | S |

**Figure 1.** The general structure of the ligands.

# 2. Experimental Procedures

## 2.1. Reagents, materials and instruments

All of the reagents used were of analytical reagent grade. The solvents were purified and dried according to the standard procedures [13]. $RuCl_3 \cdot 3H_2O$ was purchased from Loba chemie. The analysis of carbon, hydrogen, nitrogen, and sulphur were performed in a Vario EL III CHNS analyzer at Cochin University, Kerala, India. The IR spectra of the complexes were recorded in KBr pellets with a Perkin–Elmer 597 infrared spectrophotometer in the range of 4000–200 $cm^{-1}$. The electronic spectra were recorded in dichloromethane with a Systronics Double beam UV-Vis Spectrophotometer 2202. The $^1H$ NMR spectra were monitored on a Bruker AMX-400 NMR spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard at Indian Institute of Science, Bangalore, India. Cyclic voltammetric studies were carried out in acetonitrile using a platinum wire counter electrode and a platinum disc working electrode. All the potentials were referenced to a Ag/AgCl electrode. The molecular weights were determined by the Rast micro method. The melting points were recorded with a Raaga heating table and are uncorrected. The starting complexes $[RuCl_3(PPh_3)_3]$ [14], $[RuCl_3(AsPh_3)_3]$ [15], $[RuBr_3(AsPh_3)_3]$ [16] and the ligands [17] were prepared by the reported methods.

## 2.2. Synthesis of the new ruthenium(III) dihydropyrimidin-2(1H)-one/thione complexes

A representative procedure for the preparation of the ruthenium(III) complexes is detailed as follows. To a solution of $[RuCl_3(PPh_3)_3]$ (0.1 g; 0.1 mmol) in benzene (25 mL), 0.06 g (0.2 mmol) of $HL^1$ was added and refluxed for 5 h. The resulting solution was concentrated to ca 5 mL and the product was precipitated by the addition of petroleum ether (60-80 ºC). The precipitate was washed with petroleum ether and recrystallised from the petroleum ether-dichloromethane mixture.

## 2.3. Procedure for the catalytic oxidation of alcohols

### *2.3.1. NMO as oxidant*

To a solution of alcohol (0.07-0.13 mL, 1 mmol) and dichloromethane (20 mL), N-methylmorpholine-N-oxide (NMO) (0.35 g, 3 mmol) and the ruthenium complex (0.009 g, 0.01 mmol) were added and the solution was heated under reflux for 3 h. The mixture was then filtered and the filtrate was dried over anhydrous $Na_2SO_4$. It was then evaporated to dryness and extracted with diethyl ether. The diethyl ether extract was filtered and evaporated to yield the corresponding carbonyl compound which was then quantified as its 2,4-dinitrophenylhydrazone [13,18].

### 2.3.2. Molecular oxygen as oxidant

To a solution of alcohol (0.07 - 0.13 mL, 1 mmol) and dichloromethane (20 mL), a mixture of the ruthenium complex in dichloromethane (0.009 g, 0.01 mmol) was added and the combination was stirred under an oxygen atmosphere at ambient temperature for 6 h. The mixture was then evaporated to dryness and extracted with diethyl ether. The combined extracts were filtered and evaporated to give the corresponding carbonyl compound, which was then quantified as its 2, 4-dinitrophenylhydrazone [13,19].

## 2.4. Procedure for antibacterial activity

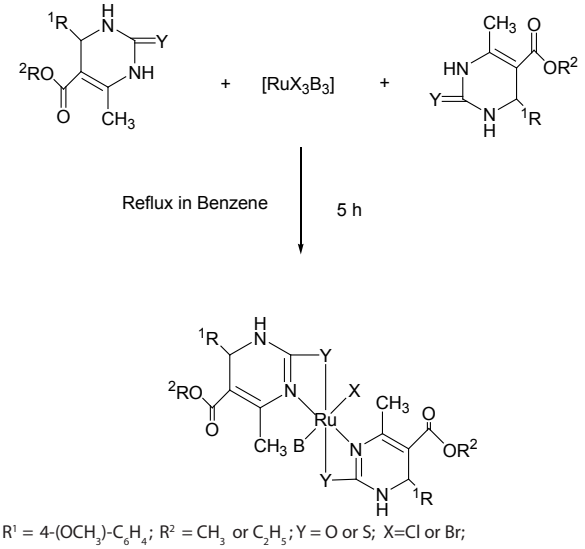
The ligands and their complexes have been tested for the in vitro growth inhibitory activity against the bacteria Escherichia Coli and Bacillus Subtilis using a disc diffusion method. The bacteria were cultured in nutrient agar medium and used as inoculum for this study. Bacterial cells were swabbed onto nutrient agar medium in Petri plates. The compounds to be tested were dissolved in DMSO at a final concentration of 0.5% (0.5 g/100 mL) and 1.0% (1.0 g/100 mL) and soaked on filter paper discs (5 mm diameter, 1 mm thick). These discs were placed on previously seeded plates and incubated at 35±2°C for 24 h. The diameter (mm) of the inhibition zone around each disc was measured after 24 h. Ampicillin was used as a standard [20].

