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Ruthenium(II) bipyridine complexes with modified phenolic Schiff base ligands. Synthesis, spectroscopic characterization and Redox properties

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Abstract—A group of stable new ruthenium(II) mixed-ligand tris-chelated complexes of the type [Ru(bpy)$_2$L]ClO$_4$ (**1–6**), (bpy = 2,2′-bipyridine; L = deprotonated form of the HL ligands, *o*-(HO)—C$_6$H$_3$(R)C(R′)=N—CH$_2$—C$_6$H$_5$ or *o*-(HO)—C$_6$H$_3$(R)C(R′)=N—NH—C$_6$H$_5$; where R = H, *p*-NO$_2$ and R′ = H, CH$_3$) have been synthesized and characterized. The complexes are essentially diamagnetic and behave as 1 : 1 electrolytes in acetonitrile solution. They display two metal-to-ligand-charge-transfer (MLCT) transitions near 500 and 400 nm respectively and intra ligand π–π^* transitions in the UV-region. In acetonitrile solution the complexes exhibit weak emission from the lowest energy MLCT band at room-temperature. The quantum yields of the complexes are found to be in the range 0.0004–0.01. In acetonitrile solution the complexes show quasi-reversible ruthenium(II)–ruthenium(III) oxidation couples in the range 0.33 → 0.70 V and irreversible ruthenium(III)–ruthenium(IV) oxidations in the range 1.53 → 1.95 V vs SCE. Two successive reversible bipyridine reductions are observed for each complex in the ranges −1.4 → −1.62 V and −1.59 → −1.85 V vs SCE respectively. The presence of trivalent ruthenium in the oxidized solution for one complex **5** is evidenced by the rhombic EPR spectrum with g values, $g_1 = 2.389$, $g_2 = 2.081$ and $g_3 = 1.810$. The EPR spectrum of the coulometrically oxidized species, **5**$^+$ has been analyzed to furnish values of axial ($\Delta = 4745$ cm^{-1}) and rhombic ($V = 3692$ cm^{-1}) distortion parameters as well as the energies of the two expected ligand field transitions ($\nu_1 = 3071$ cm^{-1} and $\nu_2 = 6819$ cm^{-1}) within the t_2 shell. One of the ligand field transitions has been observed experimentally at 6578 cm^{-1} by near-IR spectrum which is close to the computed ν_2 value. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: ruthenium; synthesis; spectra; redox; electronic structure.

The chemistry of ruthenium-bipyridine complexes has been the focus of continuous research activity since the discovery of their important redox, photophysical and photochemical properties [1]. Several ruthenium-bipyridine complexes have been exploited in solar energy schemes [2], in the oxidation of water to dioxygen [3], in the conversion of chloride ion to chlorine [4] and in the electrochemical reduction of acetylene to ethylene and ethane [5]. This has also been used to investigate photochemically induced charge-transfer [6], ligand substitution [7], stereochemical isomerization processes [8], and finally to probe important metal–ligand interactions [9]. In fact these properties have spurred the development of newer ruthenium bipyridine systems either by incorporating desired groups within the bipyridine moiety itself or by using other types of donor sites along with the [Ru(bpy)$_2$] core to form mixed ligand tris-chelates to modulate the photo-redox activities of this class of complexes.

The present work originates from our interest to introduce phenolic Schiff base ligands (HL) having CH$_2$ or NH spacer [OH—C$_6$H$_3$(R)C(R′)=N—CH$_2$—C$_6$H$_5$ or OH—C$_6$H$_3$(R)C(R′)=N—NH—C$_6$H$_5$, Scheme 1] as a third ligand in the [Ru(bpy)$_2$] core to prepare new mixed ligand ruthenium-bipyridine complexes of type [Ru(bpy)$_2$L] to understand the

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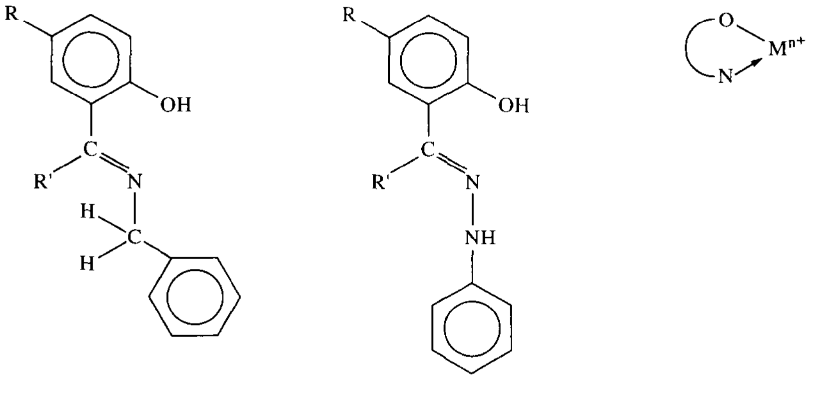

A **B** **ML**

R = H, R' = H → HL^1
R = H, R' = CH_3 → HL^2
R = NO_2, R' = H → HL^3

R = H, R' = H → HL^4
R = H, R' = CH_3 → HL^5
R = NO_2, R' = H → HL^6

Scheme 1.

effect of newly inducted groups on the redox and spectroscopic properties of the $[Ru(bpy)_2]$ core system.

Herein we report the synthesis of six complexes of the kind having RuN_5O chromophore, their redox properties, spectroelectrochemical correlation, preliminary photophysical aspects and electronic structure of one of the electrogenerated trivalent congeners.

