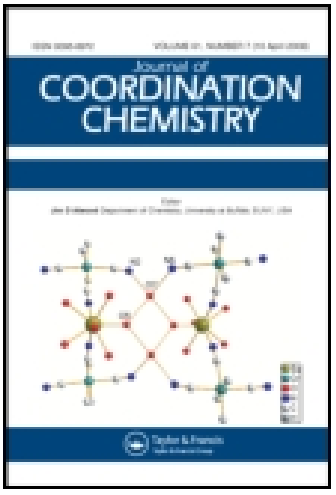

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Ruthenium(III) tetradentate Schiff-base complexes: spectral, catalytic, and its biocidal efficacy

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Ruthenium(III) tetradentate Schiff-base complexes: spectral, catalytic, and its biocidal efficacy

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New six-coordinate ruthenium(III) Schiff-base complexes of general formula $[Ru(X)(PPh_3)(L)]$ (where X = Cl/Br and L = mononucleating bibasic tetradentate ligand derived by condensing actetoacetanilide/acetoacetotoludide with *o*-aminophenol/*o*-aminothiophenol/*o*-aminobenzoic acid in 1 : 2 molar ratio in ethanol) have been synthesized and characterized by physico-chemical and spectroscopic methods. The new ruthenium(III) complexes possess 2NO/2NS metal binding sites and are catalysts for the oxidation of alcohols using molecular oxygen as co-oxidant and in C–C coupling reactions. These complexes possess good biocidal (antibacterial and antifungal) activity.

Keywords: Schiff base; Tetradentate ligands; Electrochemical; Molecular oxygen; Biocidal

1. Introduction

Design, synthesis, and structural characterization of Schiff-base complexes are of interest due to their structural, magnetic, spectral, catalytic, and redox properties [1–9]. Much research has been published concerning the use of Schiff-base ligands, which incorporate nitrogen imine, phenolate, thiophenolate, and carboxylato donors for synthesizing ruthenium complexes capable of oxidizing organic substrates [9–13]. Activation of molecular oxygen by transition metals for the catalytic oxidation of organic substrates has been of continued interest [14–16]. Particularly, the use of ruthenium complexes to catalyze oxidation of alcohols by oxygen donors has been well-documented [17, 18]. Mechanism of oxidation using hydrogen peroxide in the presence of Mo, V, W, and Ti and peracids is also studied [19]. Further, primary oxidants, such as iodobenzene [20], alkylhydroperoxides [21], *p*-cyano-*N*-*N*-dimethylaniline-*N*-oxide [22], and molecular oxygen [23] and C–C coupling [24] have been reported. It has been reported that high-valent metal-oxo species are responsible for Cytochrome P-450 catalyzed epoxidation and hydroxylation. Sharpless *et al*. [25] carried out an oriented study of oxidation of cholesterol, geraniol, etc., catalyzed by ruthenium complexes in the presence of *N*-methylmorpholine-*N*-oxide and *N*-*N*-dimethylaniline-*N*-oxide.

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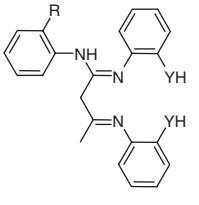
Here, we report the synthesis, spectral, catalytic, and biocidal efficacies of six-coordinate ruthenium(III) complexes incorporated with Schiff-base ligands. The Schiff bases were derived by condensation of actetoacetanilide/acetoacetotoludide with *o*-aminophenol/*o*-aminothiophenol/*o*-aminobenzoic acid in the 1 : 2 ratio. The preparation of the Schiff bases are given in scheme 1.