# 3. Results and Discussion

All of the complexes are coloured solids, stable in air,light and soluble in common organic solvents such as DMSO, dichloromethane and chloroform. The microanalytical data and the molecular weights of the complexes are shown in Table 1. The results are in good agreement with the calculated values, and therefore confirms the composition of the mixed ligand complexes. The low values of the molar conductance (6.28-13.85 $ohm^{-1} cm^2 mol^{-1}$) are in agreement with their non-electrolytic nature.

## 3.1. IR spectroscopic analysis

The mode of ligand bonding to ruthenium is inferred by comparing the IR spectra of the ligands and the complexes. In the spectra of all the ligands, the bands present at 3200$cm^{-1}$ and 1400 $cm^{-1}$ are due to $\nu_{(N-H)}$ and $\delta_{(N-H)}$ vibrations, respectively [21]. The ring $\nu_{(C=O)}$ vibration of the ligands, $HL^1$ and $HL^3$ are observed at 1700 $cm^{-1}$. These bands confirm the ligands are present in keto form. In the spectra of their corresponding complexes, these bands are absent. A new band is present in the range




$R^1$ = 4-$(OCH_3)$-$C_6H_4$; $R^2$ = $CH_3$ or $C_2H_5$; Y = O or S; X=Cl or Br; B=$PPh_3$ or $AsPh_3$

**Scheme 1.** Preparation of ruthenium(III) complexes

1539-1548 $cm^{-1}$ which is due to $\nu_{(C=N)}$, which indicates the enolisation of the HN-C=O part of the ring to N=C-OH. Further, the absence of a signal around 3500 $cm^{-1}$ due to $\nu_{(O-H)}$ and presence of a signal at 545-593 $cm^{-1}$ due to $\nu_{(Ru-O)}$ [22] confirm the deprotonation and subsequent coordination through the enolic oxygen to ruthenium. Similarly, in ligands, $HL^2$ and $HL^4$, the $\nu_{(C=S)}$ vibrations are present at 1200 and 1250 $cm^{-1}$ respectively. The absence of the $\nu_{(C=S)}$ and $\nu_{(N-H)}$ vibrations in the IR spectrum of the corresponding complexes and presence of a new band around 1539-1548 $cm^{-1}$ corresponding to $\nu_{(C=N)}$, confirm the thio-enolisation. The deprotonation of the thiol group followed by coordination to ruthenium ion through thiolate sulphur is confirmed by the presence of $\nu_{(Ru-S)}$ vibrations at 440-465 $cm^{-1}$ and absence of a band around 2600 $cm^{-1}$ due to $\nu_{(S-H)}$ [23]. A new band present around 689-696 $cm^{-1}$ corresponding to (Ru-N) vibration in the spectra of all the complexes indicates that the other coordinating mode is through nitrogen [22]. The ester carbonyl group vibrations are seen around 1724-1737 $cm^{-1}$ in the ligand spectra and they show no change in the spectra of the complexes which reflects the non-involvement of the ester carbonyl group in coordination. The $\nu_{(Ru-P)}$ / $\nu_{(Ru-As)}$ vibrations display a band around 510-520 $cm^{-1}$ / 472-474 $cm^{-1}$ in the spectra of the complexes. The $\nu_{(Ru-Cl)}$ / $\nu_{(Ru-Br)}$ absorption is seen in the 310–320 $cm^{-1}$ / 245-250 $cm^{-1}$ region [24].

