ANTIMICROBIAL STUDIES OF RUTHENIUM (II) SCHIFF BASE COMPLEXES

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ABSTRACT : The Schiff base ligands (H_2L^1 - H_2L^4) has been prepared by the reaction of acetoacetanilide with *o*-phenylenediamine and salicylaldehyde/ *o*-hydroxyacetophenone/ *o*-vanillin/ 2-hydroxy-1-naphthaldehyde and a series of mononuclear ruthenium(II) complexes of the type [Ru(CO)(PPh$_3$)L] has also been synthesized. The formation of the Schiff base ligands and its complexes have been envisaged from IR, UV-VIS, ^{1}H, ^{13}C, ^{31}P NMR, High resolution mass and Powder XRD studies. These spectral studies confirm an octahedral environment around the metal ion. The redox behavior of the complexes has also been determined. The ligands, metal precursors and the complexes were tested for their efficiency towards antimicrobial activity.

Keywords: Schiff base; ruthenium (II); mononuclear; redox; antimicrobial.

INTRODUCTION

Schiff base complexes of transition metals containing ligands with N_2O_2 donors are known to exhibit interesting electrochemical, electronic properties [1–4], significant antifungal[5], antibacterial, anticancer and catalytic activities [1–4]. In addition, some complexes containing nitrogen and oxygen donor atoms in the complexes are effective as stereospecific catalysts for oxidation [6], reduction [7] and hydrolysis [8] other transformations of organic and inorganic chemistry. A number of aldehydes and ketones have been found to react with *o*-phenylenediamine leading to the formation of an azomethine linkage exhibiting a broad spectrum of biological activities [9]. Hence, in this present work we have synthesized new ruthenium(II) complexes containing *o*-phenylenediamine Schiff bases efficient for the antimicrobial. The tetradentate Schiff base ligands [13] were derived by the reaction of acetoacetanilide with *o*-phenylenediamine and salicylaldehyde/ *o*-hydroxyacetophenone/*o*-vanillin/ 2-hydroxy-1-naphthaldehyde (Scheme 1).
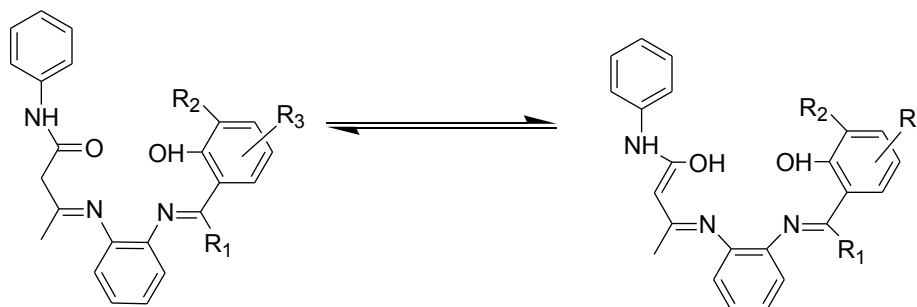
R$_1$	R$_2$	Abbreviation
H	H	H$_2$L^1
CH$_3$	*H*	*H$_2$L^2*
H	OCH$_3$	H$_2$L^3
H	H	C$_4$H$_4$

Scheme 1. keto-enol form of Schiff base ligands (H$_2$L^1 – H$_2$L^4)

EXPERIMENTAL PROCEDURE

MATERIALS

All the reagents used were of analar grade. RuCl$_3$.3H$_2$O and triphenylphosphine purchased from Loba Chemie, was used without further purification. Triphenylarsine was purchased from Sigma-Aldrich. The metal starting precursors [RuHCl(CO)(PPh$_3$)$_3$][11] were prepared according to literature methods.

Physical measurements

Melting Points

Melting points were recorded on a Veego VMP-DS melting point apparatus and are uncorrected.

Elemental analyses

The analysis of carbon, hydrogen and nitrogen were performed in Vario EL III CHNS analyzer at Cochin University, Kerala, India.

IR spectra

IR spectra were recorded as KBr pellets in the 400 - 4000 cm^{-1} region using a Perkin Elmer FT–IR 8000 spectro-photometer with a resolution of 4 cm^{-1} in transmittance mode.

