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Synthesis, spectral, electrochemical and catalytic studies of new Ru(III) tetradentate Schiff base complexes

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The synthesis and characterization of several hexa-coordinated ruthenium(III) Schiff base complexes of the type [RuX(EPh$_3$)(L)] (X = Cl or Br; E = P or As; L = dianion of the tetradentate Schiff base) are reported. IR, EPR, electronic spectra and cyclic voltammetric data of the complexes are discussed. An octahedral geometry has been tentatively proposed for all of these complexes. The new complexes have been subjected to catalytic activity in the reaction of oxidation of alcohols in the presence of *N*-methylmorpholine-*N*-oxide. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: ruthenium(III) complexes; tetradentate N_2O_2 Schiff base; electron paramagnetic resonance; electrochemistry; catalytic oxidation

INTRODUCTION

Transition metal complexes with tetradentate Schiff base ligands have been studied as catalysts for a number of organic oxidation and reduction reactions and electrochemical reduction processes.[1,2] Salen-type complexes have also been recently used as catalytically active materials to develop surface modified electrodes for sensing applications.[3,4] Tetradentate Schiff base complexes have been employed as catalysts for many reactions and as biological models in understanding the structure of bio-molecules and biological process.[5,6] They are increasingly important for designing metal complexes related to synthetic and natural oxygen carriers.[7] The synthesis and biological activities of some ruthenium complexes containing tetradentete Schiff base ligands have been reported.[8,9] Herein, we are reporting the preparation, spectral and electrochemical characterization and catalytic activity of a series of new Ru(III) complexes containing teteradentate Schiff base ligands. The general structure of the Schiff base ligands are given in Scheme 1.

EXPERIMENTAL

Materials and methods

All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to the standard procedures. $RuCl_3 3H_2O$, purchased from Loba Chemie, was used without further purification. The analyses of carbon, hydrogen and nitrogen were performed at the Central Drug Research Institute, Lucknow, India. IR spectra of the complexes were recorded in KBr pellets with a Shimadzu 8000 FT-IR spectrophotometer in the 4000–400 cm^{-1} range. The electronic spectra were recorded in CH_2Cl_2 solution with Perkin-Elmer 20/200 spectrophotometer in the 800–200 nm range. EPR spectra of the powdered samples were recorded on a Bruker E-112 Varian model instrument in X-band frequencies at room temperature using 2,2′-diphenyl-1-picrylhydrazine hydrate (DPPH) as internal standard. Magnetic susceptibilities were recorded on EG- and G-PARC vibrating sample magnetometers. The cyclicvoltammetric studies were carried out in acetonitrile solution using a glassy carbon working electrode and the potentials were referenced to silver–silver chloride electrode.

The ligands and starting complexes [$RuCl_3(PPh_3)_3$], [$RuCl_3(AsPh_3)_3$], [$RuBr_3(AsPh_3)_3$] and [$RuBr_3(PPh_3)_2$ (MeOH)] were prepared according to the reported

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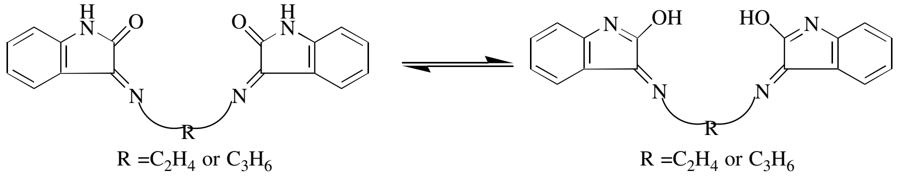
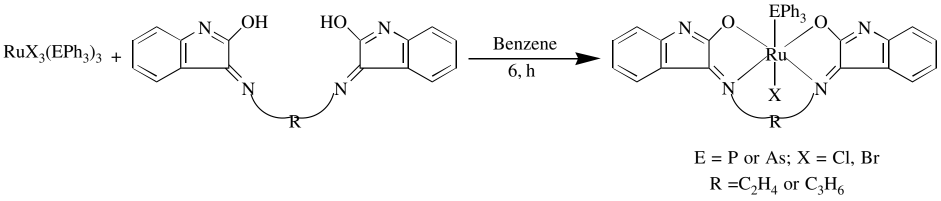


R	Abbreviation
C_2H_4	IZTen
C_6H_4	IZTph
C_3H_6	IZTpro

Scheme 1.