## 3.2. $^1$H NMR spectroscopic analysis

The $^1$H NMR spectra of the ligands confirm their structure. A triplet found at 1.08 ppm and a quartet found at 3.95 ppm of ligands, $HL^1$ and $HL^2$, were assigned to the $CH_3$ and $CH_2$ protons, respectively, of the ethoxy group. The

ligands, $HL^3$ and $HL^4$, display a singlet at 3.5 ppm for the $CH_3$ protons of the methoxy group. In the spectra of all the ligands, a singlet was found at 3.7 ppm, which was assigned to the $OCH_3$ protons of the anisaldehyde moiety. The methyl protons of the pyrimidine ring gave a singlet at 2.2 ppm [25,26]. A singlet present at 5 ppm was assigned to the proton attached to the asymmetric carbon of the pyrimidine ring. The aromatic protons of the anisaldehyde moiety gave two doublets at 6.8 and 7.2 ppm. The NH proton signals were found at 7.65 and 9.13 ppm [17].

## 3.3. Electronic spectroscopic analysis

The electronic spectra of all the complexes display several bands which were assigned to various transitions on the basis of their absorption wavelength and molar absorption coefficient. The bands which are present in the lower wavelength region are assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic ring (255 nm) and $n \rightarrow \pi^*$ transitions of the pyrimidine ring hetero atoms (296-300 nm) of the ligand moiety. In the electronic spectrum of the ligands, the bands corresponding to the $\pi \rightarrow \pi^*$ transitions occur in the same position as that of their complexes. This reflects that aromatic group is not involved in the coordination with ruthenium. There is a bathochromic shift (3-5 nm) in the position of the bands corresponding to $n \rightarrow \pi^*$ transitions. This suggests that the pyrimidine ring hetero atoms (N, O/S) are involved in coordination with ruthenium [27]. Apart from these intra ligand transitions, three other sets of bands were present in the spectra of all the complexes. The bands which are present in the wavelength range

**Table 1.** Analytical and FT-IR spectroscopic data of the complexes

| Complexes | Colour | Mol.Wt (calcd) | M.P (°C) | Yield (%) | Analytical data % found (calculated) | | | | IR ($cm^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | S | $\nu_{Ru-N}$ | $\nu_{Ru-O/Ru-S}$ | $\nu_{C=N}$ | $\nu_{Ru-P/Ru-As}$ |
| $[RuCl(PPh_3)(L^1)_2]$ | Brown | 983 (977) | 186 | 83 | 60 .02 (58.98) | 5.11 | 5.92 (5.73) | - | 690 | 574 | 1541 | 510 |
| $[RuCl(PPh_3)(L^2)_2]$ | Green | 1003 (1009) | 190 | 92 | 57.97 (57.10) | 5.04 | 5.75 (5.55) | 6.61 (6.35) | 696 | 440 | 1541 | 518 |
| $[RuCl(PPh_3)(L^3)_2]$ | Grey | 951 (949) | 198 | 80 | 60.12 (58.19) | 4.92 | 6.12 (5.90) | - | 694 | 589 | 1548 | 510 |
| $[RuCl(PPh_3)(L^4)_2]$ | Brown | 985 (981) | 190 | 90 | 56.92 (56.29) | 4.97 | 5.54 (5.71) | 6.98 (6.53) | 696 | 465 | 1541 | 520 |
| $[RuCl(AsPh_3)(L^1)_2]$ | Green | 1025 (1021) | 173 | 92 | 55.32 (56.44) | 4.98 | 5.69 (5.48) | - | 691 | 545 | 1544 | 474 |
| $[RuCl(AsPh_3)(L^2)_2]$ | Grey | 1050 (1053) | 140 | 87 | 55.67 (54.72) | 4.72 | 5.52 (5.32) | 6.33 (6.09) | 691 | 446 | 1548 | 472 |
| $[RuCl(AsPh_3)(L^3)_2]$ | Cream | 998 (993) | 180 | 75 | 56.21 (55.62) | 4.42 | 5.79 (5.64) | - | 692 | 593 | 1539 | 472 |
| $[RuCl(AsPh_3)(L^4)_2]$ | Brown | 1030 (1025) | 190 | 95 | 52.14 (53.87) | 4.44 | 5.64 (5.46) | 6.46 (6.25) | 691 | 442 | 1539 | 474 |
| $[RuBr(AsPh_3)(L^1)_2]$ | Brown | 1062 (1065) | 165 | 70 | 54.98 (54.09) | 4.71 | 5.12 (5.26) | - | 694 | 575 | 1541 | 473 |
| $[RuBr(AsPh_3)(L^2)_2]$ | Brown | 1101 (1098) | 182 | 70 | 53.67 (52.50) | 4.23 | 5.34 (5.10) | 6.01 (5.84) | 693 | 459 | 1541 | 473 |
| $[RuBr(AsPh_3)(L^3)_2]$ | Brown | 1041 (1037) | 189 | 88 | 54.83 (53.23) | 4.47 | 5. 67 (5.40) | - | 690 | 580 | 1540 | 474 |
| $[RuBr(AsPh_3)(L^4)_2]$ | Green | 1072 (1070) | 170 | 92 | 51.24 (51.64) | 4.49 | 5.51 (5.24) | 6.21 (5.99) | 689 | 459 | 1541 | 474 |

