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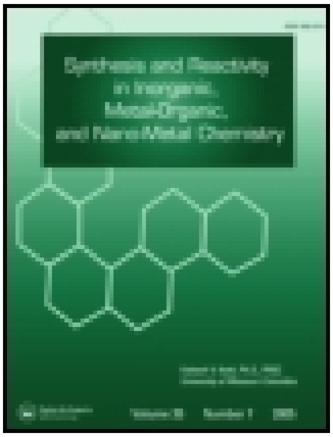

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Synthesis, Characterization, Redox, Catalytic, and Antibacterial Activities of Binuclear Ruthenium(III) Schiff Base Complexes Containing Triphenylphosphine as Co-Ligand

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Synthesis, Characterization, Redox, Catalytic, and Antibacterial Activities of Binuclear Ruthenium(III) Schiff Base Complexes Containing Triphenylphosphine as Co-Ligand

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New hexa-coordinated binuclear Ru(III) Schiff base complexes of the type $\{[(PPh_3)_2X_2Ru]_2L\}$ (where, X = Cl or Br; L = binucleating N_2O_2 Schiff bases) have been synthesized and characterized by elemental analysis, magnetic susceptibility measurement, FT-IR, UV-vis, $^{13}C\{^1H\}$-NMR, ESR, cyclic voltammetric, SEM and powder X-ray diffraction pattern. The new complexes have been used as catalyst in C—C coupling reaction and the oxidation of alcohols to their corresponding carbonyl compounds by using molecular oxygen atmosphere at ambient temperature. Further, the new Schiff base ligands and their Ru(III) complexes were also screened for their antibacterial activity against *K. pneumoniae*, *Shigella sp.*, *M. luteus*, *E. coli* and *S. typhi.* From this study, it was found out that the activity of the ruthenium(III) Schiff base complexes almost reaches the effectiveness of the conventional bacteriocide standards.

Keywords antibacterial activity, binuclear ruthenium(III), N_2O_2 donor, phenyl-phenyl coupling, oxidation reactions

INTRODUCTION

The oxidation of alcohols into corresponding aldehydes and ketones, and aryl-aryl coupling reactions is a crucial reaction in organic chemistry, both academic and industrial relevance.[1−4] Moreover, the oxidant used in the reactions generally may lead to environmental pollution. With the overgrowing environmental concerns, the development of benign catalytic processes of highly efficient oxidation of alcohols is becoming increasingly important.[5] Currently, a considerable effort is being invested in the development of new chelating ligand systems; particularly the planarity of the N_2O_2 ligand provides the means of creating vacant site, since their binucleating imino ligands are versatile and they exhibit very rich coordination chemistry, such species occupy an important position in modern coordination and inorganic chemistry, but they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials.[6−10] The incorporation of binucleating Schiff base ligand into ruthenium tertiaryphosphine complexes was initially aimed at promoting activity of such species towards oxidation of alcohols and aryl-aryl coupling, because the use of metal-*salen* derivative Schiff base complexes are known to react with oxidants like NMO, PhIO, *t*-BuOOH[11] and molecular oxygen to form metal *oxo*-species.[4] The Schiff base ligands were prepared by condensing 4,4′-diaminophenyl and *isatin* with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, *o*-hydroxyacetophenone and *o*-vanillin. As a part of our continuing efforts[4] to synthesis and characterize ruthenium chelates using simple and inexpensive Schiff base ligands, we herein describe the synthesis and characterization of a series of new class of binuclear ruthenium(III) Schiff base complexes along with their catalytic activity towards the highly efficient oxidation of a number of primary and secondary alcohols in the presence of molecular oxygen atmosphere at ambient temperature and C-C coupling reactions. Further, the ligands and their Ru(III) Schiff base complexes were also screened for their antibacterial activity against *K. pneumoniae*, *Shigella sp.*, *M. luteus*, *E. coli* and *S. typhi.*

EXPERIMENTAL

Materials and Methods

All the chemicals and solvents used were purified and dried by standard methods. IR spectra were recorded as KBr pellets with a Nicolet FT-IR spectrometer in 4000–400 cm^{-1}

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We are thankful to NMR Research Centre, Indian Institute of Science (IISc), Bangalore, India for providing $^{13}C\{^1H\}$-NMR spectra.

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range. Electronic spectra of the complexes were recorded in $CHCl_2$ solutions using Systronics double beam UV-vis spectrophotometer-2202 in the range 800–200 nm. Microanalyses were carried out with a Vario El AMX-400 elemental analyzer at STIC, Cochin University of Science and Technology, Kerala, India. EPR spectra of powdered samples were recorded with a JEOL TEL-100 instrument at X-band frequencies at room temperature. Redox potential studies were carried out with a BAS CV-27 model electrochemical analyzer in acetonitrile using glassy carbon working electrode and the potentials were referenced to Ag-AgCl electrode. Powder XRD were recorded using Shimadzu Model XRD6000 instrument with CuKα radiation (λ = 1.54060 Å) from a Cu target. Scanning electron micrography associated with energy dispersive spectrometry (SEM/EDS) was used for morphological evaluation. Magnetic moments were measured on an EG & G PARC vibrating sample magnetometer. Melting points were recorded with a Veego VMP-DS model heating table and were uncorrected. The starting complexes $[RuCl_3(PPh_3)_3]$[12] and $[RuBr_3(PPh_3)_3]$[13] and the Schiff base ligands (Scheme 1) were prepared by the reported procedure[14] with modification of the substitutions and the purity of the starting complexes and the free Schiff base ligands were checked by TLC. The analytical data, FT-IR, $^{13}C\,^{1}H$-NMR spectral data confirm the proposed molecular formula and the structure of the Schiff base ligands.

Preparation of Schiff Base Ligands

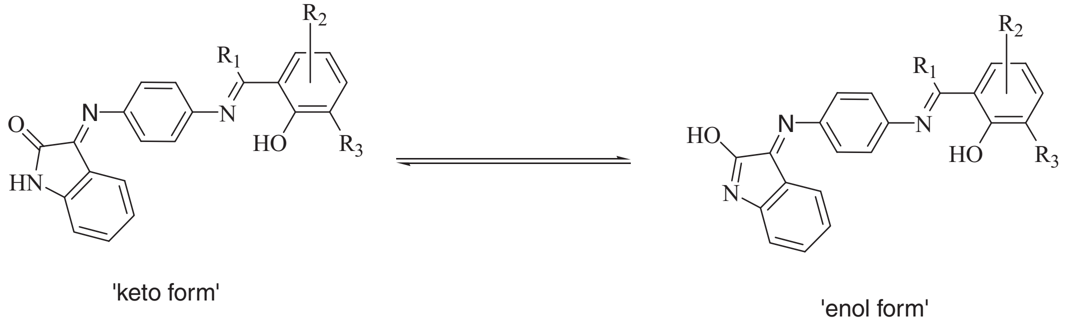
To an ethanolic solution of *p*-phenylenediamine (1.8 g; 10 mmol), salicylaldehyde/*o*-hydroxy acetophenone/*o*-vanillin/2-hydroxy-1-naphthaldehyde (10 mmol) was added and one hour for stirring. Then to the above stirring solution about 10 mmol of *isatin* was added. The mixture was stirred for about half an hour and then refluxed for about 4 hrs. The resultant product was washed with ethanol and dried in *vacuo* (Scheme 1).