UV- VIS spectra

Electronic spectra of all the ligands and their complexes were taken in dichloromethane solution in quartz cells. The concentration of the complexes ranges around 0.02 – 0.3N. The spectra were recorded on a Systronics double beam UV-vis Spectrophotometer 2202 in the range 200-800 nm at room temperature.

NMR spectra

^{1}H and ^{13}C-NMR spectra for the ligands and the complexes were recorded using Bruker 500 MHz instrument in CDCl$_3$ at room temperature in Indian Institute of Science, Bangalore. Minimum quantities of ligands were dissolved in deuterated CDCl$_3$. ^{1}H-NMR chemical shifts were referenced to tetramethylsilane (TMS) as an internal solvent standard resonance and ^{13}C-NMR chemical shifts were referenced to the internal solvent resonance. ^{31}P-NMR spectra of the complexes were obtained at room temperature using *o*-phosphoric acid as a reference. Signals are quoted in parts per million as δ downfield from internal reference.

Mass spectra

The mass spectra were recorded using Finnigan Trace DSQ Single Quadrupole MS at SITRA, Coimbatore.

Powder XRD

The powder XRD were recorded using Powder XRD were recorded using Shimadzu Model XRD6000 instrument with Cu Kα radiation (λ = 1.54060 Å) from a Cu target at Alagappa University, Karaikudi.

Cyclic voltammetry

Cyclic voltammetric studies of the complexes were carried out in dichloromethane using a glassy-carbon working electrode and potentials were referenced to standard calomel electrode at Bharathiar University, Coimbatore. Minimum quantity of the complexes was dissolved in acetonitrile and decimolar solution of TBAP was added.

Synthesis of ruthenium(II) Schiff base complexes

All the new ruthenium(II) complexes were prepared by the following general procedure given below (Scheme 2). To a solution of [RuHCl(CO)(PPh$_3$)$_3$] (0.1 mmol) in benzene (20 cm^3) the appropriate Schiff base (0.1 mmol) was added in 1:1 molar ratio and heated under reflux for about 6 hrs. The solution was then concentrated to 3 cm^3 and cooled. The complex was separated by the addition of a small amount of CH$_2$Cl$_2$/petroleum ether and dried *in vacuo*.

R_1 = H / CH$_3$; R_2 = H / OCH$_3$; R_3 = H / C$_4$H$_4$
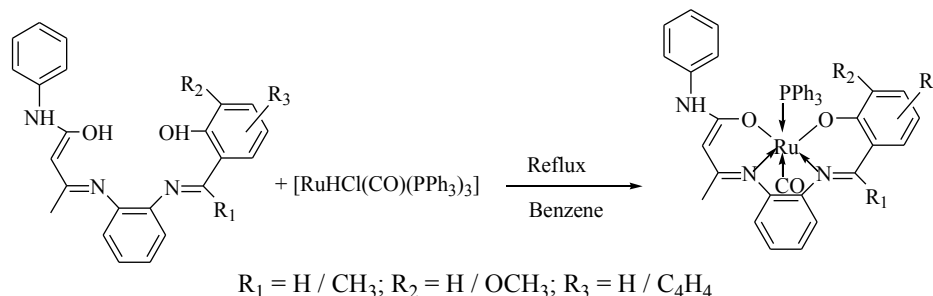
Scheme 2. Synthesis of new Ru(II) Schiff base complexes