**Table 2.** Electronic spectroscopic data of the complexes

| Complex | λ max (nm) (ε; $dm^3 mol^{-1} cm^{-1}$) | Transition Energy ($cm^{-1}$) | Assignments | $v_2 / v_1$ | 10Dq | B | C |
|---|---|---|---|---|---|---|---|
| $[RuCl(PPh_3)(L^1)_2]$ | 550 (789)<br>449 (2890)<br>394 (3521) | 18181<br>22271<br>25380 | $^2T_{2g} \rightarrow {}^4T_{1g}$<br>$^2T_{2g} \rightarrow {}^4T_{2g}$<br>$^2T_{2g} \rightarrow {}^2A_{1g}, {}^2T_{1g}$ | 1.22 | 28291 | 511 | 1888 |
| $[RuCl(PPh_3)(L^2)_2]$ | 624 (438)<br>490 (1750)<br>389 (3342) | 16025<br>20391<br>25706 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.27 | 29479 | 545 | 2681 |
| $[RuCl(PPh_3)(L^3)_2]$ | 598 (593)<br>516 (2402)<br>416 (3495) | 16722<br>19379<br>24038 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.16 | 26809 | 332 | 2106 |
| $[RuCl(PPh_3)(L^4)_2]$ | 521 (631)<br>445 (2954)<br>392 (3763) | 19193<br>22471<br>25510 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.17 | 28025 | 409 | 1695 |
| $[RuCl(AsPh_3)(L^1)_2]$ | 550 (773)<br>437 (2597)<br>394 (3075) | 18181<br>22883<br>25380 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.26 | 28368 | 587 | 1811 |
| $[RuCl(AsPh_3)(L^2)_2]$ | 610 (421)<br>494 (2750)<br>387 (5961) | 16393<br>20242<br>25839 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.23 | 29469 | 481 | 2667 |
| $[RuCl(AsPh_3)(L^3)_2]$ | 522 (450)<br>437 (2956)<br>400 (3333) | 19157<br>22883<br>25000 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.19 | 27413 | 465 | 1481 |
| $[RuCl(AsPh_3)(L^4)_2]$ | 576 (620)<br>478 (2534)<br>392 (3423) | 17361<br>20920<br>25510 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.21 | 28671 | 444 | 2271 |
| $[RuBr(AsPh_3)(L^1)_2]$ | 557 (500)<br>449 (2243)<br>389 (5732) | 17953<br>22271<br>25706 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g {}^2T_2g \rightarrow {}^2A_1g,$ | 1.24 | 28831 | 539 | 2044 |
| $[RuBr(AsPh_3)(L^2)_2]$ | 526 (567)<br>456 (2544)<br>392 (3466) | 19011<br>21929<br>25510 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.15 | 28041 | 364 | 1801 |
| $[RuBr(AsPh_3)(L^3)_2]$ | 557 (422)<br>449 (2100)<br>389 (3298) | 17953<br>22271<br>25706 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.24 | 28831 | 539 | 2044 |
| $[RuBr(AsPh_3)(L^4)_2]$ | 500 (765)<br>428 (2171)<br>401 (3532) | 20000<br>23364<br>24937 | $^2T_2g \rightarrow {}^4T_1g$<br>$^2T_2g \rightarrow {}^4T_2g$<br>$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$ | 1.17 | 27004 | 420 | 1225 |

~500-600 nm (16025-20000 $cm^{-1}$) are assigned to the $^2T_{2g} \rightarrow {}^4T_{1g}$ transitions of the metal 'd' orbitals. Similarly, bands which are present in the wavelength range of ~400-500 nm (19379 -23364 $cm^{-1}$) and ~380-400 nm (24038-25839 $cm^{-1}$) are assigned to the $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2A_{1g}$, $^2T_1g$ transitions of the metal 'd' orbitals, respectively. The ligand field parameters B, C and 10 Dq were calculated (shown in Table 2) using the above d-d transition energies and standard equations [23] for ruthenium(III) ion. The values of the ligand field parameters are comparable to those reported for other trivalent ruthenium complexes. A considerable lower value for the Racah inter electronic repulsion parameter than that of the free ruthenium ion, indicates the covalent nature of the metal ligand bond [22]. Higher Dq values are usually associated with considerable electron delocalization. The results of the electronic spectra suggest an octahedral environment around the ruthenium ion [28].