Synthesis of Binuclear Ruthenium(III) Schiff Base Complexes

To a solution of $[RuX_3(PPh_3)_3]$ (where, X = Cl/Br) (0.20 mmol) in benzene/methanol, an appropriate Schiff base ligand was (molar ratio of ruthenium complex to Schiff base was 2:1) added. The solution was heated under reflux for 6–8 hours (Scheme 2) and then it was concentrated to 5 cm^3. The new complex was separated from it by addition of 10 cm^3 of petroleum ether (60–80°C). The product was filtered, washed with petroleum ether and recrystallized from methanol/CH_2Cl_2 mixture and tried in *vacuo* (Yield ≈82 %).

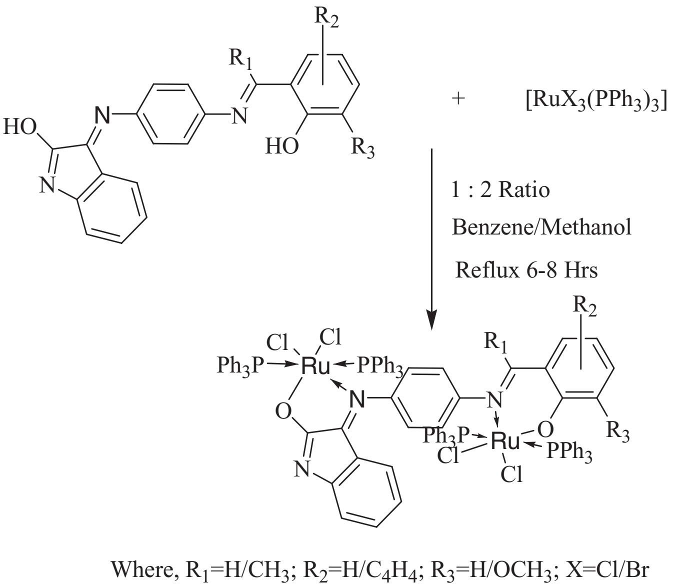
Catalytic Oxidation Reactions by Binuclear Ru(III) Schiff Base Complexes

Catalytic oxidation of alcohols to corresponding carbonyl compounds by binuclear Ru(III) Schiff base complexes



R1	R2	R3	Abbreviation
H	H	H	H_2L^1
H	C_4H_4	H	H_2L^2
CH_3	H	H	H_2L^3
H	H	OCH_3	H_2L^4

SCH. 1. Structure of Schiff base ligands.



SCH. 2. Formation of binuclear Ru(III) Schiff base complexes.

containing triphenylphosphine/triphenylarsine as co-ligands were studied in the presence of oxygen atmosphere at ambient temperature. A typical reaction using the complexes $\{[(PPh_3)_2(X)_2Ru]_2L\}$ as a catalyst and alcohols as substrates at a 1:100 molar ratio is described as follows. A solution of binuclear Ru(III) Schiff base complex (0.01 mmol) in 20 cm^3 CH_2Cl_2 was added to the solution of alcohol (1 mmol) under 1 atm oxygen atmosphere at ambient temperature. The solution mixture was stirred at room temperature for 6 hours and the solvent was then evaporated from the mother liquor under reduced pressure. The resulting carbonyl compounds was then extracted with petroleum ether (60–80°C) (20 cm^3) and was then quantified as 2,4-dinitrophenylhydrazone derivative.[15] The oxidation products are known and are commercially available.

C-C Coupling Reaction by Binuclear Ruthenium(III) Schiff Base Complexes

Magnesium turnings (0.320 g) were placed in a flask equipped with a $CaCl_2$ guard tube. A crystal of iodine was added. PhBr (0.75 cm^3 of total 1.88 cm^3) in anhydrous Et_2O (5 cm^3) was added with stirring and the mixture was heated under reflux. The remaining PhBr in Et_2O (5 cm^3) was added dropwise and the mixture was refluxed for 40 minutes. To this mixture, 1.03 cm^3 (0.01 mol) of PhBr in anhydrous Et_2O (5 cm^3) and the Ru(III) Schiff base complex (0.05 mmol) chosen for investigation were added and heated under reflux for 6 hours. The reaction mixture was cooled and hydrolyzed with a saturated solution of aqueous NH_4Cl and the ether extract on evaporation gave a crude product which was chromatographed to get pure biphenyl and compared well with an authentic sample.[15] Melting point: 69–72°C.

RESULTS AND DISCUSSION

All the complexes were isolated in high yields and are stable both in solid state and in solution. The analytical data (C, H, N) of all the Schiff base ligands and their Ru(III) complexes are in good agreement with the calculated values thus confirming the proposed binuclear composition for all the complexes (Table 1). The complexes were obtained in powder form. Various attempts have been made to obtain the single crystals of the complexes, but it has been unsuccessful. So for all the ligands and their complexes are stable at room temperature, non-hygroscopic and insoluble in water, methanol, ethanol and soluble in CH_2Cl_2, $CHCl_3$, DMF, DMSO and CH_3CN.

IR Spectra

The IR spectra of the free Schiff bases were compared with those of the ruthenium complexes in order to infer the binding mode of the Schiff base ligands in the complexes. The important IR absorption frequencies for the synthesized ligands and their complexes are shown in Table 1. The IR spectral data confirm the coordination of Schiff bases through azomethine nitrogen ($\nu_{C=N}$) by shifting the $\nu_{C=N}$ stretching frequency of free Schiff base ligands to lower frequency in the range 1612–1600 cm^{-1} in the complexes and this lowering of this wave number may be attributed to the decrease in electron density on the nitrogen atom of the azomethine group.[16,17] A medium band corresponding to phenolic oxygen (ν_{C-O}) is observed at 1390–1280 cm^{-1} for the free Schiff base ligands. On complexation this band is shifted to higher frequency in the range 1386–1368 cm^{-1} for all the ruthenium complexes.[18,19] This further supported by the disappearance of the ν_{OH} band at 3420–3416 cm^{-1} in all the complexes. Further, appearance of the bands in the region 510–490 and 474–460 cm^{-1} are probably due to formation of Ru-N and Ru-O bond, respectively.[20] In addition to other bands observed near 692, 1091 and 1435 cm^{-1} is due to triphenylphosphine fragments.