Scheme 2.

procedures.[9–13] The procedures for catalytic activity and antibacterial studies were similar to those reported in our earlier publications.[8,9]

Synthesis of new ruthenium(III) complexes

All the new complexes were prepared by following the general procedure described below (Scheme 2). To a solution of [$RuCl_3(PPh_3)_3$], [$RuCl_3(AsPh_3)_3$], [$RuBr_3(AsPh_3)_3$] or [$RuBr_3(PPh_3)_2(MeOH)$] (0.1 g; 1.0 mmol) in benzene (25 cm^3), the appropriate Schiff base ligands (0.0318–0.0356 g; 0.1 mmol) were added. The mixture was then heated under reflux for 6 h. The resulting solution was concentrated to *ca* 3 cm^3 and cooled. Light petroleum (60–80 °C) was then added, whereupon the product complex separated. The solid was filtered off, washed, recrystallized from CH_2Cl_2/light petroleum (60–80 °C) and dried *in vacuo*.

RESULTS AND DISCUSSION

All the new ruthenium(III) complexes were colored, air- and light-stable and soluble in common organic solvents. The analytical data obtained for the complexes were in good agreement with the proposed molecular formula (Table 1).

IR spectra

The IR spectra of free ligands were compared with those of the new complexes in order to confirm the coordination of Schiff base to the ruthenium metal. The free Schiff bases showed a very strong absorption band around 1652–1619 cm^{-1} in the IR spectra, which is characteristic of the azomethine (C=N) group (Table 2). In the IR spectra of the new complexes, this absorption occurred at a lower region (1614–1623 cm^{-1}), indicating that the coordination is through azomethine nitrogen.[14] The bands assigned to stretching vibration modes, $\nu_{(N-H)}$, $\nu_{(C=O)}$, $\nu_{(C=N)}$, in the free ligands disappeared in the spectra of the complexes. In addition to this, new bands were observed around 1590–1580 and 1254–1237 cm^{-1}, corresponding to $\nu_{(C=N)}$ and $\nu_{(C-O)}$ vibration modes, respectively, suggesting the enolization of the N–H hydrogen of isatin and the coordination through the oxygen of the C–O group.[9] The formation of the M–O and M–N bonds was further supported by the appearance of the $\nu_{(M-O)}$ and $\nu_{(M-N)}$ bands in the regions 455–475 and 541–480 cm^{-1}, respectively, in the spectra of the chelates. The most important conclusion drawn from the infrared spectral evidence is that the diamine–bis(isatin) Schiff base ligand acts as a chelating agent towards the central ruthenium ion as a dibasic ONNO tetradentate ligand via two azomethine nitrogen atoms and two negatively charged oxygen atoms.

Electronic spectra

The electronic spectra of all the complexes in acetonitrile showed three to six bands in the region 232–506 nm and their assignments are summarized in Table 3. The ground state of ruthenium(III) (t^5_{2g} configuration) is $^2T_{2g}$, while the first excited doublet levels in the order of increasing energy