RESULTS AND DISCUSSION

Synthesis

Six phenolic Schiff base ligands used for the present study are abbreviated HL^1–HL^6 respectively. The ligands are primarily classified into two groups, HL^1–HL^3 (**A**) and HL^4–HL^6 (**B**) depending on the nature of the spacer (CH_2 or NH) present in between the imine nitrogen and phenyl ring and within each group the three ligands differing with respect to substituents present either on the phenolic ring or on the imine fragment (Scheme 1). The anionic form of the ligands (L^-) bind to the metal ion as bidentate N, O coordinators forming six membered chelate ring (**ML**) systems.

The complexes, $[Ru(bpy)_2(L)]^+$ (**1**–**6**) (bpy = 2,2'-bipyridine) have been synthesized from $[Ru(bpy)_2CO_3]$ following the general decarbonation synthetic route shown in eqn (1):

$$Ru(bpy)_2CO_3 + HL \xrightarrow[\Delta]{MeOH} [Ru(bpy)_2L]^+ + HCO_3^- \qquad (1)$$

Ligand Complex

$L^1 \rightarrow \mathbf{1}$

$L^2 \rightarrow \mathbf{2}$

$L^3 \rightarrow \mathbf{3}$

$L^4 \rightarrow \mathbf{4}$

$L^5 \rightarrow \mathbf{5}$

$L^6 \rightarrow \mathbf{6}$

The red colored cationic complexes have been isolated as perchlorate salts and the crude products were purified by column chromatography using a silica gel column.

The microanalytical data of the complexes are shown in Table 1. The results are in very good agreement with the calculated values thus confirming the gross composition of the mixed ligand tris chelates $[Ru(bpy)_2L]ClO_4$ (**1**–**6**). The complexes exhibit 1 : 1 conductivity in acetonitrile solution (Π_M, 140–155 Ω^{-1} cm^2 M^{-1}). Solid state magnetic moment measurements at room temperature indicate that all the monocations (**1**–**6**) are essentially diamagnetic (t_{2g}^6, idealized, S = 0).

Spectral study

IR spectra. FTIR spectra of the complexes were recorded as KBr discs. The $\nu_{(C=N)}$ stretching frequency of the free ligands (HL) appears near 1630 cm^{-1} which has been shifted to 1600 cm^{-1} in accordance with the coordination of the azomethine function to the metal

Table 1. Microanalytical and electronic spectral data

Compound	Elemental analysis (%)[a] C	H	N	Electronic spectral data[b] λ_{max} (nm) (ε[c], M^{-1} cm^{-1})
1	56.65	3.93	9.77	580 (2554)[d], 510 (5108), 460 (4561)[d], 379 (7297), 330 (5472)[d], 294 (27000), 233 (24333), 212 (24446)
	(56.47)	(3.88)	(9.69)	
2	57.19	4.02	9.41	586 (1600)[d], 508 (4060), 381 (6350), 297 (29710), 245 (25790), 217 (24190)
	(57.02)	(4.07)	(9.50)	
3	53.33	3.45	11.11	480 (14030), 389 (13310), 328 (14040), 293 (48030) 241 (40670)
	(53.16)	(3.52)	(10.94)	
4	54.68	3.67	11.58	591 (2570)[d], 504 (5210), 374 (8000), 331 (6980)[d], 296 (36420), 233 (36150)
	(54.73)	(3.73)	(11.61)	
5	55.45	3.84	11.47	599 (2520)[d], 511 (4960), 375 (7980), 297 (31710), 244 (25870), 218 (23680)
	(55.32)	(3.93)	(11.38)	
6	51.67	3.32	12.87	478 (16060), 390 (14830), 323 (13810)[d], 293 (50000) 244 (37330), 215 (33280)
	(51.53)	(3.38)	(12.75)	

[a] Calculated values are in parentheses.
[b] In acetonitrile solution.
[c] Extinction coefficient.
[d] Shoulder.

ion [10]. The O—H stretch in the free ligands is observed as a prominent bond near 3400 cm^{-1}. This band is absent in the complexes as expected. A very strong and broad band near 1100 cm^{-1} and a strong and sharp vibration band near 630 cm^{-1} are observed for all the complexes due to the presence of ionic perchlorate.

^{1}H NMR spectra. ^{1}H NMR spectra of the complexes were recorded in $CDCl_3$ solvent using a 300 MHz instrument. The representative spectra of complexes **3** and **6** are shown in Fig. 1. The O—H proton of the free ligands appears as a broad peak near 14 ppm as expected [11]. The absence of OH proton of the free ligand (HL) in the spectra of the complexes suggests coordination through the phenolato oxygen. The methylene protons (—CH_2) appear as a singlet near 4.8 ppm for the free ligands (HL^1–HL^3), the same protons are observed for the corresponding complexes (**1**–**3**) as a doublet of doublet near 4.9 ppm (Fig. 1(a)). The —NH proton for the free ligands (HL^4–HL^6) appears near 5.5 ppm as a broad peak, whereas for the corresponding complexes (**4**–**6**) the same is observed as a triplet near 6.0 ppm due to the nitrogen nuclear spin ($I = 1$) (Fig. 1(b)).