UV-Vis Spectra and Magnetic Susceptibility

The electronic spectra of all the complexes in CH_2Cl_2 showed three to six bands in the region 255–644 nm and their assignments are summarized in Table 1 and Figure 1. The ground state of ruthenium(III) (t_{2g}^5 configuration) is $^2T_{2g}$, while the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$, which arise from $t_{2g}^4e_g^1$ configuration. In most of the ruthenium(III) complexes, the electronic spectra show only charge transfer bands. Since in a d^5 system and specially in ruthenium(III), which has relatively high oxidation properties, the charge transfer bands of the type $L_y \rightarrow t_{2g}$ are prominent in the low energy region and obscure the weaker bands due to d-d transition at 502–640 nm. All the binuclear ruthenium complexes display strong band in the range 466–644 nm followed by a weak shoulder in the range 363–399 nm to be the LMCT transitions. Therefore, it becomes difficult to assign conclusively the bands in the visible region. The band observed around 260 nm, which

TABLE 1
Analytical and IR spectral data of binuclear ruthenium(III) Schiff base complexes

Ligand/complexes	Decomposing temperature (°C)	molecular weight	Elemental analysis found (calcd.) %			FT-IR spectral data							
			C	H	N	$\nu_{Ph-C-OH}$ (cm^{-1})	$\nu_{C=N}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	$\nu_{C=N} + \nu_{NH}$ (cm^{-1})	ν_{Ph-C-O} (cm^{-1})	ν_{Ru-N} (cm^{-1})	ν_{Ru-O} (cm^{-1})	Bands due to PPh_3
H_2L^1	>250	341.36	74.00 (73.89)	4.51 (4.43)	12.13 (12.31)	3418	1624	1715	1510	1284	—	—	—
H_2L^2	193	391.42	76.58 (76.71)	4.39 (4.38)	10.84 (10.74)	3420	1628	1717	1512	1290	—	—	—
H_2L^3	202	355.39	74.65 (74.35)	4.48 (4.48)	11.90 (11.82)	3416	1620	1716	1511	1280	—	—	—
H_2L^4	96	371.39	71.22 (71.15)	4.53 (4.61)	11.26 (11.31)	3420	1626	1717	1512	1290	—	—	—
$\{[(PPh_3)_2Cl_2Ru]_2L^1\}$	96	1732.44	64.55 (64.48)	4.25 (4.25)	2.43 (2.43)	—	1602	—	—	1372	510	470	692,1092,1434
$\{[(PPh_3)_2Cl_2Ru]_2L^2\}$	112	1782.50	65.87 (65.36)	4.44 (4.24)	2.80 (2.36)	—	1600	—	—	1379	508	460	690,1092,1435
$\{[(PPh_3)_2Cl_2Ru]_2L^3\}$	133	1746.47	64.58 (64.65)	4.35 (4.33)	2.60 (2.41)	—	1601	—	—	1382	490	468	693,1092,1435
$\{[(PPh_3)_2Cl_2Ru]_2L^4\}$	122	1762.47	64.11 (64.06)	4.44 (4.29)	2.11 (2.38)	—	1608	—	—	1386	494	474	692,1092,1435
$\{[(PPh_3)_2Br_2Ru]_2L^1\}$	>250	1910.24	58.61 (58.47)	4.01 (3.85)	1.98 (2.20)	—	1606	—	—	1368	494	470	691,1090,1434
$\{[(PPh_3)_2Br_2Ru]_2L^2\}$	>250	1960.30	59.62 (59.43)	3.90 (3.86)	2.29 (2.14)	—	1612	—	—	1383	490	470	692,1089,1434
$\{[(PPh_3)_2Br_2Ru]_2L^3\}$	>250	1924.27	58.30 (58.67)	4.06 (3.93)	2.04 (2.18)	—	1608	—	—	1382	502	472	693,1091,1436
$\{[(PPh_3)_2Br_2Ru]_2L^4\}$	>250	1940.27	57.95 (58.19)	3.89 (3.90)	2.14 (2.17)	—	1604	—	—	1386	506	464	693,1091,1436

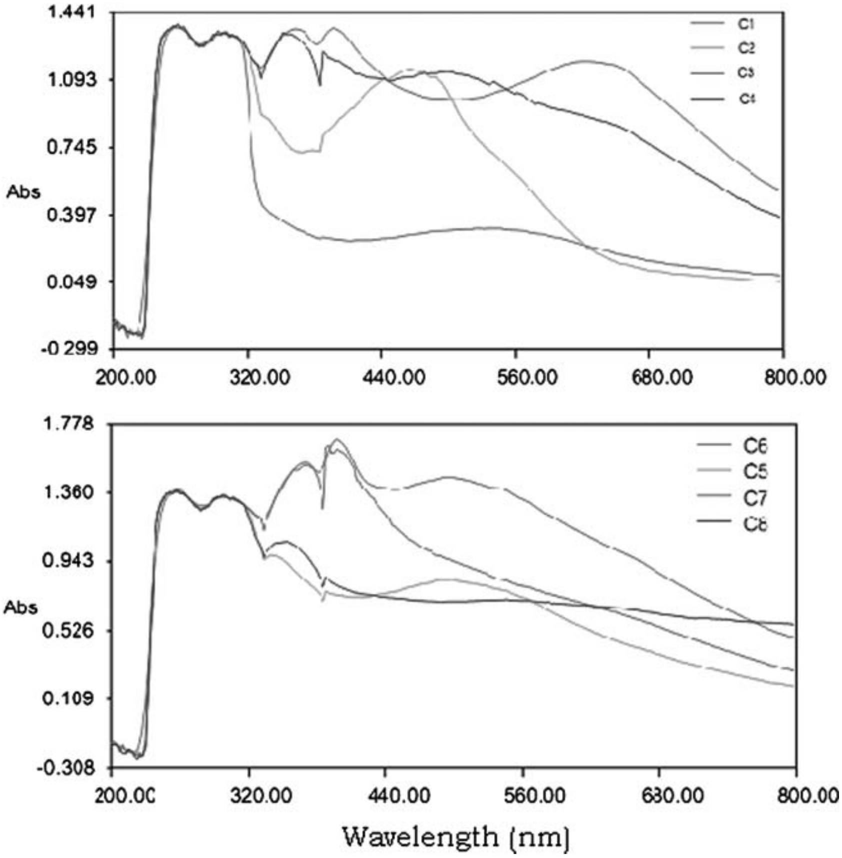


FIG. 1. Electronic spectrum of binuclear Ru(III) Schiff base complexes; C1-{$[(PPh_3)_2Cl_2Ru]_2L^1$}, C2-{$[(PPh_3)_2Cl_2Ru]_2L^2$}, C3-{$[(PPh_3)_2Cl_2Ru]_2L^3$}, C4-{$[(PPh_3)_2Cl_2Ru]_2L^4$}, C5-{$[(PPh_3)_2Br_2Ru]_2L^1$}, C6-{$[(PPh_3)_2Br_2Ru]_2L^2$}, C7-{$[(PPh_3)_2Br_2Ru]_2L^3$} and C8-{$[(PPh_3)_2Br_2Ru]_2L^4$}.