Biocidal activity

The *in vitro* antimicrobial screenings of the solvent, free ligands, metal precursors and the new ruthenium(II) complexes were tested for their effect on certain human pathogenic bacteria and fungus by disc diffusion method. The ligands, metal precursors and their ruthenium(II) complexes were stored at room temperature and dissolved in dichloromethane. The Gram –ve (*E. coli*) bacteria were grown in Mueller Hinton agar medium and incubated at 37 ºC for 48 hrs followed by frequent subculture to fresh medium and were used as test bacteria. *C. albicans* was grown in Sabourard Dextrose Agar medium were incubated at 27 ºC for 72 hrs followed by periodic sub culturing to fresh medium and was used as test fungus. Then the petriplates were inoculated with a loop full of bacterial and fungal culture and spread throughout the petriplates uniformly with a sterile glass spreader. To each disc the test samples and reference antibiotic (ciprofloxacin/co-trimazine) were added with a sterile micropipette. The plates were then incubated at 35 ± 2 ºC for 24 hrs for bacteria and at 27 ± 1 ºC for 48 hrs for fungus, respectively. Plates with disc containing respective solvents served as control. Inhibition was recorded by measuring the diameter of the inhibitory zone after the period of incubation [12].

RESULTS AND DISCUSSION

The tetradentate Schiff bases (H_2L^1-H_2L^4) react with the metal precursors of the general formula [RuHCl(CO)(PPh$_3$)$_3$] in 1: 1 molar ratio in benzene to yield the complexes of the type [Ru(CO)(PPh$_3$)L] (Scheme 2). The new complexes were soluble in most of the common organic solvents and their purity was checked by TLC. From the TLC, we obtained a single spot which confirmed that there were no isomers in the metal complexes. This fact is further supported by the analytical data obtained for all the new complexes which agreed well with proposed molecular formulae (Table 1). We have attempted to prepare single crystals of the metal complexes in different solvents, but we could not prepare convenient single crystals of the complexes.

Table.1. Analytical data of Ru(II) Schiff base complexes

Ligands and Complexes	Colour	Melting point (°C)	Emprical formula	Molecular weight	Elemental analysis Calculated (found) (%)		
					C	H	N
H_2L^1	Orange	62	$C_{23}H_{21}N_3O_2$	371.422	74.38(74.35)	5.70(5.69)	11.31(11.28)
H_2L^2	Brown	71	$C_{24}H_{23}N_3O_2$	385.449	74.79(74.73)	6.01(6.03)	10.90(10.87)
H_2L^3	Brown	69	$C_{24}H_{23}N_3O_3$	401.439	71.81(71.80)	5.76(5.77)	10.47(10.45)
H_2L^4	Orange	64	$C_{27}H_{23}N_3O_2$	421.482	76.94(76.90)	5.50(5.49)	9.97(9.95)
[Ru(CO)(PPh$_3$)L^1]	Brown	158	$RuPC_{42}H_{34}N_3O_3$	760.760	66.31(66.30)	4.50(4.48)	5.52(5.51)
[Ru(CO)(PPh$_3$)L^2]	Brown	122	$RuPC_{43}H_{36}N_3O_3$	774.787	66.66(66.64)	4.68(4.65)	5.42(5.41)
[Ru(CO)(PPh$_3$)L^3]	Green	176	$RuPC_{43}H_{36}N_3O_4$	790.777	65.31(65.30)	4.59(4.56)	5.31(5.29)
[Ru(CO)(PPh$_3$)L^4]	Brown	161	$RuAsC_{46}H_{36}N_3O_3$	854.777	64.64(64.62)	4.25(4.26)	4.92(4.94)

FT-IR spectral analysis

The preliminary identification regarding the formation of the free Schiff base ligands and its complexes were obtained from IR spectral data (Table 2). A strong band observed around 1710 cm^{-1} in the free Schiff base ligands due to $\nu_{C=O}$ completely disappeared on complexation. This may be due to the enolisation and subsequent coordination through the deprotonated enolised oxygen atom [13,14]. The free Schiff base ligand shows a very strong absorption at 1619-1664 cm^{-1} which is characteristic of the azomethine $\nu_{C=N}$ group. In the Schiff base complexes, the absorption has been shifted to the region 1599-1612 cm^{-1} indicating the coordination of the Schiff bases through the nitrogen atom of the phenolic moiety [15]. In all the complexes, the bands in the region 1433-1530 cm^{-1} have been assigned to the mixed vibrational mode arising from $\nu_{C=N}$ and $\nu_{C=CH}$. This is indicative of coordination of the Schiff base nitrogen atom to the metal ion [16]. Another medium intensity band around 3000 cm^{-1} in the free ligands due to phenolic ν_{OH} was absent in the complexes indicating the deprotonation of the Schiff bases prior to the coordination. This fact is further supported by the increase in the absorption frequency of the phenolic ν_{C-O} from 1243-1261 cm^{-1} in the free ligands to 1262-1383 cm^{-1} in the ruthenium complexes confirming the other coordination site of Schiff base is the phenolic oxygen atom [17,18]. In all the complexes, a strong band appears in the region 1936-1954 cm^{-1} owing to the terminal carbonyl group [19]. The coordination of the azomethine nitrogen and phenolic oxygen atoms are further supported by the appearance of two bands at 414-456 cm^{-1} and 516-535 cm^{-1} due to ν_{M-N} and ν_{M-O} respectively [20,21]. Characteristic bands for triphenylphosphine were also present in the expected region 1432-1435 cm^{-1} [31]. From the IR spectral data, we inferred that the Schiff bases behave as dibasic tetradentate ligands.