## 3.4. Magnetic moment and EPR spectroscopic analysis

The effective magnetic moments of the complexes were measured at room temperature using a vibrating sample magnetometer. The values are found to be in the range of 1.72-1.92 BM which indicates the presence of one unpaired electron. The EPR spectral data of the ruthenium complexes are presented in Table 3. The room temperature (RT) EPR spectra of all the complexes display two signals indicating an axial distortion. In an axial distortion, the triply degenerate '$t_2$' level ($d_{xz}d_{yz}d_{xy}$) is split up into a doubly degenerate 'e'($d_{xz}d_{yz}$) and a non-degenerate 'a' ($d_{xy}$) component. However, presence of three signals (Fig. 2) in the spectra recorded at liquid nitrogen temperature (LNT) indicates a rhombic distortion in the complexes. In a rhombic distortion, the doubly degenerate 'e' level is further split into non-degenerate components and therefore suggests the electronic configuration is $d_{xz}{}^2d_{yz}{}^2\, d_{xy}{}^1$ [29]. The RT and LNT (EPR) spectra of all the complexes indicate no hyperfine coupling with the active nuclei through Ru, N, As, or P.

## 3.5. Cyclic voltammetric analysis

The redox behaviour of some of the complexes was studied by cyclic voltammetry. The electrochemical profiles (Table 4, Fig. 3) of the complexes display a quasi-reversible ($\Delta$Ep=100-340 mV) redox process. The complexes show a well defined wave in the range, 0.85-1.22 V ($Ru^{III}$ - $Ru^{IV}$) and 0.40 - 0.75 V( $Ru^{III}$ - $Ru^{II}$ ). The redox potentials are influenced by the nature of the ligands. Complexes with pyrimidin-one ligands (oxygen as the donor atom) were oxidized at a lower potential than the complexes with pyrimidine-thione ligands (sulphur as the donor atom). This easy oxidation of the pyrimidine-one complexes, may be attributed to the presence of more electronegative oxygen [30], makes them better catalysts for a catalytic oxidation reaction.

## 3.6. Oxidation of alcohols

The oxidation of the primary/secondary alcohols was carried out using the synthesized ruthenium complexes as the catalyst, NMO / molecular oxygen as the oxidant and the alcohols were then converted into the corresponding aldehyde/ketone. The results are shown in Table 5. The oxidation reaction in the presence of NMO may proceed through a mechanism which has been previously reported for a similar type of system [31]. The proposed mechanism, in the presence of molecular oxygen, including the oxidation of alcohol by a $Ru^{n+}$ complex to form aldehyde and $Ru^{(n-2)+}$, followed by the oxidation of $Ru^{(n-2)+}$ to $Ru^{n+}$ with $O_2$ [32]. From these results, it was found that the catalytic activity of the complexes is influenced by the electronegativities of the ligands. [$RuCl(PPh_3)(L^1)_2$] showed the highest catalytic activity. This may be due to the highly electronegative chloro ligand and the electronegative oxygen donor atom in the pyrimidin-one ligand. [$RuCl(AsPh_3)(L^1)_2$] displayed decreased activity, which may be ascribed

**Table 3.** EPR spectroscopic data of the complexes

| Complex | | $g_x$ | $g_y$ | $g_z$ | <g>* |
|---|---|---|---|---|---|
| [$RuCl(PPh_3)(L^1)_2$] | | 2.50 | 2.50 | 2.29 | 2.43 |
| [$RuCl(PPh_3)(L^2)_2$] | | 2.24 | 2.24 | 2.02 | 2.17 |
| [$RuCl(PPh_3)(L^3)_2$] | | 2.60 | 2.60 | 2.39 | 2.53 |
| [$RuCl(PPh_3)(L^4)_2$] | | 2.39 | 2.39 | 2.04 | 2.27 |
| [$RuCl(AsPh_3)(L^1)_2$] | RT | 2.42 | 2.42 | 2.19 | 2.35 |
| | LNT | 2.42 | 2.20 | 2.13 | 2.25 |
| [$RuCl(AsPh_3)(L^2)_2$] | | 2.42 | 2.42 | 2.14 | 2.33 |
| [$RuCl(AsPh_3)(L^3)_2$] | | 2.49 | 2.49 | 2.29 | 2.43 |
| [$RuCl(AsPh_3)(L^4)_2$] | | 2.20 | 2.20 | 2.03 | 2.14 |
| [$RuBr(AsPh_3)(L^1)_2$] | | 2.42 | 2.42 | 2.12 | 2.32 |
| [$RuBr(AsPh_3)(L^2)_2$] | | 2.39 | 2.39 | 2.04 | 2.27 |
| [$RuBr(AsPh_3)(L^3)_2$] | RT | 2.49 | 2.49 | 2.28 | 2.42 |
| | LNT | 2.44 | 2.21 | 2.02 | 2.23 |
| [$RuBr(AsPh_3)^4L_2$] | | 2.44 | 2.44 | 2.05 | 2.32 |