is also present in free ligands, is assigned to $\pi - \pi^*$ transition from the benzene ring and the double bond of the azomethine group. The bands around 300 and 350 nm are due to n-π^* transition of non-bonding electrons present on the nitrogen of azomethine group in the binuclear ruthenium(III) complexes. The patterns of the electronic spectra of all the complexes indicate the presence of an octahedral environment around the ruthenium ion.[4,21–23]

The room temperature magnetic moments show that the ruthenium(III) complexes are one electron paramagnetic (Table 2), in the range 1.79–1.89 BM, which corresponds to the +3 state of ruthenium. It has been observed that the μ_{eff} values indicate a single unpaired electron and is consistent with non-interacting d^5 centers or the absence of any strong magnetic interactions between the two ruthenium centers of the molecule.

$^{13}C\{^1H\}$-NMR Spectra of Schiff Base Ligands

The formation Schiff base ligands were conveniently monitored by peak ratios in the ^{1}H-NMR spectra. ^{1}H-NMR spectra of all the ligands (Table 3) were taken in DMSO.d_6 solvent. The aromatic region is a set of multiplets in the range 6.6–7.8 ppm for all the Schiff base ligands, while the azomethine proton of H_2L^1, H_2L^2 and H_2L^4 ligands were observed in the range 8.2–9.0 ppm. The phenolic -OH protons of H_2L^1-H_2L^4 Schiff base ligands were observed as a singlet in the region 11.8–13.1 ppm. ^{1}H-NMR spectra exhibit a singlet peak at 1.1 ppm and 3.2 ppm for -CH_3 protons for H_2L^3 and —OCH_3 protons of H_2L^4 ligands.

^{13}C-NMR spectral data (Table 3) are consistent with ^{1}H-NMR spectral data. The methyl carbon of aliphatic substituents, azomethine (>C=N) for all the Schiff base ligands and for Ph—C—CH_3 of H_2L^3 and Ph-OCH_3 of H_2L^4 ligand around 20 ppm. The resonance observed at 132.0–168.6 ppm is assigned to phenyl group of ligands. The N=C—O and C—C=N of Indole derivatives for all the ligands observed around 130 ppm and 125 ppm.

ESR Spectra

The room temperature ESR spectra of powdered samples were recorded at X-band frequencies (Table 2 and Figure 2). The solid state ESR spectra of all the complexes exhibit an anisotropic spectra with rhombic distortion and the 'g' values measured in the range of $g_x = 2.09$–2.02, $g_y = 2.14$–2.06 and $g_z = 2.20$–2.16 with $g_{av} = 2.14$–2.09 (Table 2), which derived from $\langle g\rangle^* = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$. The ESR spectra of the present binuclear ruthenium(III) complexes are similar in

TABLE 2

EPR spectral data, cyclic voltammetric data[a], magnetic moments and UV-vis spectral data of new binuclear Ru(III) Schiff base complexes

					Cyclic voltammetry data									
	EPR data				Ru^{IV}-Ru^{III}				Ru^{III}-Ru^{II}					
Ligand/complexes	g_x	g_y	g_z	$\langle g\rangle^*$	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)	μ_{eff} (BM)	UV-Vis λ_{max} (nm)
$\{[(PPh_3)_2Cl_2Ru]_2L^1\}$	2.09	2.12	2.16	2.12	1.420	1.120	1.270	300	−1.594	−1.368	−0.113	226	1.89	255, 296, 363, 397, 620
$\{[(PPh_3)_2Cl_2Ru]_2L^2\}$	2.06	2.14	2.18	2.13	1.510	1.000	1.255	510	−1.100	−0.800	−0.150	300	1.82	258, 466, 574
$\{[(PPh_3)_2Cl_2Ru]_2L^3\}$	2.02	2.10	2.18	2.10	1.100	0.700	0.900	400	−0.800	−0.500	−0.150	300	1.80	258, 298, 529, 620
$\{[(PPh_3)_2Cl_2Ru]_2L^4\}$	2.04	2.06	2.16	2.09	1.200	0.800	1.000	400	−0.900	−0.500	−0.200	400	1.80	255, 298, 356, 399, 507, 644
$\{[(PPh_3)_2Br_2Ru]_2L^1\}$	2.07	2.06	2.16	2.10	1.100	0.700	0.900	400	−1.000	−0.700	−0.150	300	1.79	258, 303, 349, 493, 622
$\{[(PPh_3)_2Br_2Ru]_2L^2\}$	2.09	2.12	2.20	2.14	1.200	0.800	1.000	400	−0.900	−0.500	−0.200	400	1.82	258, 301, 368, 397, 495, 634
$\{[(PPh_3)_2Br_2Ru]_2L^3\}$	2.02	2.08	2.16	2.09	1.100	0.900	1.000	200	−0.800	−0.400	−0.200	400	1.84	258 296, 370, 392, 618
$\{[(PPh_3)_2Br_2Ru]_2L^4\}$	2.09	2.12	2.20	2.14	1.500	1.000	0.800	500	−0.900	−0.400	−0.250	500	1.82	255, 298, 356, 502, 620

[a] Working electrode: Glassy carbon electrode; Reference electrode: Ag/AgCl electrode: Supporting electrolyte $[NBu_4]ClO_4$ (0.01 M); Concentration of the complex: 0.001 m; Scan rate : 100 mVs^{-1}; $E_f = 0.5(E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$, Where E_{pa} and E_{pc} are anodic and cathodic potentials.
$\langle g\rangle^* = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$.

