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Synthesis, Spectral, Catalytic, and Bioactivity Studies of Ruthenium(III) Complexes Containing ONO Donor Schiff Base Ligands

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New hexa-coordinated ruthenium(III) complexes of the type $[RuX(EPh_3)_2L]$ (X = Cl or Br; E = P or As; L = deprotonated dibasic tridentate Schiff base ligand) have been synthesized by the reactions of $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$ or $[RuBr_3(AsPh_3)_3]$ with the appropriate Schiff bases. The Schiff bases were synthesized by the condensation of anthranilic acid with acetyl acetone/salicylaldehyde/*o*-vanillin/*o*-hydroxy acetophenone. The complexes were characterized by elemental analyses, spectral (FT-IR, electronic and EPR) electrochemical, and magnetic moment data. Catalytic activity of the complexes in the oxidation of alcohols and the antibacterial activity of the ligands and the complexes have also been studied.

Keywords antibacterial activity, NMO, oxidation of alcohol, ruthenium(III), Schiff base

INTRODUCTION

Oxidation of organic substrates as catalyzed by coordination complexes of transition metals in resemblance of enzymatic oxidations is an intriguing area of current research[1] Selective alcohol oxidation is a prominent reaction in laboratory and industrial synthetic chemistry and has attracted substantial recent effort. Many catalytic systems have been reported for the oxidation of alcohols. They have some drawbacks, such as instability of the oxidant at room temperature,[2] not effective for non-activated alcohols,[3] over oxidation of the alcohol to acid or production of toxic waste,[4] or not effective for unsaturated alcohols,[5] but metal nanoparticles and ionic liquids are successively used for the oxidation of alcohols.[6,7] Ruthenium complexes by virtue of their wide range of chemically accessible oxidation states have been subject of many recent investigations. Ruthenium compounds have been extensively investigated as catalysts for alcohol oxidations using a variety of primary oxidants like iodosobenzene, *N*-methylmorpholine-*N*-oxide[8,9] *tert*-butyl hydroperoxide, molecular oxygen with ruthenium supported on a $CaO–ZrO_2$ solid solution.[10] Changes in the electronic, steric, and geometric properties of the ligand alter the orbitals at the metal center, and thus affect its properties. In catalytic asymmetric systems, small changes in the donating ability of the ligand or the size of its substituents can have a dramatic effect on the catalyst efficiency and enantioselectivity.[1] The Schiff base transition metal complexes are attractive oxidation catalysts because of their cheap, easy synthesis and their chemical and thermal stability.[11] Hence, to explore the effect of the Schiff base ligands on the catalytic efficiency of ruthenium metal, and also to investigate the influence of the substituents, we have synthesized a series of ruthenium(III) complexes with four Schiff base ligands containing ONO donor atoms. Schiff base transition metal complexes find a variety of applications including biological, clinical, analytical and industrial, in addition to their important role in catalysis and organic synthesis.[11] In view of the promising physiological properties of Schiff bases, we were interested to study the biological role of metal ions on them. In connection with such studies and continuation of our research on synthesis, spectral studies, catalytic and bioactivities of ruthenium complexes with simple and inexpensive ligands,[12–14] we describe here the synthesis, characterization, and redox properties of ruthenium(III) complexes containing tridentate Schiff bases along with their reactivity towards oxidation of alcohols in the presence of NMO. The antibacterial activity studies of Schiff bases and their ruthenium complexes were also carried out. The ligands used in this study were prepared by the condensation of anthranilic acid with acetyl acetone/salicylaldehyde/*o*-vanillin/*o*-hydroxy acetophenone and they have the following structure (Figure 1).

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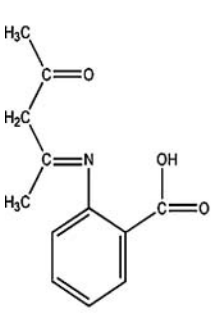
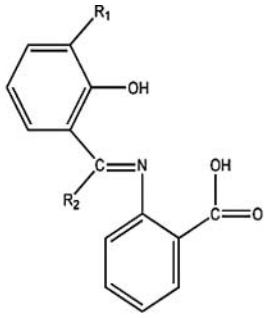


H_2Anth-acac



R^1	R^2	Acronym
H	H	H_2Anth-sal
OCH_3	H	H_2Anth-ovan
H	CH_3	H_2Anth-ohap

FIG. 1. Structure of the Schiff base ligands.

EXPERIMENTAL

Materials and Methods

All the reagents used were analytical reagent grade. Solvents were purified and dried according to the standard procedures.[15] $RuCl_3.3H_2O$ was purchased from Loba Chemie. C H N analysis were performed in Vario EL III CHNS analyzer at Cochin University, Kerala. IR spectra of the complexes were recorded in KBr pellets with a Perkin–Elmer 597 infrared spectrophotometer in the range 4000–200 cm^{-1}. Electronic spectra were recorded in dichloromethane with a Systronics double beam UV-Vis Spectrophotometer 2202. X-band EPR Spectra of powdered samples at RT and LNT were recorded with Bruker model ER-200-D Spectrometer using DPPH as g-marker at Indian Institute of technology, Chennai. Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon working electrode and potentials were referenced to standard calomel electrode using $[N(Bu)_4BF_4]$ as supporting electrolyte. Melting points were recorded on a Raaga heating table and are uncorrected. Magnetic susceptibility measurements were made with an EG and G-PARC vibrating sample magnetometer. Molecular weights were determined by Rast micro method. Molar conductivities of freshly prepared solutions were measured using Elico CM 180 conductivity meter. $[RuCl_3(PPh_3)_3]$[16] $[RuCl_3(AsPh_3)_3]$[17] $[RuBr_3(AsPh_3)_3]$[18] and ligands[19] were prepared by reported methods.