2. Experimental

2.1. *Materials and methods*

All reagents were of AnalaR grade. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie and used without purification. The starting ruthenium(III) complexes $[RuCl_3(PPh_3)_3]$ [26], $[RuBr_3(PPh_3)_3]$ [27], and the Schiff bases [28] were prepared by the methods reported in the literature. Microanalyses were performed using a Vario EL III CHNS analyzer at Cochin University, Kerala, India. Infrared (IR) spectra were recorded in KBr pellets from 400 to 4000 cm^{-1} using a Shimadzu instrument. ^{1}H-NMR spectra for the ligands were recorded with a Bruker-NRC 500 MHz in the Indian Institute of Science, Bangalore. Electronic spectra were recorded in CH_2Cl_2 with a Systronics Double beam UV-Vis Spectrophotometer-2202 from 200 to 800 nm. X-band electron paramagnetic resonance (EPR) spectra of the powdered samples were recorded on a JEOL JESFA200 EPR spectrometer at room temperature (RT) and liquid nitrogen temperature (LNT) using diphenylpicrylhydrazyl as reference. Electrochemical studies were recorded in dichloromethane using a glassy carbon working electrode and $[NBu_4]ClO_4$ as the supporting electrolyte. Catalytic and biocidal studies were carried out in the Gene-Pool Biotech Research Center. Melting points were recorded on a Veego VMP-DS melting point apparatus and are uncorrected.



Abbreviation	R	Y
H_2L^1	H	O
H_2L^2	H	S
H_2L^3	H	COO
H_2L^4	CH_3	O
H_2L^5	CH_3	S
H_2L^6	CH_3	COO

Scheme 1. Preparation of mononucleating tetradentate Schiff-base ligands.

2.2. *Preparation of Schiff-base ligands*

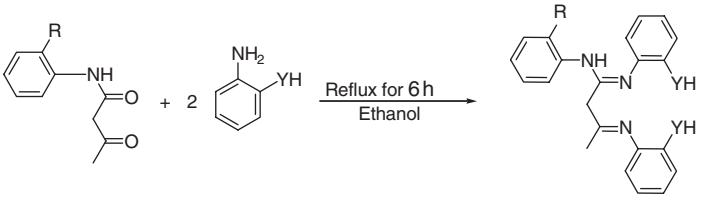
To an ethanolic solution of actetoacetanilide (0.17 g; 1 mmol)/acetoacetotoludide (0.19 g; 0.1 mmol), *o*-aminophenol(0.2 g; 2 mmol)/*o*-aminothiophenol (0.24 mL; 2 mmol)/*o*-aminobenzoic acid (0.27 g; 2 mmol) was added and the mixture was stirred for 30 min and then refluxed for 6 h (scheme 2). The resulting solution was concentrated and the product obtained was washed with ethanol and purity was checked by thin layer chromatography (TLC).

2.3. *Synthesis of new ruthenium(III) Schiff-base complexes*

All the new complexes were prepared by the following general procedure (scheme 3). To a solution of $[RuX_3(PPh_3)_3]$ (where X = Cl/Br) (1 mmol) in benzene (20 cm^3) the appropriate Schiff base (1 mmol) was added (1 : 1 molar ratio) and refluxed for 6 h. The solution was then concentrated to 3 cm^3 and cooled. The complexes were precipitated by the addition of a small quantity of petroleum ether (60–80°C), recrystallized from CH_2Cl_2/petroleum ether mixture, and dried *in vacuo*).

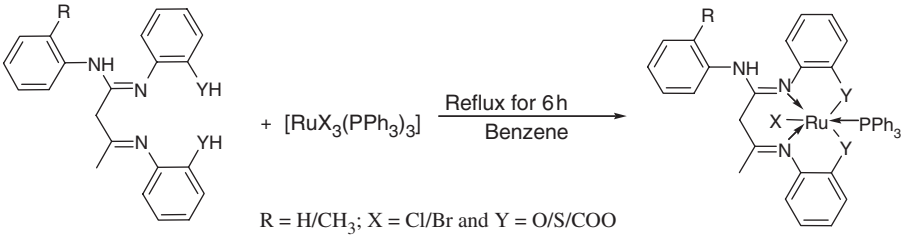
2.4. *Catalytic oxidation of alcohols*

Catalytic oxidation of alcohols (scheme 4) by the Schiff bases, ruthenium(III) starting complexes, and new ruthenium(III) Schiff-base complexes were carried and the results are given in table 1. Benzaldehyde and cyclohexanone were formed from benzyl alcohol and cyclohexanol, respectively, after stirring for 6 h in the presence of molecular



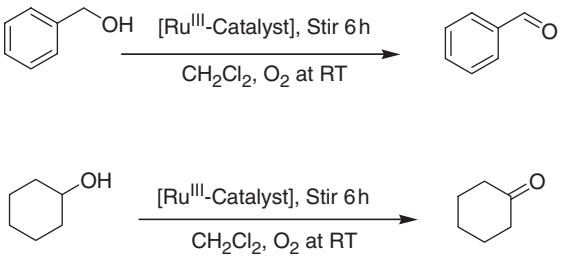
R = H/CH_3 and Y = O/S/COO

Scheme 2. Preparation of new tetradentate Schiff bases.