TABLE 3
$^{13}C\{^{1}H\}$-NMR spectra of Schiff base ligands

Ligand	^{1}H-NMR (δ ppm)		^{13}C-NMR (δ ppm)	
H_2L^1	6.6-7.8	m, aromatic (12 H)	156.5–132.0	phenyl carbons
	8.2	s, –CH=N (1 H)	20.0	>C=N–Carbon
	12.3	s, –OH (2 H)	130.1	N=C–O (Indole Carbon)
			125.6	C—C=N (Indole azomethine)
H_2L^2	6.8-7.4	*m*, aromatic (14 H)	161.0–139.8	naphthalene carbons
	8.6	*s*, –CH=N (1 H)	18.7	>C=N–Carbon
	13.1	*s*, –OH (2 H)	135.4	N=C–O (Indole Carbon)
			126.2	C–C=N (Indole azomethine)
H_2L^3	7.0-7.8	*m*, aromatic (16 H)	160.9–137.1	phenyl carbons
	12.4	*s*, –OH (2 H)	19.0	>C=N–Carbon
	1.1	*s*, CH_3 (3 H)	16.0	-methyl carbon
			133.5	N=C–O (Indole Carbon)
			124.4	C–C=N (Indole azomethine)
H_2L^4	6.8-7.6	*m*, aromatic (12 H)	168.6–140.0	Benzene carbons
	9.0	*s*, –CH=N (1 H)	19.8	>C=N–Carbon
	11.8	*s*, –OH (2 H)	58.0	-methoxy carbon
	3.2	*s*, $-OCH_3$ (3 H)	132.8	N=C–O (Indole Carbon)
			124.0	C—C=N (Indole azomethine)

nature to those of the mononuclear complexes[24–27] and this indicates that the two paramagnetic centers are equivalent and there is no super exchange between the two metal centers.[28] However, these new complexes are dimers with one unpaired electron on each ruthenium(III) atom, leading to an *S*-value of 1. The pairing of electrons is prevented by the greater distance between two ruthenium(III) atoms provided by the bridging bis-bidentate Schiff base ligands.

Cyclic Voltammogram

The cyclic voltammogram studies of binuclear Ru(III) Schiff base complexes were carried out using glassy carbon electrode and the supporting electrolyte used was $[NBu_4]ClO_4$ in CH_3CN solution versus Ag/AgCl at a scan rate of 100 mVs^{-1}. Cyclic voltammogram E_f of all the ruthenium(III) complexes exhibit in the range from 0.800 to 1.270 V (Ru^{III}-Ru^{IV}) and from −0.113 to −0.250 V (Ru^{III}-Ru^{II}), respectively (Table 2 and Figure 3). All the complexes were electroactive only with respect to the metal center. In these redox couples, electrons are gained or lost from the dπ levels orbital of the coordinated metal.[25,29,30] Complexes showed redox couples with peak-to-peak separation values (ΔE_p) ranging from 200 to 510 mV, revealing that this process is at best quasi-reversible. This is attributed to slow electron transfer and adsorption of the complexes onto the electrode surface. The first oxidation and followed by reduction was attributed to the oxidation and reduction of one of the ruthenium(III) centers to the corresponding mixed valence complex and the second to the ruthenium(IV). Hence, it is inferred from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation state of ruthenium.

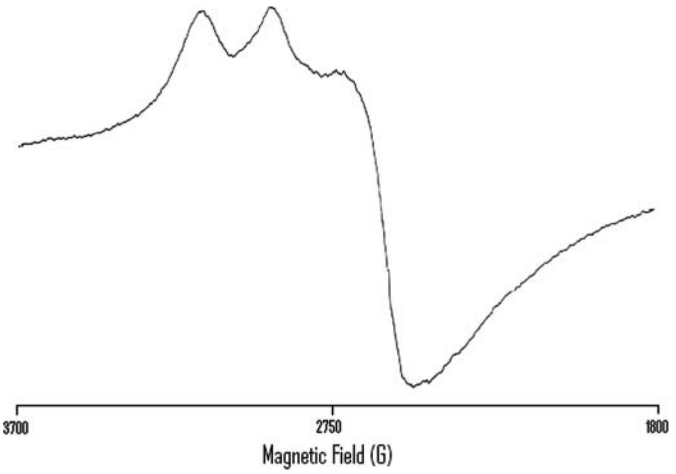


FIG. 2. EPR spectrum of binuclear $\{[(PPh_3)_2Cl_2Ru]_2L^2\}$ complex.

Powder X-ray Diffraction

X-ray diffraction was performed to obtain further evidence about the structure of the metal complexes. The diffractograms obtained for the Schiff base metal complexes are given in Figure 4 and the XRD patterns indicate crystalline nature for the Schiff base ligands and their Ru(III) complexes. The 'd' values, 2θ angles and (h k l) values are listed in Table 4. The complex crystallizes in an orthorhombic type of lattice with dimensions as a = 1.106, b = 1.242 and c =1.204 E. On the basis of above studies, an octahedral geometry for Ru(III) complexes have been proposed.[31–33]