The presence of asymmetric ligands L in the complexes make all the six aromatic rings inequivalent. The complexes **1**, **2**, **4**, **5** and **3**, **6** thus possess twenty-five and twenty-four non-equivalent aromatic protons respectively. Since the electronic environment of many aromatic hydrogen atoms are similar, their signals may appear in a narrow chemical shift range. In fact aromatic regions of the spectra are complicated due to the overlapping of several signals which has precluded the identification of individual resonances. However, the direct comparison of the intensity of the aromatic region proton signals with that of the clearly observable —CH_2 protons (δ, 4.9 ppm) for the complexes **1**–**3** reveal the presence of the expected twenty-five aromatic protons and one azomethine (CH=N) proton for the complex **1**, twenty-five aromatic protons for the complex **2** and twenty-four aromatic protons and one azomethine proton for the complex **3** (Fig. 1(a)).

Similarly the direct comparison of the intensity of the aromatic protons with that of the clearly observable —NH proton (δ, 5.8 ppm) reveals the presence of the calculated number of protons in the aromatic region for the complexes **3**–**6** (Fig. 1(b)).

Methyl (CH_3) protons for the complexes **2** and **5** have appeared as a singlet at 2.51 and 2.49 ppm respectively.

Electronic spectra. Solution electronic spectra of the complexes were recorded in acetonitrile solvent in the UV-visible region (200–700 nm). The spectral data are listed in Table 1 and the representative spectra are shown in Fig. 2. The presence of different acceptor levels in the complexes may be responsible for the observed multiple absorptions [12]. The complexes exhibit primarily two bands in the visible region near 500 nm and 400 nm respectively (Table 1).

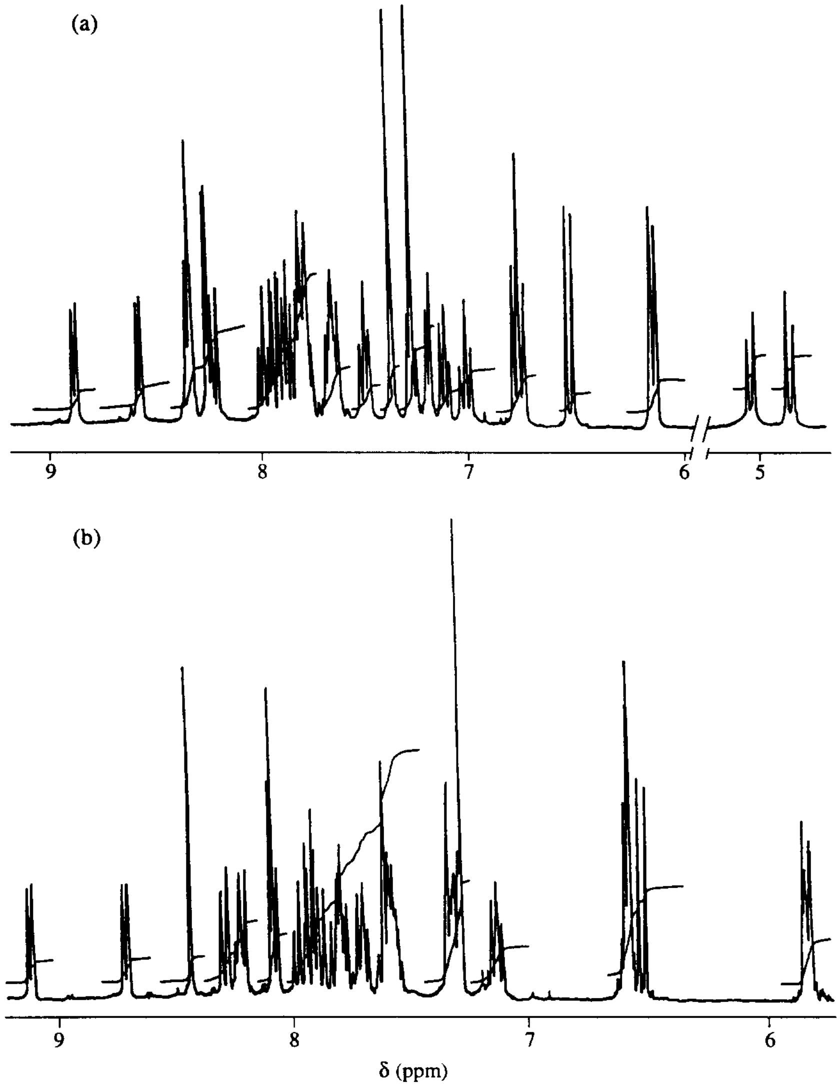

Fig. 1. ^{1}H NMR spectra of (a) [Ru^{II}(bpy)$_2$L^3]ClO$_4$, **3** and (b) [Ru^{II}(bpy)$_2$L^6]ClO$_4$, **6** in CDCl$_3$.

The origin of these two bands in the visible region has been assigned on the basis of reported spectra of Ru(bpy)$_2^{2+}$ complexes having other kinds of chelating third ligands [13]. Two different kinds of bipyridine acceptor levels, one symmetric (χ) and one antisymmetric (ψ) have developed with respect to the C_2 axis of bipyridine ligand and the transitions from metal filled dπ orbital to those two π^* orbitals result in the observed two MLCT bands. The lower energy band near 500 nm is considered to be $\pi(\mathrm{Ru}) \rightarrow \pi^*(\psi)$ and the higher energy band near 400 nm may be due to $\mathrm{d}\pi(\mathrm{Ru}) \rightarrow \pi^*(\chi)$ transitions.