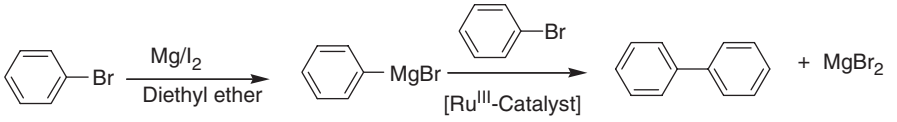


R = H/CH_3; X = Cl/Br and Y = O/S/COO

Scheme 3. Formation of new mononuclear Ru(III) Schiff-base complexes.



Scheme 4. Oxidation of alcohols in the presence of Ru(III) Schiff-base complexes.



Scheme 5. Phenyl–phenyl coupling in the presence of Ru(III) complexes.

oxygen; the resulting carbonyl compounds were quantified as 2,4-dinitrophenylhydrazone derivatives [29].

2.5. *Catalytic activity of ruthenium(III) Schiff-base complexes in aryl–aryl coupling*

Magnesium turnings (0.320 g) were placed in a two-necked round-bottomed flask 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 for 30 min. The remaining PhBr in Et_2O (5 cm^3) was added dropwise and the mixture was refluxed for 40 min. To this mixture, 1.03 cm^3 (0.01 mol) of PhBr in anhydrous Et_2O (5 cm^3) and the ruthenium complex (0.05 mmol) chosen for investigation were added and heated under reflux for 6 h. The reaction mixture was cooled and hydrolyzed with a saturated solution of aqueous NH_4Cl; the precipitated biphenyl was chromatographed to get pure sample and compared well with an authentic sample (69–72°C) [30]. The results are given in table 1 (scheme 5).

2.6. *Biocidal activity of ruthenium(III) Schiff-base complexes*

The ligands and their ruthenium complexes have been tested *in vitro* to assess their growth inhibitory activity against *Staphylococcus epidermidis*, *Escherichia coli*, *Botrytis cinerea*, and *Aspergillus niger* by the disc diffusion method [31]. *Streptomycin* and *co-trimoxazole* were used as standards. The ligands, ruthenium(III) starting complexes, and new ruthenium(III) complexes were stored at RT and dissolved in dichloromethane. Both the *S. epidermidis* and *E. coli* bacteria were grown in nutrient agar medium and incubated at 37°C for 24 h followed by frequent subculture to fresh medium and were used as test bacteria. The bacteria were cultured in nutrient agar medium in Petri plates and used as inoculum for the study. Both the *B. cinerea* and *A. niger* grown in Sabouraud dextrose agar medium were incubated at 27°C for 72 h

Table 1. Catalytic activity of ruthenium(III) Schiff-base complexes.

	Oxidation of alcohols				C–C coupling	
Complex	Substrate	Product	Yield	Turnover[a]	Yield (g)	Yield (%)
H_2L^1	A	C	03	05	0.01	3
	B	D	02	02		
H_2L^2	A	C	03	03	0.03	5
	B	D	03	05		
H_2L^3	A	C	04	05	0.02	4
	B	D	02	03		
H_2L^4	A	C	04	06	0.01	3
	B	D	05	05		
H_2L^5	A	C	02	04	0.03	5
	B	D	04	04		
H_2L^6	A	C	06	06	0.05	7
	B	D	05	07		
$[RuCl_3(PPh_3)_3]$	A	C	29	29	0.03	05
	B	D	31	33		
$[RuBr_3(PPh_3)_3]$	A	C	31	33	0.37	39
	B	D	35	36		
$[RuCl(PPh_3)(L^1)]$	A	C	75	77	0.59	61
	B	D	81	83		
$[RuCl(PPh_3)(L^2)]$	A	C	74	74	0.65	67
	B	D	85	87		
$[RuCl(PPh_3)(L^3)]$	A	C	76	77	0.68	70
	B	D	82	85		
$RuCl(PPh_3)(L^1)]$	A	C	73	75	0.62	64
	B	D	86	88		
$[RuCl(PPh_3)(L^2)]$	A	C	78	79	0.67	69
	B	D	86	86		
$[RuCl(PPh_3)(L^3)]$	A	C	78	80	0.57	59
	B	D	81	82		
$[RuBr(PPh_3)(L^1)]$	A	C	76	76	0.66	68
	B	D	81	83		
$[RuBr(PPh_3)(L^2)]$	A	C	75	77	0.68	70
	B	D	87	87		
$[RuBr(PPh_3)(L^3)]$	A	C	74	75	0.58	60
	B	D	83	84		
$[RuBr(PPh_3)(L^1)]$	A	C	76	78	0.64	66
	B	D	87	88		
$[RuBr(PPh_3)(L^2)]$	A	C	77	77	0.69	71
	B	D	89	90		
$[RuBr(PPh_3)(L^3)]$	A	C	79	80	0.67	69
	B	D	81	82		
O_2	A	C	5	7		–
	B	D	9	9		