Table 1. Analytical data of Ru^{III} Schiff base complexes

Complex	Colour	Melting point (°C)	Found (calcd) (%)		
			C	H	N
[RuCl(PPh$_3$)(IZTen)]	Brown	135	60.6 (60.5)	3.7 (3.7)	7.8 (7.7)
[RuCl(PPh$_3$)(IZTph)]	Black	116	62.9 (62.9)	3.5 (3.4)	7.7 (7.6)
[RuCl(PPh$_3$)(IZTpro)]	Brown	109	60.9 (60.9)	3.9 (3.8)	7.6 (7.5)
[RuCl(AsPh$_3$)(IZTen)]	Brown	138	56.9 (56.8)	3.5 (3.5)	7.4 (7.2)
[RuCl(AsPh$_3$)(IZTph)]	Black	136	59.5 (59.2)	3.3 (3.2)	6.9 (6.9)
[RuCl(AsPh$_3$)(IZTpro)]	Green	134	57.5 (57.4)	3.7 (3.8)	7.2 (6.9)
[RuBr(AsPh$_3$)(IZTen)]	Brown	126	53.8 (52.9)	3.3 (3.2)	6.9 (6.8)
[RuBr(AsPh$_3$)(IZTph)]	Black	130	56.4 (56.4)	3.1 (3.0)	6.5 (6.4)
[RuBr(AsPh$_3$)(IZTpro)]	Brown	137	54.3 (54.2)	3.5 (3.5)	6.8 (6.7)
[RuBr(PPh$_3$)(IZTen)]	Black	139	56.9 (56.8)	3.5 (3.4)	7.5 (7.5)
[RuBr(PPh$_3$)(IZTph)]	Black	145	59.4 (59.2)	3.3 (3.2)	6.9 (6.7)
[RuBr(PPh$_3$)(IZTpro)]	Black	128	57.4 (57.3)	3.7 (3.6)	7.2 (7.1)

Table 2. IR spectral data of Ru^{III} complexes

Complex	$\nu_{C=N}$	ν_{C-O}	ν_{M-N}	ν_{M-O}	Bands due to PPh$_3$/AsPh$_3$
[RuCl(PPh$_3$)(IZTen)]	1614	1258	480	460	694, 1089, 1436
[RuCl(PPh$_3$)(IZTph)]	1641	1243	541	455	695, 1436, 1089
[RuCl(PPh$_3$)(IZTpro)]	1622	1240	542	458	691, 1436, 1085
[RuCl(AsPh$_3$)(IZTen)]	1614	1256	540	475	692, 1086, 1436
[RuCl(AsPh$_3$)(IZTph)]	1613	1237	540	473	492, 1436, 1084
[RuCl(AsPh$_3$)(IZTpro)]	1623	1244	544	475	691, 1085, 1436
[RuBr(AsPh$_3$)(IZTen)]	1614	1257	541	475	690, 1435, 1089
[RuBr(AsPh$_3$)(IZTph)]	1615	1241	541	475	694, 1437, 1090
[RuBr(AsPh$_3$)(IZTpro)]	1623	1244	545	474	695, 1436, 1090
[RuBr(PPh$_3$)(IZTen)]	1615	1242	540	476	692, 1084, 1437
[RuBr(PPh$_3$)(IZTph)]	1616	1242	543	475	691, 1436, 1085
[RuBr(PPh$_3$)(IZTpro)]	1614	1240	541	475	692, 1085, 1438

ν in cm^{-1}.

Table 3. Electronic spectral data of Ru^{III} Schiff base complexes

Complex	λ_{max}	Assignment
[RuCl(PPh$_3$)(IZTen)]	232	Charge transfer
[RuCl(PPh$_3$)(IZTph)]	352, 236, 232, 322, 266	Charge transfer
[RuCl(PPh$_3$)(IZTpro)]	398, 294, 268, 232	Charge transfer
[RuCl(AsPh$_3$)(IZTen)]	292, 248, 230	Charge transfer
[RuCl(AsPh$_3$)(IZTph)]	388, 352, 232, 322, 336	Charge transfer
[RuCl(AsPh$_3$)(IZTpro)]	232, 265, 325	Charge transfer
[RuBr(AsPh$_3$)(IZTen)]	230, 256, 306, 506	Charge transfer
[RuBr(AsPh$_3$)(IZTph)]	230, 322, 266, 350, 336	Charge transfer
[RuBr(AsPh$_3$)(IZTpro)]	242, 300, 400	Charge transfer
[RuBr(PPh$_3$)(IZTen)]	232, 268, 294, 298	Charge transfer
[RuBr(PPh$_3$)(IZTph)]	232, 322, 268, 352, 476, 386	Charge transfer
[RuBr(PPh$_3$)(IZTpro)]	265, 232, 375	Charge transfer