Electronic spectral analysis

The electronic spectral data of the free ligands and their complexes in CH_2Cl_2 were recorded and the values are listed in Table 2. The spectra of the ligand showed two types of transitions namely π-π^* and n-π^* in the range 298-304 nm and 349-480 nm respectively for the electrons localized on the benzene ring, C=N, phenolic OH and enolic OH of the Schiff bases. The spectra of the complexes showed one to six bands in the region 254-772 nm. All the Schiff base ruthenium complexes were diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$, arising from the t^6_{2g} configuration and the excited states corresponding to the t_{2g}^5 eg^1 configuration were $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy. The electronic spectral bands in the region 772 nm were assigned as d-d transitions [22-26]. The other high intensity band in the visible region 254-484 nm was assigned as charge transfer transitions arising from the metal t_{2g} level to the unfilled π^* molecular orbital of the ligand. This pattern of the electronic spectra of all the complexes indicate the presence of an octahedral environment around the ruthenium(II) ion which is similar to other ruthenium(II) octahedral complexes [21-24].

Table.2. FT-IR, UV-vis and Electrochemical data of new Ru(II) Schiff base complexes

Ligands and Complexes	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
H_2L^1	7.0-7.7(m, ar), 3.5(s, NH), 15.0(s, enolic-OH), 2.3(s, CH), 1.2(s, CH_3), 8.6(s, HC=N), 9.9(s, Ph-OH)	119-138 (aromatic C), 70.0 (enolic C-OH), 32.2 (CH), 20.4 (CH_3), 159.2 (anilide C=N), 163.6 (phenolic HC=N)
H_2L^2	7.0-7.5(m, ar), 3.5(s, NH), 15.1(s, enolic-OH), 2.2(s, CH), 1.1(s, CH_3), 0.9(s, CH_3-C=N), 10.1(s, Ph-OH)	120-138 (aromatic C), 70.2 (enolic C-OH), 54.8 (CH), 14.9 (CH_3), 151.09 (anilide C=N), 168.59(phenolic C=N), 24.5 (CH_3)
H_2L^3	7.0-7.8(m, ar), 3.5(s, NH), 15.3(s, enolic-OH), 2.2(s, CH), 1.2(s, CH_3), 8.6(s, HC=N), 10.3(s, Ph-OH), 2.0(s, OCH_3)	119-129 (aromatic C), 65.8 (enolic C-OH), 56.3 (CH), 15.0 (CH_3), 150.08 (anilide C=N), 165.68 (phenolic HC=N), 29.82 (OCH_3)
H_2L^4	7.0-8.0(m, ar), 3.5(s, NH), 15.1(s, enolic-OH), 2.2(s, CH), 0.9(s, CH_3), 8.6(s, HC=N), 9.8(s, Ph-OH)	119-138 (aromatic C), 72.4 (enolic C-OH), 40.0 (CH), 20.2 (CH_3), 159.2 (anilide C=N), 164.6 (phenolic HC=N)
$[Ru(CO)(PPh_3)L^1]$	6.5-8.0(m, ar), 3.5(s, NH), 2.7(s, CH), 1.6(s, CH_3), 8.5(s, HC=N),	120-138 (aromatic C), 71.8 (enolic C-O), 52.3 (CH), 21.4 (CH_3), 152.3 (anilide C=N), 164.3 (phenolic HC=N), 170.3 (C=O)
$[Ru(CO)(PPh_3)L^2]$	6.9-7.7(m, ar), 3.1(s, NH), 2.1(s, CH), 1.2(s, CH_3), 0.8(s, N=C-CH_3)	119-135 (aromatic C), 70.0 (enolic C-O), 50.2 (CH), 20.0 (CH_3), 158.4 (anilide C=N), 165.8(phenolic C=N), 26.2 (CH_3), 171.2 (C=O)
$[Ru(CO)(PPh_3)L^3]$	6.8-7.7(m, ar), 3.5(s, NH), 2.2(s, CH), 1.2(s, CH_3), 8.2(s, HC=N), 1.8(s, Ph-OCH_3)	123-133 (aromatic C), 68.4 (enolic C-O), 45.0 (CH), 19.0 (CH_3), 156.3 (anilide C=N), 162.2 (phenolic HC=N), 20.5 (OCH_3), 176.1 (C=O)
$[Ru(CO)(PPh_3)L^4]$	6.9-8.2(m, ar), 3.5(s, NH), 2.2(s, CH), 0.9(s, CH_3), 8.5(s, HC=N),	109-139 (aromatic C), 76.2 (enolic C-O), 40.3 (CH), 20.4 (CH_3), 157.1 (anilide C=N), 160.5 (phenolic HC=N), 170.4 (C=O)