Error limit, 0.2–0.3% for oxidation of alcohols; 0.2–0.5% for aryl–aryl coupling. A, cyclohexanol; B, benzylalcohol; C, cyclohexanone; and D, benzaldehyde.
[a]Moles per catalyst.

followed by periodic subculturing to fresh medium and were used as test fungi. The compounds to be tested were dissolved in dichloromethane to final concentrations of 0.25%, 0.5%, and 1% and soaked in filter paper discs of 5 mm diameter and 1 mm thickness. These discs were placed on the previously seeded plates and incubated at $35^\circ C \pm 2^\circ C$ for 24 h. The diameter (mm) of the inhibitory zone around each disc was measured after 24 h. *Ciprofloxacin* and *co-trimoxazole* were

used as standards. Inhibition was recorded by measuring the diameter of the inhibitory zone after incubation.

3. Results and discussion

Stable ruthenium(III) Schiff-base complexes [RuX(PPh$_3$)(L)] (X = Cl/Br; L = dianion of the tetradentate Schiff base) have been prepared by reacting [RuX$_3$(PPh$_3$)$_3$] (X = Cl or Br) with the respective Schiff bases in a 1 : 1 molar ratio in benzene. All the complexes are soluble in common organic solvents. The analytical data (Supplementary material) obtained for the new complexes agree well with the proposed molecular formula. In all of the above reactions, the Schiff bases are bibasic tetradentate ligands.

3.1. *Spectroscopic studies*

3.1.1. FT-IR spectra. IR spectra of the free Schiff bases were compared with those of the ruthenium complexes to ascertain the binding of the Schiff base to ruthenium and the results are given in table 2. The free Schiff-base ligands showed a strong band at 1603–1667 cm^{-1}, characteristic of the azomethine $\nu_{(C=N)}$ group. Coordination of the Schiff bases to metal through nitrogen is expected to reduce the electron density in the azomethine link and lower the $\nu_{(C=N)}$ absorption frequency. The band due to $\nu_{(C=N)}$ shifts to lower frequencies 1578–1657 cm^{-1} in the complexes, indicating coordination of the azomethine nitrogen to ruthenium [12, 13, 32–34]. A strong band at 1310–1330 cm^{-1} in the free Schiff bases H_2L^1 and H_2L^4 has been assigned to the phenolic C–O stretch. On complexation, this band is shifted to higher frequency, 1437–1439 cm^{-1}, indicating coordination through phenolic oxygen [32–35]. This has been further supported by disappearance of the broad $\nu_{(OH)}$ band around 3000 cm^{-1} in [RuCl(PPh$_3$)(L^1)], [RuCl(PPh$_3$)(L^4)], [RuBr(PPh$_3$)(L^1)], and [RuBr(PPh$_3$)(L^4)], indicating deprotonation of the phenolic proton prior to coordination. A very weak absorption at 2600 cm^{-1} corresponding to $\nu_{(S-H)}$ in the free Schiff base disappears in spectra of the complexes due to coordination through sulfur after deprotonation. Moreover, the absorption due to $\nu_{(C-S)}$ of the ligand at 1212–1245 cm^{-1} shifts to higher frequency (1246–1266 cm^{-1}) in [RuCl(PPh$_3$)(L^2)], [RuCl(PPh$_3$)(L^5)], [RuBr(PPh$_3$)(L^2)], and [RuBr(PPh$_3$)(L^5)] indicating that coordination is through the phenolic sulfur [11]. For the anthranilic acid moiety, the free Schiff bases H_2L^3 and H_2L^6 show $\nu_{(O-H)}$ at 3300 cm^{-1} and $\nu_{(C=O)}$ of the carbonyl at 1680 cm^{-1}, and also shows the absorption bands at 1668–1671 cm^{-1} and 1419–1420 cm^{-1} for asymmetric $\nu_{(COO^-)}$ and symmetric $\nu_{(COO^-)}$, respectively. In [RuCl(PPh$_3$)(L^3)], [RuCl(PPh$_3$)(L^6)], [RuBr(PPh$_3$)(L^3)], and [RuBr(PPh$_3$)(L^6)], the bands were observed at 1654–1657 cm^{-1} and 1409–1438 cm^{-1} arising from asymmetric $\nu_{(COO^-)}$ and symmetric $\nu_{(COO^-)}$ stretching of carboxylate [13]. This indicates coordination of carboxyl to ruthenium in the complexes. The differences between the asymmetric and symmetric stretching frequencies of the coordinated carboxyl lie in the 219–245 cm^{-1} range, a clear indication of monodentate coordination [12, 35]. Characteristic bands due to triphenylphosphine were observed in the expected region.