Preparation of the Complexes

A representative procedure for the preparation of the ruthenium(III) complexes is detailed here. To a solution of $[RuCl_3(PPh_3)_3]$ (0.1 g; 0.1 mmol) in benzene (50 mL), 0.02 g (0.1 mmol) of H_2Anth-acac was added and refluxed for 6 h. The resulting solution was concentrated to *ca* 5 mL and the product was precipitated by the addition of petroleum ether (60–80°C). The precipitate was washed with petroleum ether and recrystallized from petroleum ether-dichloromethane mixture.

Catalytic Oxidation Experiments

To a solution of the alcohol (0.1–0.12 mL, 1 mmol) in 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 give the corresponding carbonyl compound, which was then quantified as its 2,4-dinitrophenylhydrazone.[15,20]

Biocidal Studies

The ligands and their complexes have been screened for the *in vitro* growth inhibitory activity against the gram negative bacteria *Escherichia coli* and the gram positive bacteria *Bacillus subtilis* using disc diffusion method. The bacteria were cultured in nutrient agar medium and used as inoculum for the 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 in filter paper discs (5 mm diameter, 1 mm thick). These discs were placed on the already 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 and was taken as a measure of inhibitory activity. Ampicillin was used as a standard.[21]

RESULTS AND DISCUSSION

All the complexes are quite stable in air and light. The analytical data and the molecular weights (Table 1) for the complexes are in good agreement with the molecular formula proposed (Table 2). The molar conductivity values for the complexes in DMSO solvent (1.0×10^{-3} mol) are in the range 7.9–12.1 ohm^{-1} cm^2 mol^{-1}. It is clear from the conductivity measurement that the complexes are non-electrolytic in nature.

IR Spectra

IR spectrum of the ligand H_2Anth-acac shows a band at 1597 cm^{-1}, which is assigned to the $\nu_{C=O}$ of the acetyl acetone moiety. Absence of this band and the appearance of a new band at 1521 cm^{-1} in the spectrum of the corresponding complexes, which may be assigned to the CH=C group, confirms the enolization of the $H_2C{-}C{=}O$ group. But these complexes do not show any peak around 3000 cm^{-1}, which indicates the deprotonation of the enolic OH. The above observations confirm the coordination of the deprotonated enolic oxygen of the

TABLE 1
Analytical and FT-IR spectral data of ruthenium(III) complexes

Complex	Color	Yield %	M.P°C	Mol.wt found (calcd)	Elemental analysis % found (calcd)			IR spectra			
					C	H	N	$\nu_{C=N}$cm $^{-1}$ cm^{-1}	$\nu_{asymCOO-}$ cm^{-1}	$\nu_{symCOO-}$ cm^{-1}	ν_{Ph-CO} cm^{-1}
[RuCl(PPh_3)$_2$(Anth-acac)]	Grey	53	186	883 (878)	66.20 (65.63)	4.72 (4.70)	1.62 (1.59)	1541	1683	1435	—
[RuCl(PPh_3)$_2$(Anth-sal)]	Green	51	188	897 (900)	66.00 (66.96)	4.12 (4.37)	1.65 (1.56)	1521	1649	1435	1313
[RuCl(PPh_3)$_2$(Anth-ovan)]	Black	92	245	926 (930)	64.20 (65.83)	4.20 (4.44)	1.38 (1.51)	1540	1699	1433	1317
[RuCl(PPh_3)$_2$(Anth-ohap)]	Black	60	221	911 (914)	67.89 (66.99)	4.70 (4.52)	1.68 (1.53)	1539	1697	1455	1316
[RuCl($AsPh_3$)$_2$(Anth-acac)]	Green	73	176	962 (966)	60.98 (59.66)	4.48 (4.28)	1.60 (1.45)	1541	1691	1435	—
[RuCl($AsPh_3$)$_2$(Anth-sal)]	Green	79	190	985 (988)	59.02 (60.76)	4.05 (3.98)	1.49 (1.42)	1537	1680	1438	1302
[RuCl($AsPh_3$)$_2$(Anth-ovan)]	Green	82	220	1022 (1018)	61.00(60.15)	4.34 (4.06)	1.43 (1.38)	1533	1700	1437	1306
[RuCl($AsPh_3$)$_2$(Anth-ohap)]	Blue	62	161	1000 (1002)	62.44 (61.11)	4.32 (4.12)	1.59 (1.40)	1541	1700	1456	1315
[RuBr($AsPh_3$)$_2$(Anth-acac)]	Black	65	215	1006 (1011)	57.87 (57.03)	4.24 (4.09)	1.29 (1.39)	1550	1670	1433	—
[RuBr($AsPh_3$)$_2$(Anth-sal)]	Brown	68	159	1027 (1032)	58.90 (58.15)	3.9 0 (3.81)	1.47 (1.36)	1523	1643	1456	1313
[RuBr($AsPh_3$)$_2$(Anth-ovan)]	Green	90	240	1059 (1063)	58.64 (57.64)	3.65 (3.89)	1.43 (1.32)	1540	1700	1436	1316
[RuBr($AsPh_3$)$_2$(Anth-ohap)]	Blue	62	129	1043 (1047)	57.43 (58.52)	3.79 (3.95)	1.43 (1.34)	1541	1700	1456	1315