$<g^*> = [1/3\, g_x^2 + 1/3\, g_y^2 + 1/3\, g_z^2]^{1/2}$

**Table 4.** Cyclic voltammetric data[a] of Ru(III) complexes

| Complex | Ru(III)-Ru(IV) | | | | Ru(III)-Ru(II) | | | |
|---|---|---|---|---|---|---|---|---|
| | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_f$ (V) | $\Delta E_p$ (mV) | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_f$ (V) | $\Delta E_p$ (mV) |
| $[RuCl(PPh_3)(L^1)_2]$ | 0.98 | 0.76 | 0.87 | 230 | 0.52 | 0.62 | 0.57 | 100 |
| $[RuCl(AsPh_3)(L^1)_2]$ | 1.0 | 0.78 | 0.89 | 220 | 0.5 | 0.64 | 0.57 | 140 |
| $[RuBr(AsPh_3)(L^1)_2]$ | 1.1 | 0.95 | 1.03 | 150 | 0.26 | 0.6 | 0.43 | 340 |
| $[RuCl(PPh_3)(L^3)_2]$ | 0.92 | 0.78 | 0.85 | 120 | 0.35 | 0.4 | 0.75 | 100 |
| $[RuCl(AsPh_3)(L^3)_2]$ | 1.0 | 0.76 | 0.88 | 240 | 0.5 | 0.6 | 0.55 | 100 |
| $[RuCl(PPh_3)(L^2)_2]$ | 1.28 | 1.15 | 1.22 | 130 | 0.3 | 0.5 | 0.40 | 200 |

[a] *supporting electrolyte $[NBu_4]ClO_4$ (0.1 M) ; all potentials are referenced to Ag/AgCl ; $E_f = 0.5(E_{pa} + E_{pc})$; $\Delta E(p) = (E_{pa} - E_{pc})$ ; where $E_{pa}$ and $E_{pc}$ are anodic and cathodic potentials respectively ; scan rate = 100 mV $s^{-1}$*

**Table 5.** Oxidation of alcohols by ruthenium(III) complexes

| Complex | Substrate | Product | NMO oxidant | | Molecular oxygen oxidant | |
|---|---|---|---|---|---|---|
| | | | [a]Yield % | [b]TON | [a]Yield % | [b]TON |
| $[RuCl(PPh_3)(L^1)_2]$ | Benzyl alcohol | Benzaldehyde | 94 | 96 | 47 | 48 |
| | Cyclohexanol | Cyclohexanone | 88 | 90 | 50 | 52 |
| | Cinnamyl alcohol | Cinnamaldehyde | 90 | 92 | 44 | 42 |
| | n-Butanol | Butyraldehyde | 75 | 77 | 41 | 42 |
| | Isobutyl alcohol | Ethyl methyl ketone | 76 | 78 | 44 | 45 |
| | n-Propanol | Propionaldehyde | 70 | 72 | 35 | 36 |
| $[RuCl(PPh_3)(L^2)_2]$ | Benzyl alcohol | Benzaldehyde | 86 | 88 | 47 | 48 |
| | Cyclohexanol | Cyclohexanone | 82 | 84 | 48 | 50 |
| | Cinnamyl alcohol | Cinnamaldehyde | 83 | 85 | 46 | 47 |
| | n-Butanol | Butyraldehyde | 70 | 72 | 41 | 42 |
| | Isobutyl alcohol | Ethyl methyl ketone | 72 | 74 | 37 | 38 |
| | n-Propanol | Propionaldehyde | 67 | 69 | 40 | 41 |
| $[RuCl(AsPh_3)(L^1)_2]$ | Benzyl alcohol | Benzaldehyde | 92 | 90 | 44 | 45 |
| | Cyclohexanol | Cyclohexanone | 87 | 89 | 47 | 49 |
| | Cinnamyl alcohol | Cinnamaldehyde | 89 | 91 | 40 | 42 |
| | n-Butanol | Butyraldehyde | 74 | 76 | 42 | 43 |
| | Isobutyl alcohol | Ethyl methyl ketone | 74 | 76 | 35 | 37 |
| | n-Propanol | Propionaldehyde | 70 | 72 | 37 | 38 |
| $[RuBr(AsPh_3)(L^1)_2]$ | Benzyl alcohol | Benzaldehyde | 88 | 90 | 38 | 39 |
| | Cyclohexanol | Cyclohexanone | 85 | 87 | 41 | 42 |
| | Cinnamyl alcohol | Cinnamaldehyde | 86 | 88 | 35 | 37 |
| | n-Butanol | Butyraldehyde | 72 | 74 | 36 | 35 |
| | Isobutyl alcohol | Ethyl methyl ketone | 74 | 76 | 33 | 34 |
| | n-Propanol | Propionaldehyde | 69 | 71 | 39 | 41 |