Table 2. IR, electronic, and EPR spectral data of ruthenium(III) Schiff-base complexes.

Complex	IR					Electronic λ_{max} nm (ε) dm^3 mol^{-1}	EPR			
	$\nu_{C=N}$	ν_{asyCOO^-}	ν_{syCOO^-}	ν_{C-O^-}	ν_{C-S^-}		g_x	g_y	g_z	$\langle g\rangle$[a]
H_2L^1	1603	–	–	1310	–	255(589), 294(843), 359(1914), 426(3283)	–	–	–	–
H_2L^2	1617	–	–	–	1245	256(706), 291(482), 369(1993), 388(704)	–	–	–	–
H_2L^3	1617	1668	1419	–	–	261(1024), 293(824), 369(501), 387(2101)	–	–	–	–
H_2L^4	1605	–	–	1330	–	256(1766), 298(845), 342(3283), 418(1680)	–	–	–	–
H_2L^5	1667	–	–	–	1212	256(1166), 296(3380), 369(662), 392(844)	–	–	–	–
H_2L^6	1615	1671	1420	–	–	261(1031), 297(1646), 369(1001), 387(846)	–	–	–	–
[RuCl(PPh$_3$)(L^1)]	1654	–	–	1437	–	256(693), 302(1113), 363(1815), 389(1035), 470(1439), 574(953)	1.82	1.9	1.94	1.9
[RuCl(PPh$_3$)(L^2)]	1654	–	–	–	1266	255(582), 291(1035), 351(426), 470(271), 504(465), 572(540)	1.83	1.83	2.03	1.9
[RuCl(PPh$_3$)(L^3)]	1597	1654	1438	–	–	256(1743), 296(1041), 359(598), 564(293)	1.9	1.9	1.92	1.91
[RuCl(PPh$_3$)(L^4)]	1620	–	–	1439	–	256(1163), 296(1685), 368(4403), 402(11894), 429(6569), 566(6831)	1.94	–	–	1.12
[RuCl(PPh$_3$)(L^5)]	1637	–	–	–	1256	256(1748), 294(3358), 348(3994), 536(525), 636(491)	1.74	1.9	1.93	1.9
[RuCl(PPh$_3$)(L^6)]	1579	1655	1438	–	–	256(1163), 297(1673), 351(3335), 644(5250)	1.65	1.8	1.96	1.81
[RuBr(PPh$_3$)(L^1)]	1654	–	–	1437	–	255(4303), 296(6100), 347(470), 473(3160), 581(4600)	1.8	1.90	1.91	1.9
[RuBr(PPh$_3$)(L^1)][b]						–	1.83	1.87	2.06	1.9
[RuBr(PPh$_3$)(L^2)]	1654	–	–	–	1260	254(4668), 287(8892), 470(2869), 503(1163), 572(1231)	1.8	1.93	1.99	1.91
[RuBr(PPh$_3$)(L^3)]	1590	1655	1438	–	–	256(1166), 296(8413), 369(9950), 401(5831), 429(6950), 573(5545)	2.2	–	–	1.27
[RuBr(PPh$_3$)(L^4)]	1624	–	–	1437	–	256(6930), 300(4800), 366(9875), 404(15992), 430(1620), 551(1696)	1.9	–	–	1.1
[RuBr(PPh$_3$)(L^5)]	1657	–	–	–	1246	254(7030), 294(8500), 364(1953), 388(3558), 518(1209), 638(2133)	1.9	1.9	2.2	2
[RuBr(PPh$_3$)(L^6)]	1578	1657	1409	–	–	254(1178), 293(1686), 359(1252), 388(1621), 431(2538), 639(3447)	1.65	1.93	1.9	1.82