The higher energy bands in the UV-region are of intra-ligand (π–π^*) type or charge-transfer transitions involving energy levels which are higher in energy than the ligand lowest unoccupied molecular orbital (LUMO).

The lowest energy MLCT band of [Ru(bpy)$_3$]$^{2+}$ appears at 450 nm in acetonitrile solution [14]. Thus the replacement of one strong π-acidic symmetric bipyridine ligand by an asymmetric phenolato Schiff base ligand (L) in the complexes (**1**–**6**) decreases the energy of the same transition. Lower ligand field strength of the ligands L compared to the bipyridine ligand and the overall lowering of the molecular symmetry while going from [Ru(bpy)$_3$]$^{2+}$ to complexes **1**–**6** might be the probable reasons for the observed shift of MLCT band. The observed red shifts of the lowest energy MLCT bands for the complexes **3** and **6** (where nitro group is present in the ligands L^3 and L^4) as compared to [Ru(bpy)$_3$]$^{2+}$ are not as much as that of the other four complexes (**1**, **2**, **4**, **5**) (Table 1).

Room temperature emission spectra. Emission properties of the complexes have been studied in acetonitrile solvent at room temperature. Excitations of the complexes in acetonitrile solution, at the top of

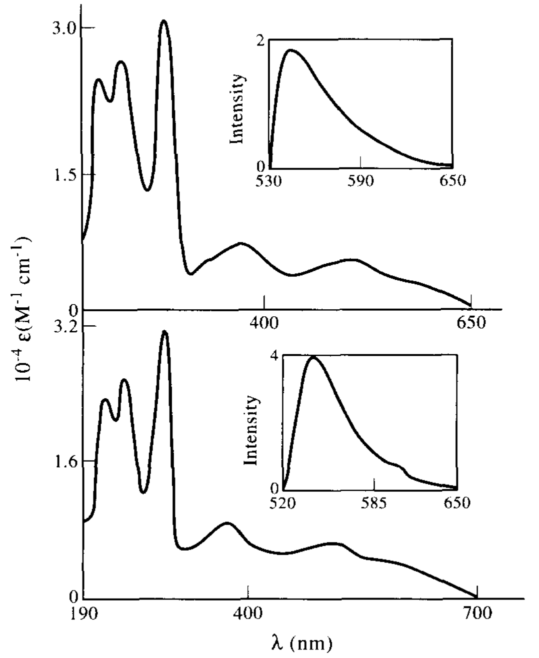

Fig. 2. Electronic spectra of (a) $[Ru^{II}(bpy)_2L^2]ClO_4$, **2** and (b) $[Ru^{II}(bpy)_2L^5]ClO_4$, **5** in acetonitrile. The insets show the emission spectra of the corresponding complexes at 298 K in acetonitrile.

the lowest energy MLCT bands (λ_{max}, near 500 nm for the complexes **1**, **2**, **4**, **5** and near 480 nm for the complexes **3** and **6**) exhibit weak emissions near 550 nm (Table 2, Fig. 2). The origin of these emission spectra are further confirmed by the excitation spectra of the corresponding same solutions. Intensity of the observed emission spectra of the complexes under each class of ligands L, **A** and **B** follows the order **3** < **1** < **2** and **6** < **4** < **5** respectively. The complexes having keto based Schiff base ligands, **2** and **5** are exhibiting the strongest emissions and within the two classes of ligands, **A** and **B**, the complexes having ligands of type **B** (phenyl hydrazine derived Schiff base) are more effective from an emission point of view.

The quantum yields of the complexes are determined by comparison with the reported quantum yield of $[Ru(bpy)_3][PF_6]_2$ complex in acetonitrile solution ($\phi_{em,r} = 0.062$) [15]. For the calculation of quantum yield of the complexes, the excitation wave lengths are chosen such that the standard reference and sample absorptions are equal. The quantum yield of the emission process is calculated by following the reported method, eqn (2), where A_s, A_r are the absorption values of sample and reference, I_s, I_r are the emission intensities of sample and reference and n_s, n_r are the refractive indices of sample and reference.

$$\phi_{em,s} = \phi_{em,r}(A_r/A_s)(I_s/I_r)(n_s/n_r)^2 \qquad (2)$$

Since A_s and A_r are equal and the refractive indices are assumed to be similar, eqn (2) can then be modified to eqn (3).

$$\phi_{em,s} = \phi_{em,r}(I_s/I_r) \qquad (3)$$

The calculated quantum yields for the complexes are listed in Table 2. The quantum yields for the complexes **2** and **5** are much higher than the rest (Table 2).

Redox properties

Redox properties of the complexes have been studied in acetonitrile solution by cyclic voltammetry (CV) using a platinum working electrode. Complexes are electroactive with respect to metal as well as ligand centers and display four redox processes in the potential range ±2 V vs saturated calomel electrode (SCE). Representative voltammograms are shown in Fig. 3 and the reduction potentials data are depicted in Table 3. The assignments of the responses to specific couples in Table 3 are based on the following considerations.

The ruthenium(III)–ruthenium(II) couple. All the complexes display one reversible oxidation process (Fig. 3) which is assigned to the metal oxidation, eqn (4). The one-electron nature of the responses is estab-

Table 2. Emission data[a]

Compound	λ_{max} (excitation) (nm)	λ_{max} (emission) (nm)	Relative intensity	Quantum yield[b]
1	510	556	1.5×10^2	0.0004
2	508	547	1.8×10^3	0.005
3	480	541	0.4×10^2	0.0001
4	504	554	1.7×10^3	0.005
5	511	548	4.0×10^3	0.01
6	478	547	0.5×10^3	0.002

[a] In acetonitrile.
[b] Calculated by using eqn (3).