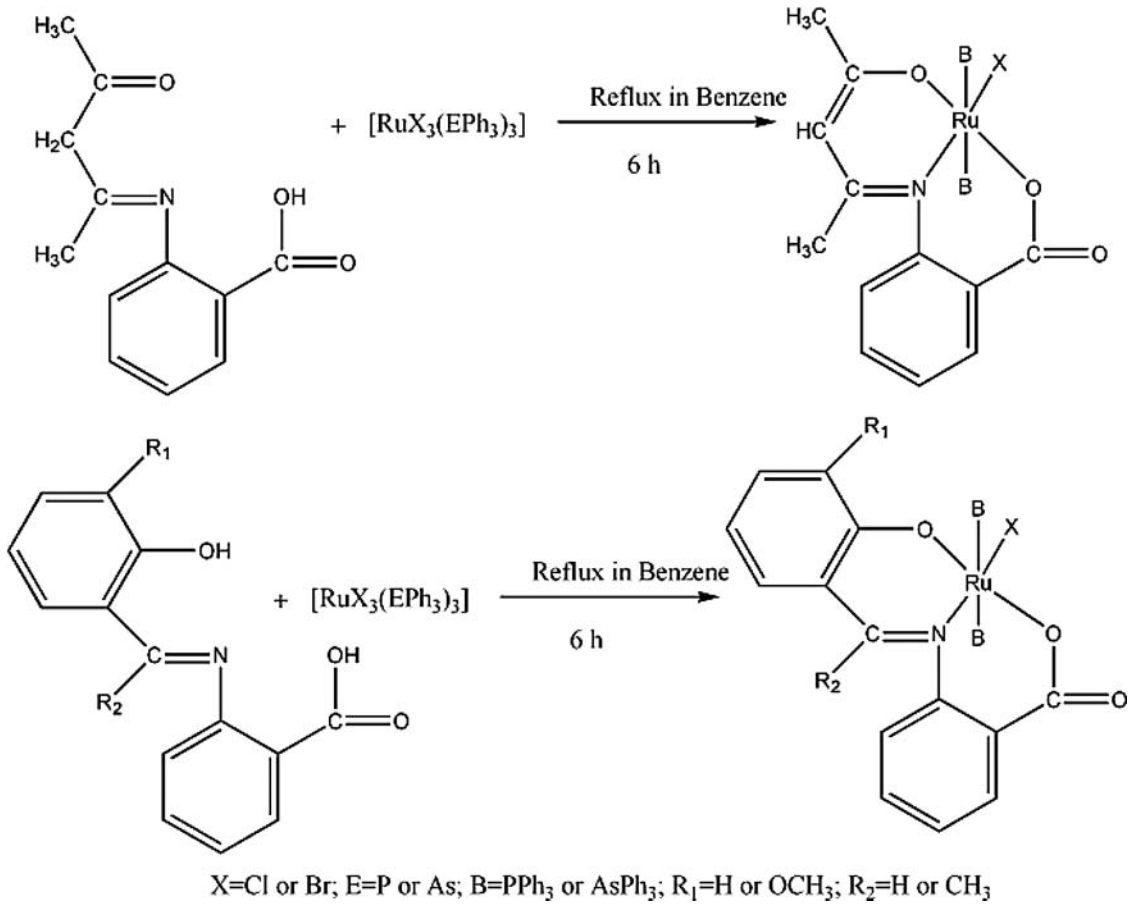


FIG. 2. Preparation of ruthenium(III) complexes.

ligand H_2Anth-acac to the ruthenium. Similarly, coordination of the deprotonated phenolic oxygen of the ligands H_2Anth-sal, H_2 Anth-ovan and H_2 Anth-ohap to ruthenium is indicated by the following observations. Disappearance of the band around 3400 cm^{-1}, which is due to phenolic $\nu_{(O-H)}$ and the appearance of $\nu_{(C-O)}$ band of the phenolic group at a higher wave number, from 1292–1299 cm^{-1} to 1302–1317 cm^{-1}.[22] In all the ligands, the band found around 1560–1577 cm^{-1} is assigned to $\nu_{(C=N)}$. This band undergoes a negative shift (1521–1550 cm^{-1}) in the spectrum of the complexes suggesting the azomethine nitrogen coordination to ruthenium[22] The band due to$\nu_{(O-H)}$ of the carboxylic acid group which is present in the spectra of the ligands disappears in the spectrum of the complexes. A band observed around 1687–1732 cm^{-1} due to the carboxylic carbonyl group in the ligands is observed at 1643–1700 cm^{-1} and at 1433–1456 cm^{-1} in the complexes arising from ν_{asy} and ν_{sym} frequencies of the COO^- group, respectively. The difference between ν_{asy} and ν_{sym} frequencies has been found to be ~250 cm^{-1}. This is a clear indication of the monodentate coordination of the carboxyl group with free carbonyl group after deprotonation[23] Coordination of the Schiff base ligands through nitrogen and oxygen to ruthenium is further confirmed by the bands present at 440–458 cm^{-1} and at 413–421 cm^{-1}, which are due to ν_{Ru-N} and $\nu_{Ru-O,}$ respectively.[24] Thus, in all the complexes, the Schiff bases behave as dibasic tridentate ligands. $\nu_{(Ru-Cl)}/\nu_{(Ru-Br)}$ absorption has been found in the 310–320 cm^{-1} /245–250 cm^{-1} region and $\nu_{(Ru-P)}/\nu_{(Ru-As)}$ vibrations display a band around 514–523 cm^{-1}/470–484 cm^{-1} in the spectra of the complexes.[25] Characteristic bands of $PPh_3/AsPh_3$ are observed in the spectra of all the complexes at 1440, 1080, 740, and 680 cm^{-1}.