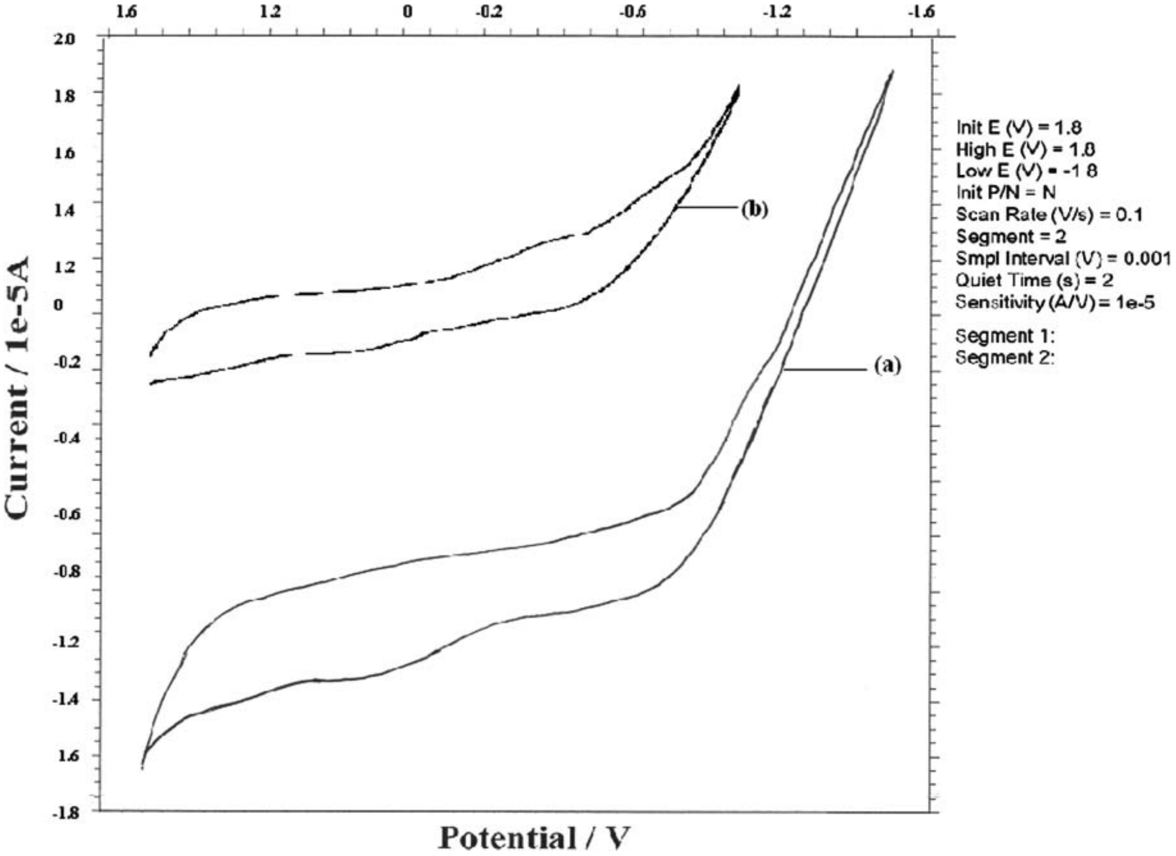


FIG. 3. Cyclic voltammogram of binuclear $\{[(PPh_3)_2Cl_2Ru]_2L^1\}$ and $\{[(PPh_3)_2Cl_2Ru]_2L^5\}$ complexes.

Scanning electron micrography (SEM)

Scanning electron micrography is used to evaluate morphology and particle size of the Schiff base metal complexes. SEM images of the synthesized Schiff base ligand (H_2L^2) and their corresponding ruthenium complex $[(PPh_3)_2Cl_2Ru]_2L^3$ are illustrated in Figure 5. From the SEM images, we noted that there is a uniform matrix of the synthesized complexes, i.e., the complexes are homogeneous phase material. A single phase formation having layer by layer like morphologies with particle size 10 μm is observed in the free Schiff base ligand and its complex. An ice square like shape is observed in the complex with the particle size of 10 μm. In general, the SEM photographs of all the complex show single phase formation withwell-defined shape and particle size in the range of 10 μm.

TABLE 4
X-ray powder diffraction data of $\{[(PPh_3)_2Br_2Ru]_2L^2\}$

Peak	2θ	Lattice spacing (d) Å	h k l
1	6.235	24.7412	2 3 1
2	8.126	18.4168	1 0 6
3	10.450	16.5254	4 3 2
4	11.110	15.3754	3 2 4
5	13.960	13.8672	4 1 2
6	18.230	8.9426	2 1 4
7	20.135	4.6847	3 4 6
8	26.468	1.64987	3 4 5
9	33.541	1.0842	4 5 6
10	40.754	1.0128	3 4 6
11	45.349	1.0102	3 5 4
12	46.346	1.0101	4 3 4

C-C Coupling and Oxidation Reactions

The C-C coupling reactions by the synthesized binuclear ruthenium(III) Schiff base complexes $\{[(PPh_3)_2X_2\text{-}Ru]_2L\}$ were carried out and the results of this study are listed in Table 5. The system chosen for our study is the coupling of phenylmagnesium bromide with bromobenzene was first converted into the corresponding Grignard reagent. Then bromobenzene, followed by the complex chosen for the investigation, was added to the above reagent and the mixture was heated under reflux for 6 hours. After work up, the mixture yielded biphenyl. Only a very little amount of biphenyl is formed when the reaction is carried out without the catalyst. This is an insignificant amount compared to the yields of biphenyl that have been

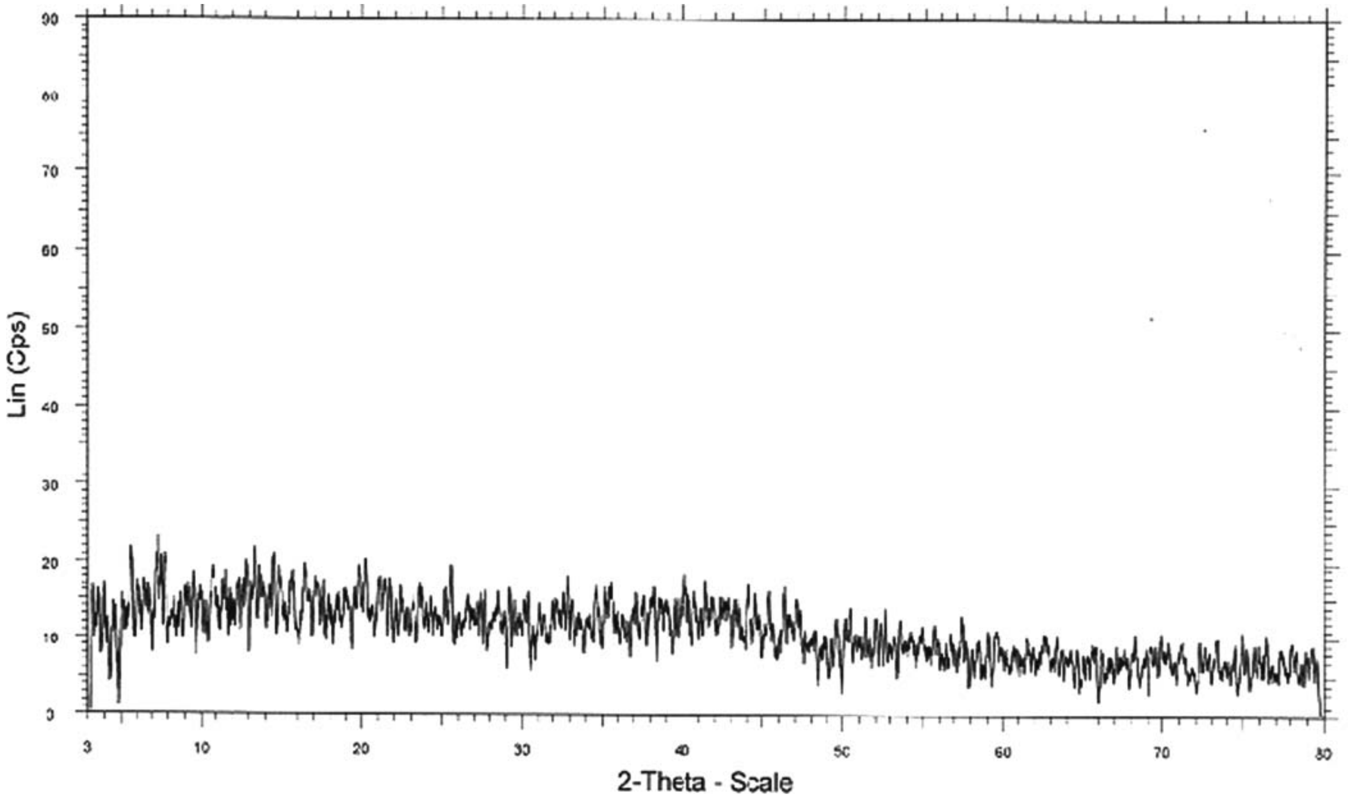


FIG. 4. Powder X-ray Diffraction pattern of binuclear $\{[(PPh_3)_2Cl_2Ru]_2L^2\}$ complex.