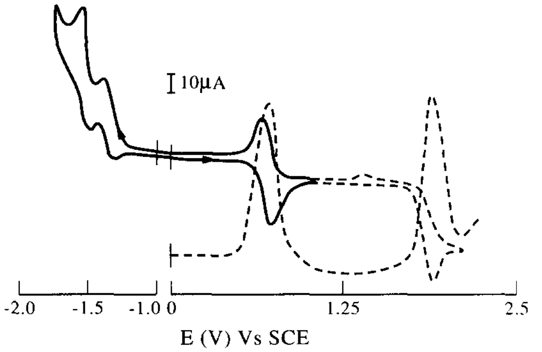

Fig. 3. Cyclic voltammograms of ~10^{-3} M solution of the complex **3** in acetonitrile at 298 K.

lished by current height and constant potential coulometry data.

$$[\mathrm{Ru^{III}(bpy)_2L}]^{2+} + e^- \rightleftharpoons [\mathrm{Ru^{II}(bpy)_2L}]^+ \qquad (4)$$

The presence of trivalent ruthenium in the oxidized solution is confirmed by characteristic rhombic EPR spectrum of the ruthenium(III) congener (see later). The formal potential of the couple (eqn 4) varies depending on the nature of ligands L. The complexes having phenyl hydrazine derived ligands L (**4**–**6**) are exhibiting lower reduction potentials compared to the corresponding complexes derived from benzylamine based ligands L (**1**–**3**) and within each class the reduction potential follows the order **3** > **1** > **2** and **6** > **4** > **5** respectively as expected. Thus a potential shift of maximum 300 mV has been observed in each class depending on the substituents present (Table 3), which implies the stability of the bivalent ruthenium in the case of NO_2 substituted ligand (L^3 or L^6) is more as compared to the others.

Under identical experimental conditions, the ruthenium(III)–ruthenium(II) reduction potential of $[\mathrm{Ru(bpy)_3}]^{2+}$ appears at 1.29 V [13,14]. Thus substitution of one bipyridine ligand from the $[\mathrm{Ru(bpy)_3}]^{2+}$ by a σ-donating phenolato Schiff base ligand, L, results in a decrease of ruthenium(III)–ruthenium(II) potential by 0.6–1 V depending on the particular R and R′ groups present in the ligands L. The reduction of overall charge of the complex cation from +2 in $[\mathrm{Ru(bpy)_3}]^{2+}$ to +1 in the present complexes provides further electrostatic stabilization of the oxidized trivalent $\mathrm{Ru^{III}}$—L species which has possibly originated from the σ-donor character of the phenolato group [16]. This decrease of metal oxidation potential ($\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$) while going from $[\mathrm{Ru(bpy)_3}]^{2+}$ to $[\mathrm{Ru(bpy)_2L}]^+$ complexes and the reversible nature of the voltammograms (Fig. 3) suggests the possibility of isolating trivalent congeners of the complexes under the present mixed ligand tris chelated environment.

Although the ruthenium(II)–ruthenium(III) oxidation potentials for the present complexes are reasonably low, the oxidized trivalent congeners are not too stable to isolate (see later section).

Table 3. Electrochemical data at 298 K[a]

Compound	$\mathrm{Ru^{III}}$–$\mathrm{Ru^{II}}$ couple E^0_{298} (V) (ΔE_p (mV))	n^b	$\mathrm{Ru^{III}}$–$\mathrm{Ru^{IV}}$ E^c_{pa} (V)	Ligand reduction E^0_{298} (V) (ΔE_p (mV))	ΔE^0 (V)^d	ν_{MLCT} (cm^{-1})	
						Cal.^{e}	Obs.^{f}
1	0.43 (80)	1.02	1.60	−1.58 (80) −1.85 (90)	2.01	19210	19608
2	0.38 (70)	1.04	1.55	−1.57 (70) −1.81 (90)	1.92	18726	19685
3	0.70 (70)	0.98	1.91	−1.40 (80) −1.59 (80)	2.10	19936	20833
4	0.39 (70)	0.95	1.55	−1.59 (80) −1.79 (90)	1.98	18968	19685
5	0.33 (70)	1.01	1.53	−1.62 (80) −1.80 (90)	1.95	18726	19569
6	0.62 (90)	0.97	1.75	−1.49 (70) −1.68 (80)	2.11	20017	20920

[a] Condition: solvent acetonitrile; supporting electrolyte, TEAP; reference electrode, SCE; solute concentration, ~10^{-3} M; working electrode, platinum wire.

[b] $n = Q/Q'$, where Q' is the calculated coulomb count for 1 e^- transfer and Q is the coulomb count found after exhaustive electrolysis of ~10^{-2} M solution of the complex.

[c] E_{pa} values are considered due to the irreversible nature of the voltammograms.

[d] Calculated by using eqn (8) of text.

[e] Calculated by using eqn (7) of text.

[f] In acetonitrile solution.