[a] *Yield based on substrate ;* [b] *Moles of product per mole of catalyst; TON – turn over number*

to the presence of a triphenylarsine ligand, which is more electron donating than a triphenylphosphine ligand. A further decrease in activity was observed for the complex $[RuBr(AsPh_3)(L^1)_2]$, which can be attributed to the presence of a less electronegative bromo ligand. Among the complexes that were tested for the catalytic activity, $[RuCl(PPh_3)(L^2)_2]$, showed the lowest activity and that is due to the presence of less electronegative sulphur donor atom in the pyrimidine-thione ligand. From the above results and discussion it may be concluded that the electron withdrawing ligands increase the catalytic activity of their corresponding complexes and this is in line with the literature [33]. This can be also interrupted by saying that the electron withdrawing or

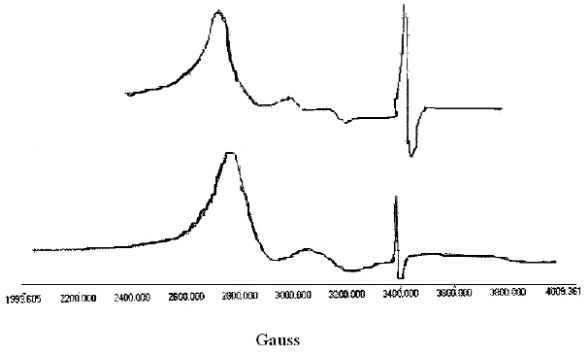



**Figure 2.** The RT and LNT epr spectrum of $[RuCl(AsPh_3)(L^1)_2]$

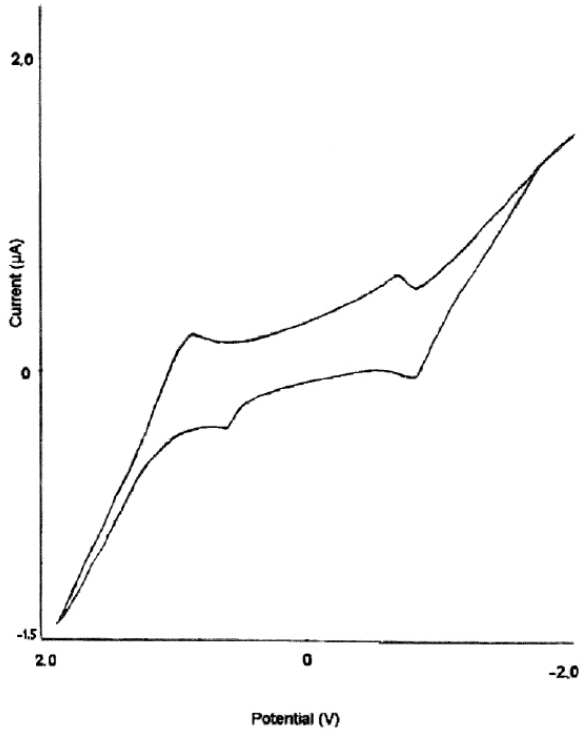



**Figure 3.** The cyclic voltammogram of $[RuCl(AsPh_3)(L^3)_2]$

electronegative ligands makes the metal centre more electron deficient thereby facilitating the formation of highvalent metal-oxo complex.

From an economical and environmental point of view, we have tested the catalytic efficiency of synthesized ruthenium(III) complexes with molecular oxygen as oxidant, but the yields and the turnover numbers were moderate when compared with NMO. This is indicated by the low product yield when molecular oxygen is employed as the oxidant which is in accordance with a previous observation [34].