obtained from the reactions catalyzed by ruthenium complexes. The catalytic properties of the new binuclear complexes have also been compared with those already reported binuclear complexes. It has been observed that the binuclear Ru(III) Schiff base complexes are better catalyst than already reported binuclear complexes. The possible mechanism for the coupling of PhMgBr with PhBr catalysed by Ru(III) complexes has already reported.[34]

The catalytic oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones by the synthesized binuclear ruthenium(III) Schiff base complexes $\{[(PPh_3)_2X_2\text{-}Ru]_2L\}$ were carried out in the presence of oxygen atmosphere at ambient temperature and the results of this study are listed in Table 5. The primary and secondary alcohols (1 mmol) were effectively oxidized by using 0.01 mmol of the catalyst in the coexistence of 1 atm pressure of oxygen atmosphere at ambient temperature in CH_2Cl_2. All the complexes oxidized the primary alcohols and secondary alcohols to their corresponding aldehydes and ketones[35,36] with high yield. This reaction provides an environmentally friendly route to the

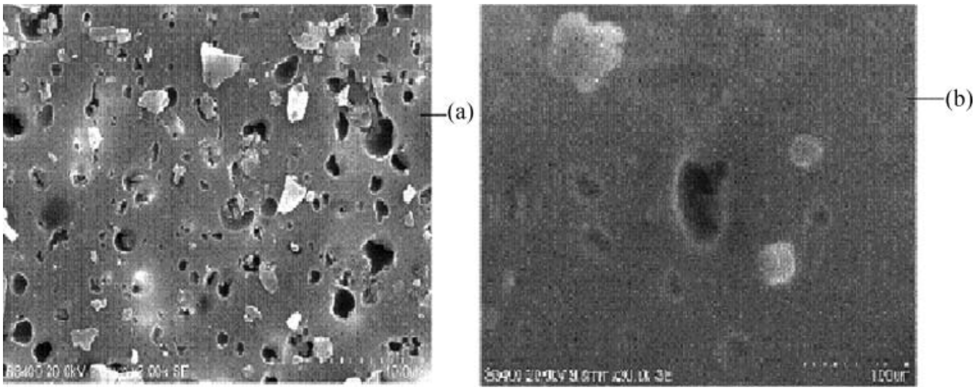


FIG. 5. SEM image of binuclear $\{[(PPh_3)_2Cl_2Ru]_2L^3\}$ complex (a) 10.00 μm, (b) 1.00 μm.

TABLE 5
Catalytic activity data of new binuclear Ru(III) complexes

	Catalytic oxidation of alcohols				C–C coupling reaction	
Complexes	Substrate	Product	Yield (%)	Turnover number[a]	Yield (mg)	Yield (%)
$\{[(PPh_3)_2Cl_2Ru]_2L^1\}$	Cinnamyl alcohol	Cinnamaldehyde	78.32	82	0.382	41.24
	Benzyl alcohol	Benzaldehyde	71.14	74		
	Cyclohexanol	Cyclohexanone	90.66	94		
	Propan-1-ol	Propionaldehyde	60.10	63		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	65.28	69		
$\{[(PPh_3)_2Cl_2Ru]_2L^2\}$	Cinnamyl alcohol	Cinnamaldehyde	75.23	78	0.264	28.41
	Benzyl alcohol	Benzaldehyde	69.00	72		
	Cyclohexanol	Cyclohexanone	53.52	56		
	Propan-1-ol	Propionaldehyde	51.18	54		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	58.56	61		
$\{[(PPh_3)_2Cl_2Ru]_2L^3\}$	Cinnamyl alcohol	Cinnamaldehyde	82.74	86	0.402	44.10
	Benzyl alcohol	Benzaldehyde	73.14	76		
	Cyclohexanol	Cyclohexanone	66.53	70		
	Propan-1-ol	Propionaldehyde	55.42	57		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	60.19	62		
$\{[(PPh_3)_2Cl_2Ru]_2L^4\}$	Cinnamyl alcohol	Cinnamaldehyde	59.48	63	0.194	20.23
	Benzyl alcohol	Benzaldehyde	52.56	55		
	Cyclohexanol	Cyclohexanone	40.44	44		
	Propan-1-ol	Propionaldehyde	38.09	42		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	64.50	67		
$\{[(PPh_3)_2Br_2Ru]_2L^1\}$	Cinnamyl alcohol	Cinnamaldehyde	92.28	96	0.311	35.66
	Benzyl alcohol	Benzaldehyde	88.44	92		
	Cyclohexanol	Cyclohexanone	85.69	89		
	Propan-1-ol	Propionaldehyde	59.43	63		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	66.72	70		
$\{[(PPh_3)_2Br_2Ru]_2L^2\}$	Cinnamyl alcohol	Cinnamaldehyde	72.56	75	0.258	29.50
	Benzyl alcohol	Benzaldehyde	67.10	69		
	Cyclohexanol	Cyclohexanone	56.60	59		
	Propan-1-ol	Propionaldehyde	54.15	57		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	67.12	70		
$\{[(PPh_3)_2Br_2Ru]_2L^3\}$	Cinnamyl alcohol	Cinnamaldehyde	78.21	81	0.418	42.30
	Benzyl alcohol	Benzaldehyde	70.52	73		
	Cyclohexanol	Cyclohexanone	48.43	51		
	Propan-1-ol	Propionaldehyde	56.56	59		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	60.83	64		
$\{[(PPh_3)_2Br_2Ru]_2L^4\}$	Cinnamyl alcohol	Cinnamaldehyde	76.75	80	0.369	36.48
	Benzyl alcohol	Benzaldehyde	74.63	77		
	Cyclohexanol	Cyclohexanone	48.19	51		
	Propan-1-ol	Propionaldehyde	50.33	53		
	2-methyl propyl alcohol	2-Methyl-propionaldehyde	65.20	67		