Electronic Spectra

The electronic spectra of the free ligands show two types of transitions, the first one appears at 255–297 nm (ε = 13820–21580 $dm^3mol^{-1}cm^{-1}$), which can be assigned to $\pi \rightarrow \pi^*$ transition of the phenolic chromophore. These peaks are shifted to lower wavelength (2–14 nm) in the spectra of the complexes. This may be due to the donation of a lone pair of electrons by the oxygen of the phenoxy group to the metal atom.[26] The second type of transition appears at 351–399 nm (ε =15800–24730 $dm^3mol^{-1}cm^{-1}$), which can be assigned to n $\rightarrow \pi^*$ transition of the C=N chromophore. These peaks appear at a lower wavelength (5–29 nm) in the spectra of the complexes. This indicates that the imine group nitrogen atom is coordi-

TABLE 2
Electronic spectral data of ruthenium(III) complexes

Complex	λmax (nm) (ε; $dm^3mol^{-1}cm^{-1}$)	Transition energy (cm^{-1})	Assignments	ν_2/ν_1	10Dq	B	C
	663 (767)	15083	$^2T_2g \rightarrow {}^4T_1g$				
$[RuCl(PPh_3)_2(Anth\text{-}acac)]$	519 (2687)	19268	$^2T_2g \rightarrow {}^4T_2g$	1.28	26358	523	2165
	432 (2380)	23148	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	639 (876)	15649	$^2T_2g \rightarrow {}^4T_1g$				
$[RuCl(PPh_3)_2(Anth\text{-}sal)]$	520 (2885)	19231	$^2T_2g \rightarrow {}^4T_2g$	1.23	26678	448	2198
	424 (3591)	23585	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	635 (819)	15748	$^2T_2g \rightarrow {}^4T_1g$				
$[RuCl(PPh_3)_2(Anth\text{-}ohap)]$	516 (2854)	19380	$^2T_2g \rightarrow {}^4T_2g$	1.23	26357	454	2085
	428 (2904)	23364	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	638 (872)	15674	$^2T_2g \rightarrow {}^4T_1g$				
$[RuCl(AsPh_3)_2(Anth\text{-}acac)]$	515 (2698)	19417	$^2T_2g \rightarrow {}^4T_2g$	1.24	26251	468	2059
	430(2874)	23256	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	690 (842)	14493	$^2T_2g \rightarrow {}^4T_1g$				
$[RuCl(AsPh_3)_2(Anth\text{-}sal)]$	519 (2753)	19267	$^2T_2g \rightarrow {}^4T_2g$	1.33	27740	597	2566
	417(2954)	23981	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	665 (704)	15038	$^2T_2g \rightarrow {}^4T_1g$				
$[RuBr(AsPh_3)_2(Anth\text{-}acac)]$	520 (2652)	19231	$^2T_2g \rightarrow {}^4T_2g$	1.28	26022	524	2091
	437(3852)	22883	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	688 (719)	14535	$^2T_2g \rightarrow {}^4T_1g$		25977		
$[RuBr(AsPh_3)_2(Anth\text{-}sal)]$	520 (2787)	19230	$^2T_2g \rightarrow {}^4T_2g$	1.32		587	2127
	441(4450)	22676	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	657 (798)	15221	$^2T_2g \rightarrow {}^4T_1g$				
$[RuBr(AsPh_3)_2(Anth\text{-}ovan)]$	514 (2851)	19455	$^2T_2g \rightarrow {}^4T_2g$	1.28	26608	529	2185
	428 (4390)	23364	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				
	657 (876)	15221	$^2T_2g \rightarrow {}^4T_1g$				
$[RuBr(AsPh_3)_2(Anth\text{-}ohap)]$	517 (2856)	19342	$^2T_2g \rightarrow {}^4T_2g$	1.27	27416	515	2405
	417 (4298)	23981	$^2T_2g \rightarrow {}^2A_1g, {}^2T_1g$				

nated to the metal atom.[27] The transitions observed at 417–520 nm (ε =2380–4450 $dm^3mol^{-1}cm^{-1}$) in the spectra of the complexes can be assigned to charge transfer transitions. These bands obscure the weak d-d transitions occurring in this region. The weak transitions observed at 635–690 nm (ε =704–876 $dm^3mol^{-1}cm^{-1}$) can be attributed to d-d transition in the metal orbitals. Octahedral low spin d^5 complexes have the $^2T_{2g}$ ground state corresponding to the electronic state t_{2g}^5 and the observed bands correspond to the transitions $^2T_2g \rightarrow {}^4T_1g$ (14493–15748 cm^{-1}), $^2T_2g \rightarrow {}^4T_2g$ (19230–19455 cm^{-1}), $^2T_2g \rightarrow {}^2A_1g$, ^2T_1g (22676–23981 cm^{-1}). Values of Racah inter electronic repulsion parameters B and C and 10Dq (Table 2) are calculated for the above transitions, and the values of these ligand field parameters are comparable to those reported for other trivalent ruthenium(III) octahedral complexes.[28] Considerable lower value of the Racah inter electronic repulsion parameter than that of the free ruthenium ion indicates the covalent nature of the metal ligand bond.[29] Higher Dq values are usually associated with considerable electron delocalization. Results of the electronic spectra suggest an octahedral environment around the ruthenium ion.

Magnetic Moment and EPR Spectra

The magnetic susceptibilities of all the complexes lie between 1.73 and 1.94 BM indicating the presence of one unpaired electron. It is inferred from these values that ruthenium is in the +3 oxidation state.[30] The observed magnetic susceptibilities and the electronic spectra of the complexes suggest an octahedral structure for the complexes.