Search for ruthenium(IV)–ruthenium(III) couple. The complexes exhibit a second irreversible oxidation process in the range 1.5–1.9 V vs SCE (Fig. 3). Although the current height of this irreversible process is ~1.5 times more than the previous one-electron process ($\mathrm{Ru^{III}} \rightleftharpoons \mathrm{Ru^{II}}$), the one-electron nature of this second oxidation process has been established with the help of the differential pulse voltammetry (Fig. 3). This second oxidation process could be due to either $\mathrm{Ru^{III}} \rightarrow \mathrm{Ru^{IV}}$ oxidation or oxidation of the coordinated ligand L. The potential difference between the two successive processes, in the range ~1.1–1.2 V, is comparable well with the reported observed potential difference between the two successive redox processes for the ruthenium center ($\mathrm{Ru^{II/III}}$–$\mathrm{Ru^{III/IV}}$) in mononuclear systems [17,10,16]. Since the free ligands (HL) do not show any redox activity within the specified potential range (±2 V), therefore it may be reasonable to consider the second irreversible oxidative process as ruthenium(III) → ruthenium(IV) oxidation.

Ligand reductions. The complexes display two successive reductions in the ranges $-1.40 \rightarrow -1.62$ V and $-1.57 \rightarrow -1.85$ V (Table 3, Fig. 3). The one-electron nature of these couples has been established by current height consideration. The observed two reductions are assigned to be due to the reductions of the coordinated bipyridine ligands. 2,2′-bipyridine is a well known potential electron-transfer center and each bipyridine can accept two electrons in one electrochemically accessible LUMO [18]. Since the complexes (**1**–**6**) have two bipyridine units, four one-electron reductions are therefore expected. However, in practice we have observed two reductions corresponding to eqns (5) and (6) within the ±2 V potential range.

$$[\mathrm{Ru^{II}(bpy)_2(L)}]^+ + e^- \rightleftharpoons [\mathrm{Ru^{II}(bpy)(b\overset{-}{p}y)(L)}] \quad (5)$$

$$[\mathrm{Ru(bpy)(b\overset{-}{p}y)(L)}] + e^- \rightleftharpoons [\mathrm{Ru(b\overset{-}{p}y)(b\overset{-}{p}y)(L)}]^- \quad (6)$$

The other expected two reductions could not be seen possibly due to solvent cut-off.

Spectroelectrochemical correlation. The lowest energy metal to ligand charge-transfer (MLCT) bands of the complexes (**1**–**6**) are observed in the range 510–475 nm (Table 1). The reduction potentials of the reversible ruthenium(III)–ruthenium(II) couple for the complexes and the first ligand reduction (reduction of the diimine fragment) have been detected in the ranges $0.33 \rightarrow 0.70$ V and $-1.40 \rightarrow -1.62$ V vs SCE respectively. The lowest energy MLCT transition involves excitation of the electron from the filled t_{2g}^6 orbital of ruthenium(II) to the lowest π^* orbital of the bipyridine ligand (dominated by the diimine, —N=C—C=N— fragment). Now the associated energy of the MLCT band for each complex can be predicted from the experimentally observed electrochemical data by considering the following eqns (7) and (8) [19].

$$\nu_{\mathrm{MLCT}} = 8065(\Delta E^0) + 3000 \quad (7)$$

$$\Delta E^0 = E^0_{298}(\mathrm{Ru^{III}/Ru^{II}}) - E^0_{298}(\mathrm{L}) \quad (8)$$

Here, E^0_{298} ($\mathrm{Ru^{III}/Ru^{II}}$) and E^0_{298} (L) are the formal potentials (in V) of the ruthenium(III)–ruthenium(II) couple and the first ligand reduction respectively. The ν_{MLCT} is the frequency of the lowest energy MLCT transition (in $\mathrm{cm^{-1}}$). The factor 8065 in eqn (7) is used to convert potential difference, ΔE from volt to $\mathrm{cm^{-1}}$ and the term 3000 $\mathrm{cm^{-1}}$ is of empirical origin. The calculated and experimentally observed ν_{MLCT} transition frequencies for the complexes are depicted in Table 3 and there is a linear relationship between the ν_{MLCT} and ΔE (Fig. 4). Here, the calculated values for all the complexes lie within the 900 $\mathrm{cm^{-1}}$ of the experimentally observed MLCT energies which are in very good agreement with the previously observed correlation in the other mixed ligand ruthenium bipyridine and other related systems [20].

Electrogeneration of trivalent ruthenium congener and distortion parameters. Chemical oxidation of the complexes (**1**–**6**) in acetonitrile solvent by aqueous cerric ammonium sulfate or cerrium(IV) in 0.1 M aqueous $\mathrm{HClO_4}$ resulted initially in a green solution corresponding to the trivalent congener of the complexes and which then eventually decomposed to an unidentified product even at 273 K.

In order to trap the trivalent analogues of (**1**–**6**) we have tried to oxidize the complexes by a constant potential coulometric technique. Coulometric oxidations of the complexes at a potential 200 mV positive to the corresponding E_{pa} of $\mathrm{Ru^{II}/Ru^{III}}$ couple in acetonitrile solution at 273 K produced a green solution in all cases. The observed coulomb count corresponds to 1 e^- transfer for all the complexes (Table 3). The coulometrically oxidized species ($\mathbf{1}^+$–$\mathbf{6}^+$) are not stable enough to be isolated in pure solid state and this has precluded its further characterization.