[a] $\langle g\rangle = \left[1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2\right]^{1/2}$.

[b] Recorded at LNT.

3.1.2. Electronic spectra. The electronic spectra of all the ligands and complexes in dichloromethane showed 4–6 bands in the 254–644 nm regions (table 2). The electronic spectra of free ligands showed two types of transitions, the first at 255–298 nm which can be assigned to π–π^* transition due to transitions involving molecular orbitals located on the oxygen of the phenolic/carboxylic or thiophenolic sulfur chromophore. These peaks shift in spectra of the complexes due to donation of a lone pair of electrons from the oxygen of the phenolic/carboxylic or thiophenolic sulfur group to ruthenium. This reveals that one coordination site is oxygen of the phenolic and carboxylic and sulfur of the thiophenolic groups. The second type of transitions at 342–426 nm are assigned to $n \rightarrow \pi^*$ transition due to azomethine and benzene of the ligands. These bands also shift in spectra of the new complexes indicating involvement of imine nitrogens in coordination. Spectra of all the complexes showed another transition in the range 254–473 nm which can be assigned to ligand-to-metal charge transfer followed by intra-ligand transitions, respectively, based on the extinction coefficients ($\varepsilon = 271$–$15{,}992\ \mathrm{dm^3\,mol^{-1}}$) which are characteristic of ruthenium(III) octahedral complexes [36, 37]. The other types of bands in the visible region 503–644 nm can be attributed to d–d transitions involving the metal orbitals [38].

3.1.3. ^{1}H-NMR spectra of the Schiff-base ligands. ^{1}H-NMR spectra of the ligands in $CDCl_3$ (Supplementary material) show multiplets at 6.3–8.1 ppm for aromatic protons. The –NH proton, $–CH_2$ proton, and methyl protons appear as singlets in the regions 8.6–10.1 ppm, 2.4–3.5 ppm, and 1.8–2.2 ppm for all the ligands. In H_2L^1 and H_2L^4, the phenolic OH appears as a singlet at 10.8–10.9 ppm. In H_2L^2 and H_2L^5, the thiophenolic SH appears as a singlet at 3.6–3.7 ppm. In H_2L^3 and H_2L^6, the COOH proton appears as a singlet at 9.6–10.8 ppm.

3.1.4. EPR spectra. EPR parameters observed for the complexes at RT and LNT (table 2) were recorded at X-band frequencies. Three of the complexes [RuCl(PPh_3)(L^4)], [RuBr(PPh_3)(L^3)], and [RuBr(PPh_3)(L^4)] have isotropic spectra with "g" of 1.9–2.2. Such isotropic lines are usually observed either due to intermolecular spin exchange which can broaden the lines or due to occupancy of the unpaired electrons in degenerate orbitals. In addition, the nature and position of the lines in the spectra of these complexes are similar to those of the other octahedral complexes [34]. [RuCl(PPh_3)(L^2)], [RuCl(PPh_3)(L^3)], and [RuBr(PPh_3)(L^5)] exhibited spectra with $g_x = g_y \neq g_z$, indicative of a tetragonal distortion in octahedral complexes [16]. [RuCl(PPh_3)(L^1)], [RuCl(PPh_3)(L^5)], [RuCl(PPh_3)(L^6)], [RuBr(PPh_3)(L^1)], [RuBr(PPh_3)(L^2)], and [RuBr(PPh_3)(L^6)] at RT exhibited three lines with different "g" values, indicating magnetic anisotropy. The presence of three "g" values is indicative of a rhombic distortion [39]. The spectra of [RuBr(PPh_3)(L^1)] (figure 1) at RT and LNT shows no variation.