The EPR spectra of powdered samples were recorded at room temperature. Two representative spectra are shown in Figures 3 and 4. The complexes showed no indication of any hyperfine interaction of Ru with N, As, P, Cl and Br. The spectra of all the complexes except complex $[RuCl(AsPh_3)_2(Anth\text{-}ovan)]$ showed single isotropic resonance with g values of 2.04–2.53 (Table 3). Such isotropic lines are usually observed either due to intermolecular spin-spin exchange, which can broaden the lines or due to occupancy of the unpaired electron in a degenerate orbital[31] corresponding to the electronic configuration $(d_{xz})^2$, $(d_{yz})^2$, $(d_{xy})^1$. However, the spectra of complex $[RuCl(AsPh_3)_2(Anth\text{-}ovan)]$ show axial symmetry with $g_\perp = 2.01$ and $g_{||} = 2.28$. EPR spectra for

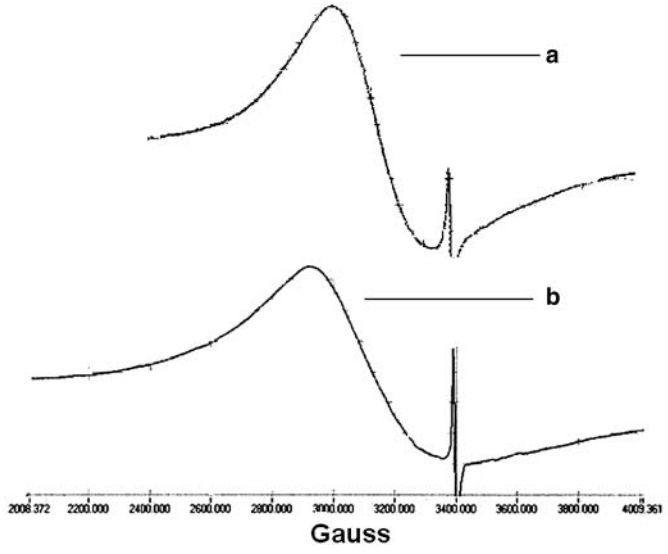


FIG. 3. EPR spectra of [RuBr(AsPh$_3$)$_2$(Anth-ovan)] **a**. at RT; and **b**. at LNT.

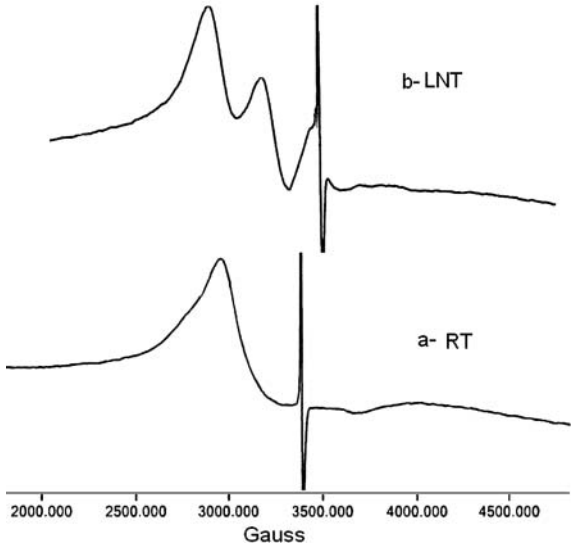


FIG. 4. EPR spectra of [RuCl(PPh$_3$)$_2$(Anth-sal)] **a**. at RT; and **b**. at LNT.

the complexes [RuCl(PPh$_3$)$_2$(Anth-acac)], [RuCl(PPh$_3$)$_2$(Anth-sal)], [RuCl(PPh$_3$)$_2$(Anth-ohap)], [RuCl(AsPh$_3$)$_2$(Anth-ovan)], [RuCl(AsPh$_3$)$_2$(Anth-ohap)], [RuBr(AsPh$_3$)$_2$(Anth-sal)] and [RuBr(AsPh$_3$)$_2$(Anth-ovan)] were recorded at liquid nitrogen temperature. The LNT epr spectra of [RuCl(PPh$_3$)$_2$(Anth-ohap)] and [RuBr(AsPh$_3$)$_2$(Anth-ovan)] show no variation from their corresponding RT epr spectra.

However the LNT epr spectra of the complexes [RuCl(PPh$_3$)$_2$(Anth-acac)], [RuCl(PPh$_3$)$_2$(Anth-sal)], [RuCl (AsPh$_3$)$_2$(Anth-ovan)], [RuCl(AsPh$_3$)$_2$(Anth-ohap)] and [RuBr(AsPh$_3$)$_2$(Anth-sal)] displayed two signals. Presence of two signals indicates an axial distortion in the complexes. For an octahedral field with axial distortion $g_x = g_y \neq g_z$. The axial distortion splits the triply degenerate t_2 level into a and e. Thus the energy level order is $d_{xy} > d_{xz}, d_{yz}$ with the unpaired electron in d_{xy}.[32]

Redox Behavior

The redox behavior of some of the complexes was studied by cyclic voltammetry (Table 4). A representative cyclic voltammogram is shown in Figure 5. The electrochemical profiles of the complexes display a quasi-reversible (ΔEp = 80–400 mV)