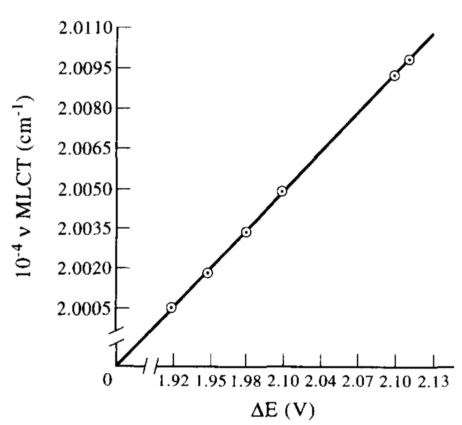

Fig. 4. Least squares plot of the lowest energy metal-to-ligand charge-transfer band (ν_{MLCT}, $\mathrm{cm^{-1}}$) vs the difference in potential (ΔE, (V)) between the $\mathrm{Ru^{II/III}}$ couple and the first bipyridine reduction.

However, in the case of complex 5^+ the situation is better to some extent which has allowed us to record the EPR and electronic spectrum of the oxidized species (5^+). X-band EPR spectrum of 5^+ is recorded by quickly freezing the green solution (liquid N_2). The rhombic nature of the spectrum (Fig. 5) at 77 K ($g_1 = 2.389$, $g_2 = 2.081$ and $g_3 = 1.810$) is characteristic of trivalent ruthenium(III) in a distorted octahedral environment (low-spin Ru^{III}, t_{2g}^5, $S = 1/2$) [21]. In the UV-visible region electronic spectrum of the oxidized complex, 5^+ shows one broad ligand to metal charge transfer (LMCT) band at 774 nm [11] and ligand based transitions in the UV region (Fig. 6).

The theory of EPR spectra of distorted octahedral low-spin d^5 (idealized t_{2g}^5, ground term $^2T_{2g}$) complexes are documented in literature [22,10,16,17,21]. The distortion of pseudo-octahedral complexes is expressed as the sum of axial (Δ) and rhombic (V) components. The t_2 orbital consists of the components $t_2(xy)$, $t_2^+(xz)$ and $t_2^-(yz)$. The degeneracy of t_2 orbital is partially removed by axial distortion (Δ), which placed t_2^0 (b) above t_2^+/t_2^- (e). The superimposed rhombic distortion (V) then further splits (e) into t_2^+ and t_2^-.

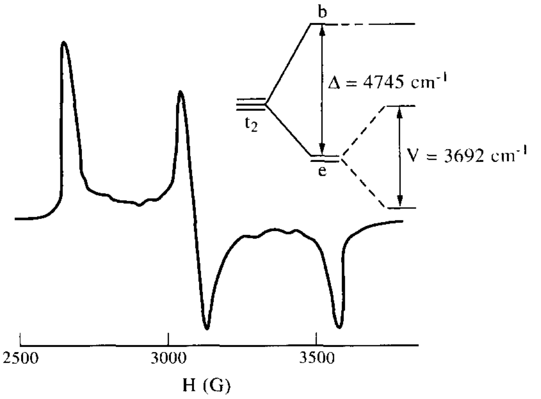

Fig. 5. X-band EPR spectrum and t_2 splittings of the coulometrically oxidized complex $[Ru^{III}(bpy)_2L^5]^{2+}$, 5^+ in acetonitrile solution at 77 K.

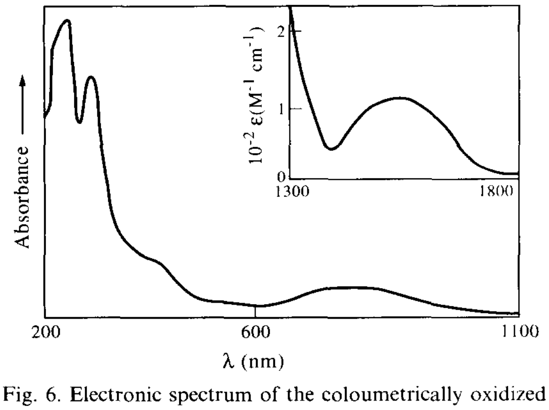

Fig. 6. Electronic spectrum of the coloumetrically oxidized complex $[Ru^{III}(bpy)_2L^5]^{2+}$, 5^+ in acetonitrile. The inset shows the electronic spectrum of 5^+ in the range 1300–1800 nm.

The distortion parameter (Δ and V) and the energies of two optical transitions (ν_1 and ν_2) from ground to upper Kramers doublets can be obtained from the analysis of EPR spectrum using the g tensor theory of low-spin d^5 ions.

The EPR spectrum provides only the absolute g values and so neither their signs nor the correspondence of g_1, g_2 and g_3 to g_x, g_y and g_z are known. There are forty-eight possible combinations based on the labelling (x, y, z) and signs chosen for the experimentally observed g values. For the present case we have chosen the combination $-g_1 > -g_2 > g_3$ as this particular set gives the reasonable value of orbital reduction factor, ($k < 1.0$). The value of k for all other combinations of g parameters does not fall within the limit ($k < 1.0$) and hence is rejected. The computed values of orbital reduction factor (k), axial distortion (Δ), rhombic distortion (V) and the two optical transitions (ν_1 and ν_2) for the complex, 5^+ are 0.606 cm^{-1}, 4745 cm^{-1}, 3692 cm^{-1}, 3071 cm^{-1} and 6819 cm^{-1} respectively. The spin-orbit coupling constant (λ) of the ruthenium(III) is taken as 1000 cm^{-1} [22].