^{1}H, ^{13}C and ^{31}P NMR spectral analysis

The ^{1}H NMR spectra of the free Schiff base ligands and the complexes (Table 3) were recorded in $CDCl_3$ solution. In the Schiff base ligands, the aromatic protons appear as multiplet in the range 7.0-8.0 ppm. The NH, enolic OH, methine and methyl protons of the acetanilide moiety appears as singlet in the range 3.5, 15.0-15.3, 2.2-2.3 and 0.9-1.2 ppm respectively. The azomethine proton of the ligands H_2L^1, H_2L^3 and H_2L^4 appear as a singlet at 8.6 ppm. The –N=C-CH_3 protons of H_2L^2 ligand appear as singlet at 0.9 ppm. In H_2L^3 ligand, the methoxy protons appear as singlet at 2.0 ppm. The phenolic OH proton appears as singlet in the range 9.8-10.3 ppm.

Table 3. ^{1}H and ^{13}C – NMR spectral data of Ru(II) Schiff base complexes

Ligands and Complexes	IR spectra(cm^{-1})				λ_{max}(nm)	^{a}Electrochemical data (Ru^{II} - Ru^{I})				(Ru^{II}-Ru^{III})
	$\nu_{C=N}$	$\nu_{Ph\text{-}C\text{-}O}$	$\nu_{C=CH}+\nu_{C=N}$	$\nu_{C\equiv O}$		E_{pa}(V)	E_{pc}(V)	E_f(V)	ΔE_p(mV)	E_{pc}(V)
H$_2$L^1	1664	1261	-	-	299,368,395	-	-	-	-	-
H$_2$L^2	1641	1243	-	-	298,304,362,395,458	-	-	-	-	-
H$_2$L^3	1619	1255	-	-	299,349	-	-	-	-	-
H$_2$L^4	1620	1245	-	-	304,368,414,445,480	-	-	-	-	-
[Ru(CO)(PPh$_3$)L^1]	1599	1319	1433	1940	254,301,366,405	-1.432	-0.404	-0.918	1028	1.10
[Ru(CO)(PPh$_3$)L^2]	1599	1301	1434	1951	258	-1.518	-1.414	-1.466	104	0.82
[Ru(CO)(PPh$_3$)L^3]	1603	1383	1474	1936	254,297,369,409,484	-0.427	-0.161	-0.294	266	0.91
[Ru(CO)(PPh$_3$)L^4]	1601	1358	1462	1938	258,294,369,394,448,772	-0.505	-0.459	-0.482	46	0.82

^{a}Supporting electrolyte: [NBu$_4$]ClO$_4$ (0.1M); Scan rate, 0.1 mV^{-1}; reference electrode, Ag-AgCl. $\Delta E_p = E_{pa} - E_{pc}$; $E_{1/2} = 0.5 (E_{pa} + E_{pc})$, Where E_{pa} and E_{pc} are the anodic and cathodic peak potentials in Volts, respectively.