λ in nm.

are $^2A_{2g}$ and $^2T_{1g}$, which arise from $t^4{}_{2g}\,e^1{}_g$ configuration. In most of the ruthenium(III) complexes, the electronic spectra show only charge transfer bands. Since in a d^5 system and especially 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. Therefore, it becomes difficult to assign conclusively the bands of ruthenium(III) complexes which appear in the visible region. Hence all the bands that appear in this region have been assigned to charge transfer transitions which are in conformity with the assignment made for similar ruthenium(III) complexes.[9]

Magnetic moments

The effective magnetic moments (μ_{eff}) of some of the complexes were measured at room temperature using vibrating sample magnetometer (Table 4). The μ_{eff} values of complexes ranged from 1.71 to 1.76 BM corresponding to a single unpaired electron in a low-spin $4d^5$ configuration.

EPR spectra

The room temperature spectra of powdered samples were recorded at the X-band frequencies. The g values of the complexes are listed in Table 5. Five complexes showed a single isotropic resonance with a g value in the 2.01–2.35 range. The isotropic lines of this type usually observed are either due to intermolecular spin exchange, which may broaden the lines, or to the occupancy of the unpaired electron in a degenerate orbital. The nature and pattern of the EPR spectra suggests an almost perfect octahedral environment around the ruthenium ion in these complexes. Four complexes exhibit two different g values ($g_x = g_y \neq g_z$), which are indicative of a tetragonal distortion in these octahedral complexes (Fig. 1). The presence of two g values also indicates an axial symmetry for these complexes and, hence, the *trans* positions were assigned for triphenylphosphine/triphenylarsine groups.

Cyclic voltammetric studies

Cyclic voltammetric studies were carried out for these Ru(III) complexes in acetonitrile solution at a glassy-carbon working electrode. The oxidation and reduction of each complex were characterized by well-defined waves with E_f values in the range from 0.225 to 0.525 V (oxidation) and from −0.075 to −0.782 (reduction) against a silver–silver chloride electrode (Table 6). All the complexes were electroactive only with respect to the metal center. Complexes showed redox couples with peak-to-peak separation values (ΔE_p) ranging from 165 to 350 mV, revealing that this process is at best quasi-reversible (Fig. 2).[15] This is attributed to slow electron transfer and adsorption of the complexes onto the electrode surface.[16] Some complexes showed only reduction potentials.

Table 4. Magnetic moments of Ru$^{\mathrm{III}}$ Schiff base complexes

Complex	μ_{eff} (BM)
[RuCl(PPh_3)(IZTph)]	1.71
[RuCl($AsPh_3$)(IZPro)]	1.76
[RuBr($AsPh_3$)(IZTph)]	1.71

Table 5. EPR spectral data of Ru$^{\mathrm{III}}$ Schiff base complexes

Complex	g_x	g_y	g_z	$<g>^a$
[RuCl(PPh_3)(IZTen)]	2.2	2.2	2.2	2.2
[RuCl(PPh_3)(IZTph)]	2.34	2.34	2.08	2.25
[RuCl(PPh_3)(IZTpro)]	2.29	2.29	2.08	2.2
[RuBr($AsPh_3$)(IZTen)]	2.35	2.35	2.35	2.35
[RuBr($AsPh_3$)(IZTph)]	2.04	2.04	2.51	2.2
[RuCl($AsPh_3$)(IZTen)]	2.31	2.31	2.31	2.31
[RuCl($AsPh_3$)(IZTph)]	2.29	2.29	2.29	2.29
[RuCl($AsPh_3$)(IZTpro)]	2.01	2.01	2.01	2.01
[RuBr(PPh_3)(IZTph)]	2.07	2.07	2.37	2.17

$^a <g> = [1/3g^2 + 1/3g_y{}^2 + 1/3g_z{}^2]^{1/2}$.