TABLE 3
EPR spectral data of ruthenium(III) complexes

Complex	Room temperature				Liquid nitrogen temperature			
	g_x	g_z	g_y	<g>*	g_x	g_z	g_y	<g>*
[RuCl(PPh$_3$)$_2$(Anth-acac)]	—	2.31	—		2.60	2.19	2.60	2.47
[RuCl(PPh$_3$)$_2$(Anth-sal)]	—	2.24	—		2.44	2.05	2.44	2.32
[RuCl(PPh$_3$)$_2$(Anth-ovan)]	—	2.38	—					
[RuCl(PPh$_3$)$_2$(Anth-ohap)]	—	2.10			—	2.10	—	
[RuCl(AsPh$_3$)$_2$(Anth-acac)]	—	2.53	—					
[RuCl(AsPh$_3$)$_2$(Anth-sal)]	—	2.28	—					
[RuCl(AsPh$_3$)$_2$(Anth-ovan)]	2.28	2.01	2.28	2.10	2.69	2.22	2.69	2.54
[RuCl(AsPh$_3$)$_2$(Anth-ohap)]	—	2.14	—		2.65	2.09	2.69	2.48
[RuBr(AsPh$_3$)$_2$(Anth-acac)]	—	2.33	—					
[RuBr(AsPh$_3$)$_2$(Anth-sal)]	—	2.27	—		2.39	2.04	2.39	2.27
[RuBr(AsPh$_3$)$_2$(Anth-ovan)]	—	2.29			—	2.28	—	
[RuBr(AsPh$_3$)$_2$(Anth-ohap)]	—	2.04	—					

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

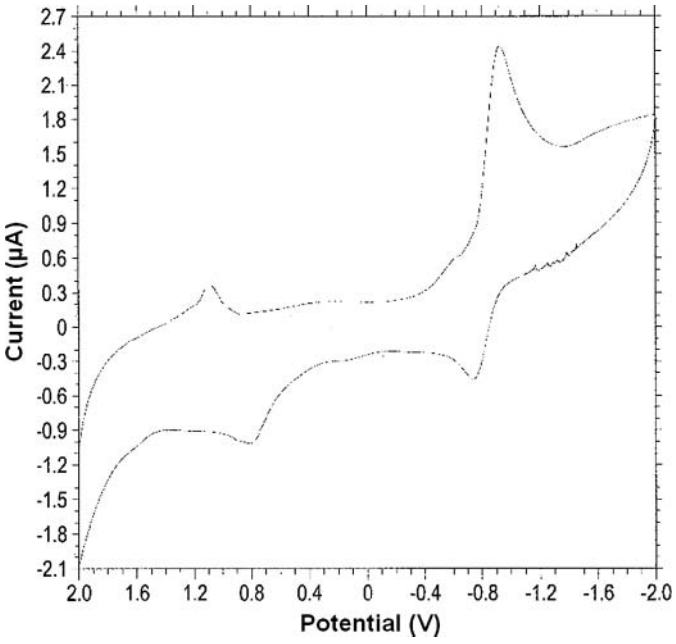


FIG. 5. Cyclic voltammogram of [RuCl($AsPh_3$)$_2$(Anth-ohap)].

redox process. The complexes showed well defined waves in the range, 0.74 to 1.28 V (Ru^{III}- Ru^{IV}) and −0.77 to − 0.90 V (Ru^{III} − Ru^{II}). The redox potentials are influenced by the nature of the ligands. Complexes with ligands having electron releasing substituents were oxidized and reduced at a lower potential[33] than the complexes with electron withdrawing ligands.

Catalytic Oxidation Studies

The oxidation of primary/secondary alcohols was carried out using the synthesized ruthenium complexes as catalyst and NMO as an oxidant. Alcohols were converted into their corresponding aldehydes/ketones. Results are shown in Table 5. The proposed mechanism[34] for the oxidation in the presence of NMO is shown in Figure 6. NMO behaves as a two electron oxidant. Reaction proceeds through the formation of Ru(V)- oxo species. This is evidenced from the IR spectrum, which shows a weak band at 805 cm^{-1} (Figure 7) and the appearance of a peak at 380 nm in the UV spectrum (Figure 8) that would account for a loose oxo complex of ruthenium.[35]

Among the ruthenium complexes that have been analyzed, the order of catalytic activity in terms of yield and turnover number was [RuBr($AsPh_3$)$_2$(Anth-acac)] > [RuBr($AsPh_3$)$_2$(Anth-ohap)] > [RuCl(PPh_3)$_2$(Anth-sal)] > [RuCl(PPh_3)$_2$(Anth-ovan)]. In terms of substituents present in the Schiff base moiety, the order of activity is $2CH_3$ > CH_3 > H > OCH_3. Hence, it is inferred that inductive effect of the substituents play a major role in deciding the catalytic activity of their corresponding complexes. Presence of two methyl groups in the ligand H_2Anth-acac makes its corresponding complex a better catalyst. Relatively lesser catalytic efficiency was observed for the complex containing the ligand H_2Anth-ohap, which contains one -CH_3 group as substituent. The last member in the above order contains -OCH_3 group as substituent in its ligand, H_2Anth-ovan. The –I effect of the -OCH_3 group makes this complex lesser active than the other three complexes. It is further inferred from the results that the $AsPh_3$/ PPh_3, Br/Cl ligands may also influence the catalytic efficiency by their electron donor-acceptor nature. High donor ability of the triphenylarsine group and the lesser electronegativity of the bromine might have augumented the influence of the ligands H_2Anth-acac and H_2Anth-ohap on their complexes. Similarly, the lesser donor ability of the triphenylarsine group and the higher electronegativity of the chlorine might have decreased the influence of the ligands H_2Anth-sal and H_2Anth-ovan on their complexes. Hence, it is inferred from the above discussion that electron releasing groups increase the catalytic activity and electron withdrawing groups decrease the catalytic activity of their corresponding ruthenium complexes. This is in line with a previous observation.[36]

The relatively higher product yield obtained for oxidation of benzyl alcohol compared to cyclohexanol is due to the fact that α-CH unit of benzyl alcohol is more acidic