The computed ν_2 band has been observed experimentally by near IR spectrum in the expected position, 6578 cm^{-1} (ε, M^{-1} cm^{-1}, 110) (Fig. 6). In view of the involved approximation in the theory, the agreement between the experimentally observed ν_2 and the calculated ν_2 band value is excellent [23]. Due to instrumental limitation (maximum wavelength scan up to 2200 nm) it has not been possible to compare the ν_1 band. Here axial distortion (Δ) is ~1.3 times more than the rhombic (V) distortion.

CONCLUSIONS

We have thus observed the effect of the presence of phenolic Schiff base ligands having CH_2 or NH spacer (**A** or **B**) as a third ligand in the $[Ru(bpy)_2]$ core with respect to redox and photophysical aspects. The presence of both the classes of ligands (**A** and **B**) in the complexes (**1**–**6**) facilitate the successive ruthenium(II) $\rightleftharpoons$ ruthenium(III) and ruthenium(III) → ruthenium(IV) oxidations and make the complex environment susceptible to undergo room temperature emission from the lowest energy metal-to-ligand-charge-transfer (MLCT) band. In general, the complexes (**4**–**6**) having the third ligand with NH spacer (Class **B**), are more effective than the ligands with CH_2 spacer (Class **A**) from the emission point of view and in particular ketone based third ligands (L^2 and L^5) in both the classes (**A** and **B**) are more suitable with respect to emission efficiency. In addition, correlations between the energies of the lowest MLCT absorption bands and the electrochemical redox potentials of the complexes follow an excellent linear relationship in accordance with the other $Ru(bpy)_2L$ systems.

EXPERIMENTAL

Materials

Commercial ruthenium trichloride (S.D. Fine Chemicals, Bombay, India) was converted to $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. The *cis*-$[Ru(bpy)_2CO_3]$ was prepared according to the reported procedure [24]. 2-hydroxy-5-nitrobenzaldehyde, benzylamine and 2-hydroxyacetophenone were obtained from Aldrich, U.S.A. Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) used for chromatography was purchased from S.D. Fine Chemicals, Bombay, India. For spectroscopic and electrochemical studies HPLC grade solvents were used. Commercial tetraethylammonium bromide was converted to pure tetraethyl ammonium perchlorate (TEAP) by following an available procedure [25].

Physical measurements

Solution electrical conductivity was checked using a Systronic conductivity bridge, 305. Electronic spectra (700–200 nm) were recorded using a Shimadzu UV 265 spectrophotometer. Near IR spectrum was recorded by using a Hitachi 330 spectrophotometer. Infrared (4000–400 cm^{-1}) spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility was checked with a PAR vibrating sample magnetometer. ^1H NMR spectra were obtained with the use of a 300 MHz Varian FT-NMR spectrometer. Cyclic voltammetric measurements were carried out using a PAR model 362 scanning potentiostat electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. TEAP was the supporting electrolyte and the solute concentration was $\sim 10^{-3}$ M. The half wave potential E^0_{298} was set equal to 0.5 $(E_{pa}+E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials respectively. The scan rate used was 50 mV s^{-1}. The coulometric experiments were done with a PAR model 370-4 electrochemistry apparatus incorporating a 179, digital coulometer. A platinum wire gauze working electrode was used in coulometric experiments. All experiments were carried out under dinitrogen atmosphere and are uncorrected for junction potentials. EPR measurement was made with a Varian model 109 E-line X-band spectrometer fitted with a quartz dewar for measurements at 77 K (liquid nitrogen). The spectrum was calibrated by using tetracyanoethylene (TCNE) ($g = 2.0037$). The elemental analyses were carried out with a Carlo Erba (Italy) elemental analyzer. Solution emission properties were checked using a SPEX-fluorolog spectrofluorometer.

CAUTION! Perchlorate salts of metal complexes are generally explosive. Care should be taken while handling such complexes.

Treatment of EPR data

An outline of the procedure can be found in our recent publications [16].

Synthesis of ligands and complexes

The ligands HL^1–HL^3 and HL^4–HL^6 were prepared by condensing benzylamine and phenylhydrazine respectively with appropriate 2-hydroxyaldehydes and ketone at 273 K in methanol solvent.

The complexes (**1**–**6**) were achieved using general methods. Yields varied in the range 70–75%. Specific details are given for one representative case.

Bis(2,2′-bipyridine)(N-benzyl salicylideneimine) ruthenium(II) perchlorate $[Ru(bpy)_2L^1]ClO_4$ (**1**). $Ru(bpy)_2CO_3$ (200 mg, 0.42 mmol) was dissolved in 20 cm^3 of methanol and heated to reflux for 10 min. To this solution the ligand HL^1 (173 mg, 0.84 mmol) was added. The resulting mixture was heated to reflux over a period of 5 h. The initial violet solution gradually turned to a red color. The progress of the reaction was monitored periodically by TLC. The volume of the solvent was then reduced under reduced pressure and the concentrated solution was treated with an excess of saturated aqueous sodium perchlorate solution. The dark red colored precipitate thus obtained was collected by filtration and washed thoroughly with cold methanol and a little ice-cold water. The solid mass was then dried *in vacuo* over P_4O_{10}.

The crude product was then purified by column chromatography on a silica gel (60–120 mesh) column. Unreacted excess ligand was eluted first with benzene and was rejected. The pure complex was eluted with a 2 : 1 ratio of benzene and acetonitrile solvents. On removal of the solvent mixture under reduced pressure fine crystalline complex $[Ru(bpy)_2(L^1)]ClO_4$ was obtained. Yield: 75%.

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