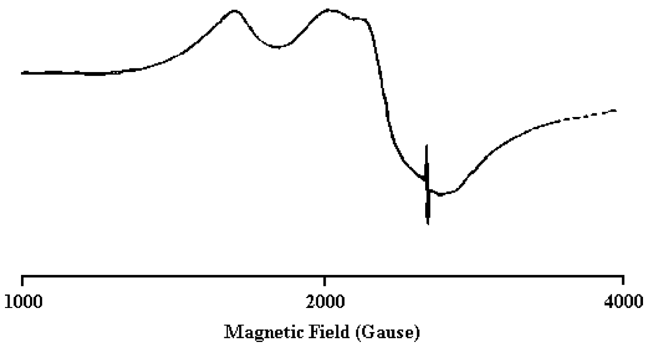


Figure 1. EPR spectrum of [RuBr(PPh_3)(IZTph)].

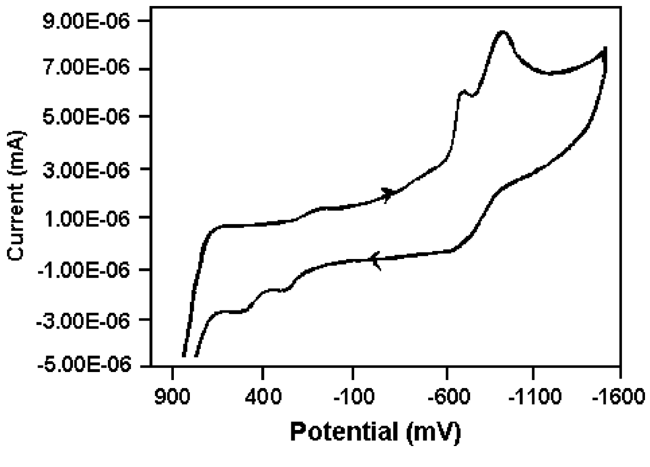


Figure 2. Cyclic voltammogram of [RuBr(PPh_3)(IZTen)].

Table 6. Cyclic voltammetry data[a] for some Ru^{III} complexes

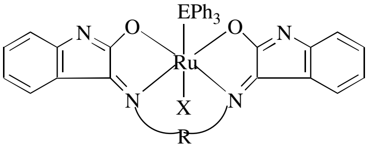
Complex	Ru^{IV} – Ru^{III}				Ru^{III} – Ru^{II}			
	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)	E_{pq} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)
[RuCl(PPh$_3$)(IZTph)]	—	—	—	—	−0.050	−0.200	−0.075	250
[RuCl(AsPh$_3$)(IZTph)]	0.600	0.450	0.525	150	−0.300	−0.050	−0.125	250
[RuBr(AsPh$_3$)(IZTen)]	—	—	—	—	−0.050	−0.300	−0.175	250
[RuBr(PPh$_3$)(IZTen)]	0.050	0.400	0.225	350	−0.825	−0.660	−0.782	165
[RuBr(PPh$_3$)(IZTpro)]	—	—	—	—	−0.200	−0.550	−0.325	350

[a] Working electrode: glassy carbon electrode; reference electrode: Ag–AgCl electrode; supporting electrolyte: [NBu$_4$]ClO$_4$ (0.05 M); scan rate: 100 mV s^{-1}; $E_f = 0.5\ (E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic potentials respectively.