TABLE 4
Cyclic voltammetry[a] data of ruthenium(III) complexes

	Ru (III-IV)				Ru (III- II)			
Complex	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)
[RuBr($AsPh_3$)$_2$(Anth-acac)]	0.78	0.70	0.74	80	−1.07	−0.73	−0.90	340
[RuBr($AsPh_3$)$_2$(Anth-ohap)]	1.10	0.70	0.90	400	−0.99	−0.70	−0.845	290
[RuCl($AsPh_3$)$_2$(Anth-ohap)]	1.10	0.78	0.94	320	−0.92	−0.75	−0.835	170
[RuCl(PPh_3)$_2$(Anth-sal)]	1.32	1.14	1.23	180	−0.90	−0.70	−0.80	200
[RuCl(PPh_3)$_2$(Anth-ovan)]	1.38	1.10	1.24	280	−0.9	−0.68	−0.79	220
[RuCl($AsPh_3$)$_2$(Anth-ovan)]	1.38	1.18	1.28	200	−0.90	−0.64	−0.77	260

[a]Supporting electrolyte [$N(Bu)_4$]BF_4 (0.1M); all potentials are referenced to SCE; E_f = 0.5 (Epa+ Epc); ΔEp = (Epa –Epc); where Epa and Epc are anodic and cathodic potentials respectively; scan rate = 100 mVs^{-1}

TABLE 5
Catalytic oxidation of alcohols by ruthenium(III) complexes

Complex	Substrate	Product	Yield[a] %	Turnover number[b]
	Benzylalcohol	Benzaldehyde	95	97
$[RuBr(AsPh_3)_2(Anth\text{-}acac)]$	Cyclohexanol	Cyclohexanone	76	78
	Cinnamyl alcohol	Cinnamaldehyde	97	99
	Benzylalcohol	Benzaldehyde	92	94
$[RuBr(AsPh_3)_2(Anth\text{-}ohap)]$	Cyclohexanol	Cyclohexanone	72	74
	Cinnamyl alcohol	Cinnamaldehyde	94	96
	Benzylalcohol	Benzaldehyde	89	91
$[RuCl(PPh_3)_2(Anth\text{-}sal)]$	Cyclohexanol	Cyclohexanone	68	70
	Cinnamyl alcohol	Cinnamaldehyde	92	94
	Benzylalcohol	Benzaldehyde	86	88
$[RuCl(PPh_3)_2(Anth\text{-}ovan)]$	Cyclohexanol	Cyclohexanone	65	68
	Cinnamyl alcohol	Cinnamaldehyde	90	92

[a] yields based on substrate.
[b] moles of product per moles of catalyst.

than cyclohexanol.[37] An important characteristic of the ruthenium/NMO system results in the selective oxidation at the alcoholic group of unsaturated cinnamyl alcohol to cinnamaldehyde, tolerating the double bond.[35]

Biocidal Studies

Inhibition activity of the test compounds were assessed on the basis of the corresponding zone of inhibition developed by them. The higher the zone of inhibition, the greater the antibacterial activity (Table 6). The results of the antimicrobial activity studies show that the ruthenium chelates are more toxic when compared with their parent ligands against the same microorganisms under the identical experimental conditions. Under conditions of balanced growth, a bacterium must duplicate every cellular constituent during its cell cycle. But in the presence of ruthenium metal, bacterial DNA loses its replication ability

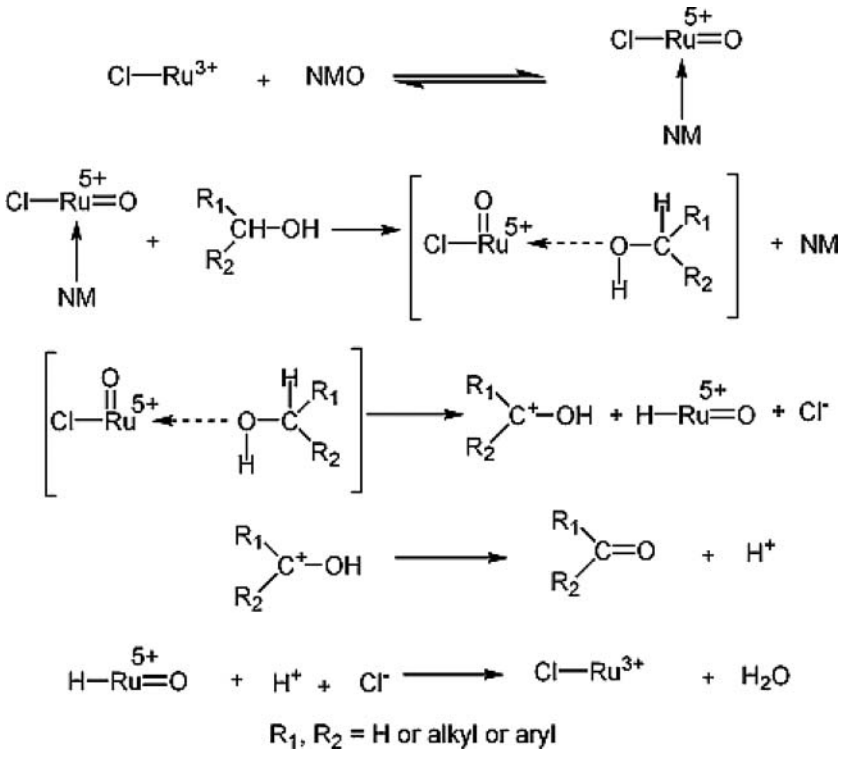


FIG. 6. Proposed mechanism for the oxidation of alcohols by Ru(III)/NMO.