For the ruthenium(II) complexes, multiplets observed in the range 6.5-8.2 ppm have been assigned for the aromatic protons of phenyl, naphthalene, triphenylphosphine, triphenylarsine and pyridine moieties [26]. In all the complexes, the NH, methine and methyl protons of the acetanilide moiety appear as a singlet in the region 3.0-3.5, 1.2-2.7 and 0.8-1.6 ppm respectively. For the complexes of the corresponding H$_2$L^1, H$_2$L^3 and H$_2$L^4 ligands, the azomethine proton appear as singlet at 8.1-8.7 ppm. The azomethine methyl carbon of the phenolic moiety for the complex [Ru(CO)(PPh$_3$)L^2] appear as singlet at 0.8 ppm. For the complex [Ru(CO)(PPh$_3$)L^3] the methoxy carbon appear as a singlet at 1.8 ppm.

The ^{13}C NMR spectra of the ligands and the complexes (Table 3) were recorded in CDCl$_3$ solution and revealed the presence of expected number of signals corresponding to different types of carbon atoms present in the complexes. In the free ligands, the aromatic carbons appear in the range 119-138 ppm. The enolic, methine and methyl carbons of the acetanilide moiety appear at 65.8-72.4, 32.2-56.3 and 14.9-20.4 ppm respectively. The azomethine carbon of the acetanilide moiety appears at 150.08-159.2 ppm. For all the ligands, the azomethine carbon of the phenolic moiety appears at 163.6-168.6 ppm. The methyl and methoxy carbons of the phenolic moiety for the ligands H$_2$L^2 and H$_2$L^3 appears at 24.5 ppm and 29.8 ppm respectively.

For the complexes, the aromatic carbons appear at 109-139 ppm. The enolic, methine and methyl carbons of the acetanilide moiety appear at 68.4-76.2, 40.3-52.3 and 18.2-24.5 ppm respectively. The azomethine carbon of the acetanilide moiety appears at 152.3-158.4 ppm. The azomethine carbon of the phenolic moiety appears in the range 160.5-165.8 ppm. The methyl and methoxy carbon for the corresponding complexes of the ligands L^2 and L^3 appear at 26.2 and 20.5 ppm. For all the complexes, the free C≡O carbon appears in the range 170.3-176.1 ppm.

The ^{31}P NMR spectra (Figure 1) were recorded for two complexes in order to confirm the presence of PPh$_3$ group. The appearance of a singlet at 29.44 ppm for the complex [Ru(CO)(PPh$_3$)L^2] indicates the presence of one triphenylphosphine group [26].
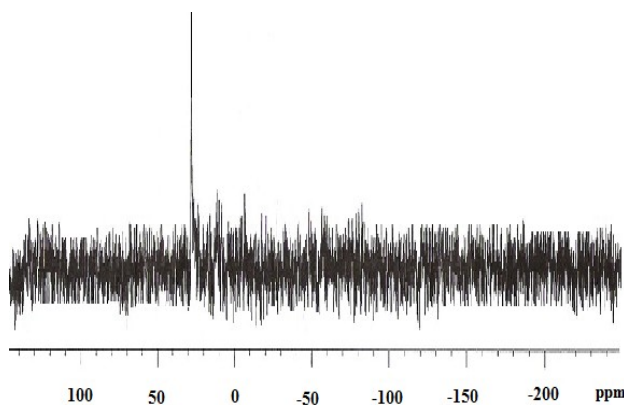
Figure 1. ^{31}P NMR spectra of the complex [Ru(CO)(PPh$_3$)L^2]

Mass spectral analysis

The high resolution mass spectra of [Ru(CO)(PPh$_3$)L^4]displayed molecular ion peak at m/z 810.8200. These molecular ion peaks are consistent with the proposed molecular formula of the corresponding ruthenium(II) Schiff base complexes [27].