[a] Moles of product per mole of catalyst.

conversion of alcoholic functions to carbonyl groups and water is the only by- product during the course of the reaction which was removed by using molecular sieves. The aldehydes and ketones formed after 3–6 hours of stirring were isolated and quantified as their 2,4-dinitrophenylhydrazone derivatives.[37] The relatively higher product yield obtained for the oxidation of cinnamyl alcohol is due to the presence of more acidic α-CH unit in cinnamyl alcohol. Further, the oxidation of cinnamyl alcohol to

TABLE 6
Antimicrobial activities of new Schiff base ligands and their binuclear Ru(III) complexes

	Inhibition zone concentration in cm																								
	K. Pneumoniae					*Shigella sp.*					*M. Luteus*					*E.Coli*					*S.typhi*				
Ligand/complex	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %
H_2L^1	0.7	0.8	0.8	0.9	0.9	0.6	0.6	0.7	0.7	0.8	0.7	0.6	0.8	0.8	0.7	0.7	0.7	0.8	0.8	0.9	0.9	0.9	1.0	1.0	1.1
H_2L^2	0.5	0.8	0.8	0.8	0.8	0.5	0.6	0.5	0.8	0.8	0.7	0.7	0.6	0.8	0.8	0.6	0.7	0.7	0.6	0.8	0.9	0.9	0.8	1.0	1.0
H_2L^3	0.8	1.0	1.0	1.0	0.8	0.6	0.6	0.5	0.9	0.9	0.7	0.8	0.8	0.9	1.0	0.5	0.5	0.8	0.8	0.8	0.6	0.8	0.8	0.7	1.0
H_2L^4	0.5	0.8	0.6	0.9	0.7	0.6	0.6	0.8	0.9	0.9	0.8	0.8	0.8	0.9	1.0	0.8	0.8	0.9	1.0	1.0	0.6	0.9	1.0	1.0	1.0
$\{[(PPh_3)_2Cl_2Ru]_2L^1\}$	0.8	1.0	1.0	1.0	1.0	0.8	0.9	0.9	0.9	1.0	0.5	07	0.7	0.7	0.7	0.9	1.0	1.0	1.1	1.0	0.5	0.8	0.9	1.0	1.4
$\{[(PPh_3)_2Cl_2Ru]_2L^2\}$	0.8	0.9	1.1	1.1	1.1	0.9	0.9	0.9	1.1	1.0	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.7	0.7	0.7	0.6	0.6	0.6	0.8	1.0
$\{[(PPh_3)_2Cl_2Ru]_2L^3\}$	1.1	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.7	0.8	0.9	0.9	0.9	0.9	0.7	0.7	0.8	0.9	1.0
$\{[(PPh_3)_2Cl_2Ru]_2L^4\}$	0.8	0.9	0.7	0.6	0.8	0.7	0.9	0.9	0.8	0.9	0.9	0.9	1.1	1.1	1.0	0.8	0.9	0.9	0.9	0.8	0.8	0.7	0.9	1.0	1.2
$\{[(PPh_3)_2Br_2Ru]_2L^1\}$	0.9	0.8	0.9	1.0	1.1	0.8	0.9	0.9	0.9	0.9	0.8	0.8	0.9	1.2	1.0	0.9	0.9	0.9	0.7	0.9	0.8	0.8	1.0	0.9	0.8
$\{[(PPh_3)_2Br_2Ru]_2L^2\}$	0.5	0.8	0.8	0.8	0.9	0.9	0.9	0.9	1.1	1.0	0.8	0.8	0.9	0.9	0.9	0.8	0.8	0.8	1.2	1.2	0.9	0.9	1.0	1.0	1.0
$\{[(PPh_3)_2Br_2Ru]_2L^3\}$	0.9	0.9	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.0	1.0	1.0	1.0	1.0	0.8	0.8	0.7	0.9	0.9	0.9	1.1	1.1	1.1	1.0
$\{[(PPh_3)_2Br_2Ru]_2L^4\}$	0.9	0.9	0.9	0.9	0.9	0.8	0.8	1.2	1.1	1.2	1.0	1.0	1.0	1.0	1.0	0.9	1.3	1.3	1.2	1.2	1.2	0.9	1.0	1.2	1.2
Standards	D	E	A_x	A_k	S	D	E	A_x	A_k	S	D	A_k	A_x	S	E	D	E	A_x	A_k	S	A_k	A_x	E	S	D
	—	1.2	0.8	2.3	1.7	—	1.6	1.0	2.1	1.0	—	1.5	—	0.9	1.6	—	—	—	—	—	1.6	—	1.0	—	0.8

Where, D = DMSO, E = Erythromycin, A_x = Amoxycilin, A_k = Ampicillin and S = Streptomycin.

cinnamaldehyde takes place with retention of C=C double bond which is in important characteristic of ruthenium/O_2 system.[4,38,39] The triphenylphosphine ruthenium(III) complexes possess greater catalytic activity than the triphenylarsine complexes.[37,40]

Antibacterial Activities

The Schiff base ligands and their binuclear ruthenium(III) complexes have been tested *in vitro* to access their growth inhibitory activity against *K. pneumoniae*, *Shigella sp.*, *M. luteus*, *E. coli* and *S. typhi* by Agar-Well diffusion method.[41] The test organisms were grown on nutrient agar medium in petri plates. The compounds to be tested were dissolved in DMSO and soaked in filter paper disc of 5 mm diameter and 1mm thickness. The concentrations used in this study were 0.5, 1.0, 1.5, 2.0 and 2.5% (Table 6 and Figure 5). The discs were placed on the previously seeded plates and incubated at 37°C for 24 hrs. *Amoxycilin*, *ampicillin*, *erythromycin* and *streptomycin* was used as standards with different concentrations. 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.[42] In general, the complexes are more active than that of parent ligands and ruthenium(III) starting complexes. The increase in the antibacterial activity of the metal chelates with increase in concentration is due to the effect of metal ion on normal cell process. Such increase activity of the metal chelates can be explained on the basis of Overtone's concept[43] and Chelation theory.[44,45] According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only rapid soluble materials due to which liposolubility has important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups. Further, it increases the delocalization of π-electrons over the whole chelate ring and enhances the liphophilicity enhances the penetration of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocking the metal binding sites on enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which further the restrict growth of the organism. Furthermore, the mode of action of the complexes may involve formation of hydrogen bond through >C=N group with the active centers of cell constituents resulting in interference with the normal cell process.[46] Though the Schiff base ligands and their ruthenium(III) complexes possess activity, it could not reach the effectiveness of the standard drugs. The variation in the effectiveness of the different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells.[47]

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