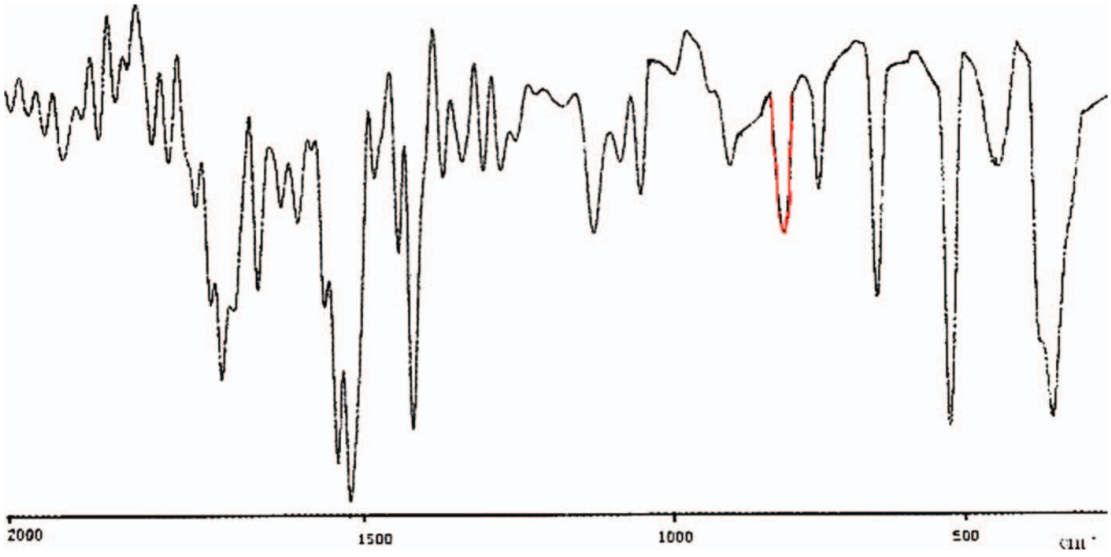


FIG. 7. IR spectra of the ruthenium(V)-Oxo active intermediate of [$RuCl(PPh_3)_2$(Anth-sal)].

and cellular proteins become inactivated. The mode of action may include induction of filamentous growth in the bacteria as well as induction of phage production from lysogenic strains of the bacteria[38] and also the interference in the mitochondnial calcium transport.[39] The possible mechanism of action of the ruthenium complexes is by binding to DNA, which reduces the synthesis of new DNA.

A possible mode of toxicity increase may also be considered in the light of Tweedy's chelation theory. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible p electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of the cell membrane. It has been suggested that the ligands with the N and O donor system might have inhibited enzyme production, since enzymes that require a free hydroxyl group for their activity appear to be especially susceptible to deactivation by the ions of the complexes.[40] It was also inferred that all four Schiff base ligands had the same activity against the organisms, and the magnitude of their influence in their corresponding complexes were also same. The inhibition activity was reinforced with the increment of concentration. Though

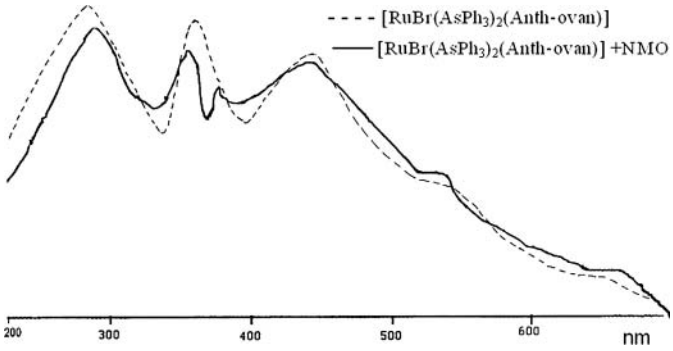


FIG. 8. UV-Vis spectra of the ruthenium(V)-Oxo active intermediate of [$RuBr(AsPh_3)_2$(Anth-ovan)].

TABLE 6
Antimicrobial activity data of Schiff bases and ruthenium(III) complexes

	Diameter of inhibition zone *Bacillus sp. E. Coli*			
Ligand/Complex	0.5%	1%	0.5%	1%
H_2Anth-acac	10	14	12	15
[$RuCl(PPh_3)_2$(Anth-acac)]	15	20	16	22
[$RuCl(AsPh_3)_2$(Anth-acac)]	18	24	17	24
[$RuBr(AsPh_3)_2$(Anth-acac)]	16	21	16	21
H_2Anth-sal	12	14	10	13
[$RuCl(PPh_3)_2$(Anth-sal)]	16	20	14	18
[$RuCl(AsPh_3)_2$(Anth-sal)]	20	25	16	21
[$RuBr(AsPh_3)_2$(Anth-sal)]	17	22	15	20
H_2Anth-ovan	10	14	11	16
[$RuCl(PPh_3)_2$(Anth-ovan)]	16	22	14	19
[$RuCl(AsPh_3)_2$(Anth-ovan)]	15	20	15	22
[$RuBr(AsPh_3)_2$(Anth-ovan)]	17	21	14	20
H_2Anth-ohap	12	17	10	16
[$RuCl(AsPh_3)_2$(Anth-ohap)]	17	22	15	22
[$RuCl(AsPh_3)_2$(Anth-ohap)]	18	23	16	22
[$RuBr(AsPh_3)_2$(Anth-ohap)]	17	22	18	23
Ampicillin	24	28	26	30

0.5% and 1.0% indicate 0.5 g and 1.0 g of the substance in 100 mL of DMSO respectively.

the complexes possess inhibition activity, it could not reach the effectiveness of the standard drug, Ampicillin.

CONCLUSION

In conclusion, it has been observed that variations in the side arms of the imine compartment and substituent of the phenyl ring influence the electrochemical, magnetic and catalytic properties of the ruthenium(III) complexes. The stability, easy preparation, mild reaction conditions, and high yields of the products and the reaction under non-aqueous condition make this reagent a useful method for the oxidation of alcohols.

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