Powder XRD

The XRD pattern (Figure 2) of the complexes [Ru(CO)(PPh$_3$)L^1] and [Ru(CO)(PPh$_3$)L^2] were compared with the XRD of the metal precursor [RuHCl(CO)(PPh$_3$)$_3$] [28]. The peaks for these complexes have been moved towards the right from the margin of the intensity that was obtained for the precursor. This confirms that the Schiff base ligands have been coordinated with the metal atom. The 'd' values, 2θ angles and (h k l) values are listed in the Table 4. The complex crystallizes in an orthorhombic type of lattice with dimensions as a = 1.104, b = 1.245 and c =1.201 Å. The similar (h k l) values of the complexes with the precursor indicate an octahedral geometry for the Ru(II) complexes.
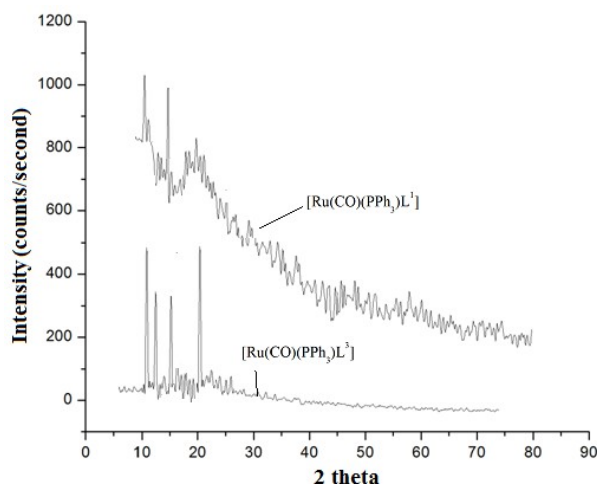

Figure 2. Powder XRD pattern of the complexes [Ru(CO)(PPh$_3$)L^1] and [Ru(CO)(PPh$_3$)L^3]

Table 4. Powder X-ray diffraction data of the complexes [Ru (CO)(PPh$_3$)L^1] and [Ru(CO)(PPh$_3$)L^3]

Complexes	2Ө	Theoritical 'd' value	Experimental 'd' value	(h k l)
[Ru(CO)(PPh$_3$)L^1]	10.701	8.2587	8.2481	(1 1 0)
	14.732	6.0068	6.0070	(2 0 0)
[Ru(CO)(PPh$_3$)L^3]	10.873	8.1280	8.1220	(1 0 1)
	12.995	6.8057	6.8053	(1 1 1)
	16.040	5.5188	5.5180	(2 0 0)
	21.506	4.1294	4.1300	(2 2 0)

Electrochemical studies

Electrochemical study were carried out for all the complexes in dichloromethane solution at a glassy carbon working electrode and the potentials were expressed with reference to Ag-AgCl (Table 2). The reduction of each complex was characterized by well defined waves with E_f values observed in the range -0.482 to -1.466 mV (reduction). The complexes [Ru(CO)(PPh$_3$)L^1], [Ru(CO)(PPh$_3$)L^2] and [Ru(CO)(PPh$_3$)L^3] showed reduction couples with peak to peak separation values (ΔE_p) ranging from 104-1028 mV revealing that this process is quasi-reversible in nature. This is attributed to slow electron transfer and adsorption of the complexes onto the electrode surface [21]. For the remaining complexes, the peak to peak separation value (ΔE_p) fell in 46 mV suggesting a reversible one-electron transfer process. The oxidation couple for the entire complex is irreversible. The reason for the irreversibility of these complexes may be due to oxidative degradation or the short-lived oxidized state of the metal ion[29].

Microbial activity

The *in vitro* antimicrobial screenings of the free ligands, metal precursors and its ruthenium (II) complexes were tested for their effect on certain human pathogenic bacteria and fungus (Table 5). The variation in the effectiveness of the different compounds against different organisms depends on their impermeability of the microbial cells or on the difference in the ribosome of the microbial cells [30]. All the complexes show better antibacterial and antifungal activity when compared to the free ligands and metal precursors.