**Table 6.** Antibacterial activity of ruthenium(III) complexes[a]

| Complex /Ligand | Zone of inhibition (mm) | | | |
|---|---|---|---|---|
| | Bacillus Subtilis | | Escherichia Coli | |
| | 0.5% | 1.0% | 0.5% | 1.0% |
| $HL^1$ | 11 | 15 | 10 | 15 |
| $[RuCl(PPh_3)(L^1)_2]$ | 14 | 19 | 15 | 20 |
| $[RuCl(AsPh_3)(L^1)_2]$ | 15 | 18 | 15 | 20 |
| $[RuBr(AsPh_3)(L^1)_2]$ | 14 | 20 | 16 | 21 |
| $HL^2$ | 14 | 18 | 16 | 19 |
| $[RuCl(PPh_3)(L^2)_2]$ | 20 | 23 | 20 | 23 |
| $[RuCl(AsPh_3)(L^2)_2]$ | 21 | 25 | 21 | 24 |
| $[RuBr(AsPh_3)(L^2)_2]$ | 20 | 24 | 20 | 24 |
| $HL^3$ | 12 | 16 | 12 | 14 |
| $[RuCl(PPh_3)(L^3)_2]$ | 15 | 20 | 16 | 20 |
| $[RuCl(AsPh_3)(L^3)_2]$ | 16 | 20 | 15 | 21 |
| $[RuBr(AsPh_3)(L^3)_2$ | 15 | 19 | 16 | 22 |
| $HL^4$ | 15 | 19 | 15 | 20 |
| $[RuCl(PPh_3)(L^4)_2]$ | 19 | 23 | 19 | 24 |
| $[RuCl(AsPh_3)(L^4)_2]$ | 22 | 24 | 19 | 25 |
| $[RuBr(AsPh_3)(L^4)_2)$ | 20 | 24 | 22 | 26 |
| Ampicillin | 24 | 28 | 26 | 30 |

*[a] 0.5% and 1.0% indicate 0.5 g and 1.0 g of the compound in 100 mL of the solvent*

## 3.7. Antibacterial activity

The antibacterial activities of ruthenium(III) and the standard drug, ampicillin, were screened by the disc diffusion method in DMSO at concentrations of 0.5 and 1.0% and were checked against gram positive bacteria B Subtilis and gram negative bacteria E Coli (results shown in Table 6). The results of this study are, (i) ruthenium complexes are more active in killing the bacteria than their ligands, since chelation makes the ligand a powerful bactericidal agent. (The mechanism the complexes reacts with the bacteria is likely to be that the complexes disturb the respiration process of

the cell and thus block the synthesis of proteins which restricts further growth of the organism.) (ii) the degree of inhibition increases with increasing concentration of the complexes from 0.5 to 1.0%. (Beyond that concentration, there is no change in inhibition.) (iii) the sulphur containing ligands exhibit higher inhibition than the corresponding oxygen analogues [35]. The variation in the effectiveness of the compounds against different organisms depends either on the impermeability of the cells of the microbes or the difference in ribosomes of microbial cells [36].

## 4. Conclusions

This paper describes the synthesis, characterization and application studies of Ru(III) mixed ligand complexes containing triphenylphosphine/triphenylarsine and 3,4-dihydropyrimidin-2(1H)-one/thione. The elemental analysis and molecular weight determination revealed the proposed stoichiometry of the complexes. The IR spectroscopic analysis indicates the N, O/S-bidentate coordination of the ligands by replacing the two Cl/Br and the two $PPh_3$/$AsPh_3$ ligands from the metal starting complexes. An octahedral structure has been proposed for all the complexes based on the results from electronic spectra, EPR spectra and magnetic moment studies. A remarkable catalytic efficiency of the prepared complexes were observed with NMO as the oxidant. However, the efficiency was decreased when molecular oxygen was used as the oxidant. In the case of antibacterial analysis, the results revealed that all the ruthenium(III) complexes have shown higher inhibition activity than their corresponding ligands.

In conclusion, in this study we have introduced a new and mild reagent for the oxidation of different types of alcohols in refluxing dichloromethane. The stability, easy preparation, mild reaction conditions, high yields of the products and non-aqueous reaction conditions make this pathway a useful method for the oxidation of alcohols. The scope of our catalyst system is illustrated by the highly selective oxidation of nonactivated aliphatic alcohols as well as activated benzyl alcohol and the secondary alcohols in excellent yields.

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