3.2. *Cyclic voltammetry*

Complexes were electrochemically examined at a glassy carbon working electrode in dichloromethane using cyclic voltammetry (Supplementary material). The oxidation and reduction of each complex were characterized by well-defined waves with E_f values

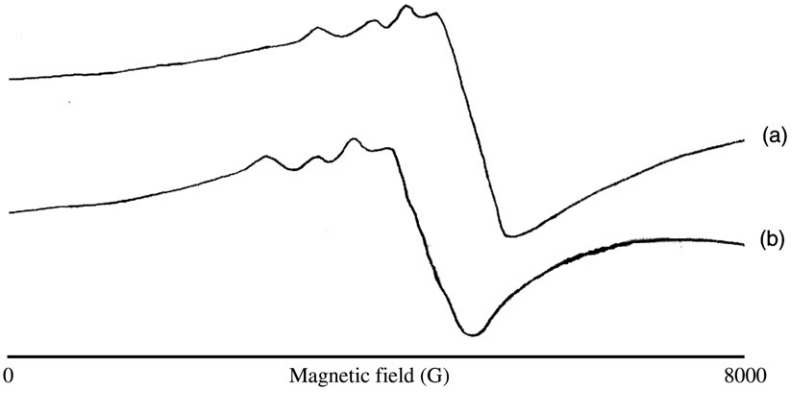


Figure 1. EPR spectra of [RuBr(PPh_3)(L^1)] at (a) RT and (b) LNT.

in the range from 0.3 to 1.25 mV (oxidation) and from −3.4 to −1.45 mV (reduction) against Ag/AgCl electrode. [RuCl(PPh_3)(L^4)], [RuBr(PPh_3)(L^3)], [RuBr(PPh_3)(L^5)], and [RuBr(PPh_3)(L^1)] show reversible oxidations in the range 80–100 mV. [RuBr(PPh_3)(L^2)] shows reversible reduction at 90 mV and [RuCl(PPh_3)(L^2)] showed reduction only. Other complexes showed redox couples with peak-to-peak separation values (ΔE_p) ranging from 120 to 790 mV revealing that this process is at best quasi-reversible [40], attributed to slow electron transfer and adsorption of the complex on to the electrode surface; a representative picture is provided in "Supplementary material."

3.3. *Catalytic activity*

3.3.1. Oxidation of alcohols. Catalytic oxidations of alcohols (scheme 4) by the new ruthenium(III) Schiff-base complexes are given in table 1. Benzaldehyde and cyclohexanone were formed from benzyl alcohol and cyclohexanol, respectively, after stirring for 6 h. Only a very little amount of carbonyl compound is formed when the reaction is carried out in the presence of Schiff bases under oxygen atmosphere at ambient temperature without the catalyst. The relatively higher product obtained for oxidation of benzyl alcohol compared with cyclohexanol due to α-CH of benzyl alcohol is more acidic than cyclohexanol [41]. The catalytic activity of the ruthenium(III) starting complexes is higher than that of the Schiff bases but lower than that of the chelate complexes. The reaction was repeated four times and the corresponding carbonyl compound was produced at the same rate as in the first run. The error limit was found to be 0.2–0.3%.

3.3.2. Aryl–aryl coupling. The new ruthenium(III) complexes have been used as catalysts for phenyl–phenyl coupling reactions (scheme 5) and the results are given in table 1. The system chosen for the study is the coupling of phenyl magnesium bromide with bromobenzene to give biphenyl. Bromobenzene was first converted into the Grignard reagent, followed by the addition of the complex chosen for investigation,

Table 3. Antimicrobial activity of ruthenium(III) Schiff-base complexes.