Table 5. Antibacterial and antifungal activities of Ru (II) complexes

Ligands, Metal starting precursors and Complexes	Diameter of inhibition zone (mm)							
	Antibacterial activity (*E. coli*)				Antifungal activity (*C. albicans*)			
	0.25%	0.5%	1.0%	2.0%	0.25%	0.5%	1.0%	2.0%
[RuHCl(CO)(PPh$_3$)$_3$]	8	8	8	9	5	5	6	6
[RuHCl(CO)(Py)(PPh$_3$)$_2$]	7	8	9	9	5	7	7	7
[RuHCl(CO)(AsPh$_3$)$_3$]	5	6	6	6	4	4	5	5
H$_2$L^1	2	2	3	3	-	-	-	1
H$_2$L^2	2	3	3	4	-	-	1	3
H$_2$L^3	-	3	3	3	-	-	-	2
H$_2$L^4	1	2	2	3	-	1	2	2
[Ru(CO)(PPh$_3$)L^1]	14	14	14	15	8	9	9	9
[Ru(CO)(PPh$_3$)L^2]	12	13	15	15	12	12	13	13
[Ru(CO)(PPh$_3$)L^3]	13	14	15	15	12	13	13	14
[Ru(CO)(PPh$_3$)L^4]	13	14	14	16	11	11	12	12
	20	20	21	21	15	17	19	20
Standard	Ciprofloxacin				Co-trimazine			

The increase in the microbial activity of the metal complexes with increase in concentration is due to the effect of metal atom on normal cell process. Such increased activity of the metal complexes can be explained on the basis of overtone's concept [31] and chelation theory [32,33]. According to overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which liposolubility has an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal atom will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of metal atom with donor groups. Further, it increases the delocalization of π electrons over the whole chelate ring and enhances the liphophilicity which enhances the penetration of the complexes. This increased liphophilicity enhances the penetration of the complexes into lipid membrane and blocking the metal binding-sites on enzymes of microorganisms. These complexes may disturb the respiration process of the cell and thus block the synthesis of proteins which restrict the further growth of the organism [34]. The complexes $[Ru(CO)(Py)L^1]$ and $[Ru(CO)(Py)L^2]$ showed higher biological activity than other complexes. Among them the complex $[Ru(CO)(Py)L^2]$ showed higher activity due to the presence of electron donating methyl group in the phenyl substituent of the Schiff base ligands [35,36].

CONCLUSIONS

New diamagnetic ruthenium(II) complexes of the type $[Ru(CO)(PPh_3)(L)]$ were synthesized and characterized by elemental analysis, spectral (FT-IR, UV-VIS , ^1H, ^{13}C, ^{31}P-NMR and Mass) and cyclic voltammetric studies. Based on the analytical and spectroscopic studies, an octahedral geometry has been tentatively proposed for all the ruthenium(II) complexes (Scheme 3).

The biocidal efficiency of the complexes has also been evaluated and found that the Ru(II) Schiff base complexes show better biological activity when compared with the Schiff base ligands and the metal precursors. The complex [Ru(CO) $(PPh_3)L^2]$) showed higher biological efficiency when compared to the remaining complexes and it also reached the effectiveness of the standards *Ciprofloxacin* and *Co-trimazine*.

$$R_1 = H / CH_3; R_2 = H / OCH_3; R_3 = H / C_4H_4$$
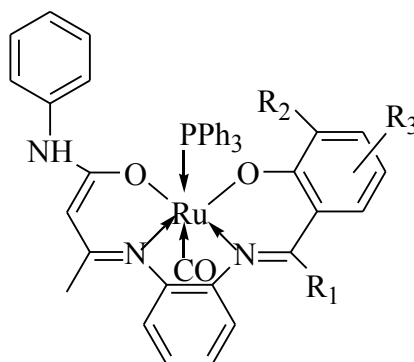
Scheme 3. General structure of Ru(II) Schiff base complexes

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