Table 7. Catalytic oxidation of alcohols by Ru^{III} complexes in the presence of NMO

Complex	Substrate	Product	Yield[a] (%)	Turnover[b]
[RuCl(PPh$_3$)(IZTen)]	Cinnamyl alcohol	E	68.2	70.1
	Benzyl alcohol	A	59.3	61.2
	Cyclohexanol	K	47.2	49.3
[RuCl(PPh$_3$)(IZTph)]	Cinnamyl alcohol	E	70.4	72.3
	Benzyl alcohol	A	61.3	64.6
	Cyclohexanol	K	51.2	54.7
[RuCl(PPh$_3$)(IZTpro)]	Cinnamyl alcohol	E	69.3	71.6
	Benzyl alcohol	A	59.9	61.6
	Cyclohexanol	K	49.3	51.4
[RuCl(AsPh$_3$)(IZTen)]	Cinnamyl alcohol	E	63.7	65.6
	Benzyl alcohol	A	54.6	56.9
	Cyclohexanol	K	43.2	45.7
[RuCl(AsPh$_3$)(IZTph)]	Cinnamyl alcohol	E	65.6	67.4
	Benzyl alcohol	A	56.3	59.0
	Cyclohexanol	K	45.7	47.7
[RuCl(AsPh$_3$)(IZTpro)]	Cinnamyl alcohol	E	63.7	65.9
	Benzyl alcohol	A	54.4	55.6
	Cyclohexanol	K	42.9	44.0
[RuBr(AsPh$_3$)(IZTen)]	Cinnamyl alcohol	E	62.5	64.0
	Benzyl alcohol	A	51.7	53.9
	Cyclohexanol	K	42.3	44.7
[RuBr(AsPh$_3$)(IZTph)]	Cinnamyl alcohol	E	63.6	65.9
	Benzyl alcohol	A	52.8	54.2
	Cyclohexanol	K	43.5	45.7
[RuBr(AsPh$_3$)(IZTpro)]	Cinnamyl alcohol	E	62.8	64.7
	Benzyl alcohol	A	52.0	54.5
	Cyclohexanol	K	42.9	44.5
[RuBr(PPh$_3$)(IZTen)]	Cinnamyl alcohol	E	65.7	67.8
	Benzyl alcohol	A	53.8	55.5
	Cyclohexanol	K	44.6	46.4
[RuBr(PPh$_3$)(IZTph)]	Cinnamyl alcohol	E	66.6	68.2
	Benzyl alcohol	A	54.7	57.0
	Cyclohexanol	K	45.0	47.3
[RuBr(PPh$_3$)(IZTpro)]	Cinnamyl alcohol	E	66.0	68.1
	Benzyl alcohol	A	54.2	56.9
	Cyclohexanol	K	45.1	47.8

[a] Yields based on substrate;
[b] moles of product per mole of catalyst.
E = cinnamaldehyde; A = benzaldehyde; K = cyclohexanone.



E = P or As; X = Cl, Br
R =C_2H_4 or C_3H_6

Scheme 3.

Based on the analytical, IR, electronic, EPR and cyclic voltammetry data the octahedral structure of the complexes has been proposed, as shown in Scheme 3.

Catalytic activity

The oxidation of cinnamyl alcohol, benzyl alcohol and cyclohexanol was carried out with new ruthenium(III) complexes in the presence of NMO as oxidant and dichloromethane as solvent. The data of catalytic oxidation are given in Table 7. Cinnamaldehyde, banzaldehyde and cyclohexanone were formed from cinnamyl alcohol, benzyl alcohol and cyclohexanol, respectively, after stirring for about 4 h, and then quantified as 2,4-dinitrophenylhydrazone derivatives. In no case was there any detectable oxidation of alcohols in the presence of NMO alone and without the ruthenium complex.

The relatively higher product yield obtained for oxidation of benzyl alcohol compared with cyclohexanol was due to the fact that the α-CH unit of benzyl alcohol is more acidic than cyclohexanol.[17] The triphenylphosphine ruthenium(III) complexes possess greater catalytic activity than the triphenylarsine complexes. The same observation has been made recently.[8]

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