	Antibacterial activity						Antifungal activity					
	S. epidermidis			*E. coli*			*B. cinerea*			*A. niger*		
Complex	0.25%	0.5%	1%	0.25%	0.5%	1%	0.25%	0.5%	1%	0.25%	0.5%	1%
$[RuCl_3(PPh_3)_3]$	21	21	23	24	24	26	22	23	23	20	21	21
$[RuBr_3(PPh_3)_3]$	20	23	23	23	23	25	21	22	22	23	23	23
H_2L^1	4	5	5	3	3	5	4	4	4	2	3	3
H_2L^2	7	7	8	6	5	5	7	7	7	5	5	6
H_2L^3	3	3	4	5	5	5	6	6	7	2	2	2
H_2L^4	3	5	5	4	5	5	2	2	3	4	5	4
H_2L^5	6	5	5	7	8	8	5	5	5	6	7	7
H_2L^6	3	3	3	5	5	6	6	6	7	5	5	6
$[RuCl(PPh_3)(L^1)]$	27	27	27	29	29	30	31	31	32	35	35	35
$[RuCl(PPh_3)(L^2)]$	29	29	29	26	27	27	28	29	29	26	26	26
$[RuCl(PPh_3)(L^3)]$	30	30	30	29	29	30	28	28	29	27	27	27
$[RuBr(PPh_3)(L^4)]$	27	29	29	27	28	29	30	28	28	26	26	26
$[RuBr(PPh_3)(L^5)]$	27	27	29	26	27	27	29	29	30	26	25	26
$[RuBr(PPh_3)(L^6)]$	26	26	26	28	28	30	28	29	29	28	29	28
Standard	*Streptomycin* (22)						*Co-trimoxazole* (21)					
Dichloromethane	No activity											

Error limit, 0.2–0.5 mm.

and the mixture was heated under reflux for 6 h. Only little biphenyl was isolated when the reaction was carried out without the catalyst; an insignificant amount compared to biphenyl was obtained from the reaction catalyzed by ruthenium(III) complexes [42]. The catalytic activity of the ruthenium(III) starting complexes is higher than that of the Schiff bases but lower than that of the chelate complexes. The experiment was repeated thrice and the error limit was found to be 0.2–0.5%.

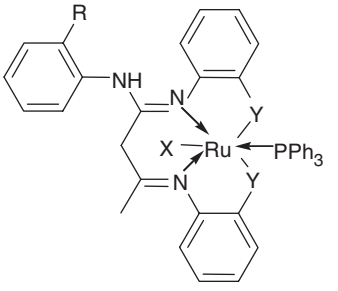
3.4. *Biocidal activity of ruthenium(III) Schiff-base complexes*

The *in vitro* cytotoxicity of ligands and complexes were screened in order to evaluate the activity against *S. epidermidis*, *E. coli*, *B. cinerea*, and *A. niger* at 0.25%, 0.50%, and 1% concentrations (table 3). The ruthenium(III) Schiff-base complexes are more active than the parent ligands, ruthenium(III) precursors, and standard reference against the same microbes under identical experimental conditions [43, 44]. The microbial screening was repeated twice and the error limit was found to be 0.2–0.5 mm.

Based on the physico-chemical and spectroscopic data, an octahedral structure has been proposed for the mononuclear ruthenium(III) complexes (scheme 6).

4. Conclusion

New six-coordinate ruthenium(III) complexes have been synthesized using Schiff bases formed by condensing actetoacetanilide/acetoacetotoludide with *o*-aminophenol/*o*-aminothiophenol/*o*-aminobenzoic acid in 1 : 2 stoichiometric ratio. The new



R=H/CH_3; X=Cl/Br and Y=O/S/COO

Scheme 6. Proposed structure for the new mononuclear ruthenium(III) complexes.

complexes have been characterized by analytical and spectral (IR, electronic, and EPR) studies. An octahedral structure has been proposed for all the complexes. All complexes show good catalytic and antimicrobial activities. Our Schiff-base complexes show better activity in catalysis and biocidal studies [11, 34, 36]. In these articles, oxidation of alcohols was carried out using *N*-methylmorpholine-*N*-oxide as oxidant. But *N*-methylmorpholine-*N*-oxide releases oxides of nitrogen which leads to pollution. In our study, we prefer molecular oxygen as the oxidant, which is a greener technique. Synthesis, characterization, and crystal data have been reported [45, 46], but we have carried out application studies. Ruthenium(III) Schiff-base complexes in the literature [47] have poor antibacterial activities, but our complexes have better inhibitory activity against bacteria and fungi than the standard compounds.

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