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Heterochelates of ruthenium(II): electrochemistry, absorption spectra, and luminescence properties

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Abstract—A series of heterochelates $[Ru(bpy)_2(L\text{-}X)](ClO_4)$ (**1**–**6**) derived from the schiff bases of *o*-aminophenol and *p*-substituted (X) benzaldehydes, HL-X (X = NO_2, Cl, F, Me, OMe and NMe_2) have been synthesized and characterized. Cyclic voltammograms of all the complexes, except **6** (X = NMe_2), exhibit a reversible Ru^{II}/Ru^{III} and an irreversible Ru^{III}/Ru^{IV} oxidation processes. In the case of **6**, both the oxidation processes take place reversibly. A linear correlation is obtained by plotting the $E_{1/2}$ value of Ru^{II}/Ru^{III} couple against the Hammett σ^+ parameters. The absorption spectra of the complexes are similar showing absorption bands due to $d\pi$–π^* (bpy), Schiff base n–π^* and π–π^* intraligand transitions. A linear correlation is also obtained between $\bar{\nu}_{max}$ (MLCT) and $\Delta E_{1/2}$ (separation between the first oxidation and first reduction couples). The effect of solvents on the MLCT and n–π^* absorption bands have been studied. Fluorescent spectral studies have shown that all the complexes luminesce at room temperature and the observed emission bands are due to metal-perturbed ligand-centred transitions. © 1997 Elsevier Science Ltd

Keywords: Ru^{II} complexes; bidentate ligand complexes; heterochelates of Ru^{II}; phenolate Schiff bases; electrochemistry; photophysics.

There is a great deal of interest with luminescent and redox-active ruthenium(II) complexes because they may be assembled to construct photochemical molecular devices that are capable of performing light-induced functions [1–5]. The highly attractive photophysical and redox properties of the archetype ruthenium(II) *tris*-bipyridine $Ru(bpy)_3^{2+}$, have led to stupendous growth of activities on polypyridine systems [6–10]. In order to tune the functions of $Ru(bpy)_3^{2+}$ lot of studies have been made by substituting one or more bpy with other chelating ligands, especially those with conjugated —N=C—C=N— units [2,3,10]. As opposed to the mostly studied homo- and heterochelates of the type $Ru(N\text{–}N)_3^{2+}$ derived from π electron deficient ligands, we have been interested to study $[Ru(N\text{–}N)_2(N,O^-)]^+$ type heterochelates, specifically of electron-rich phenolate Schiff bases which act as both σ- and π-donors in contrast to σ-donor but π-acceptor polypyridyls. Herein we report the redox activities and absorption and emission spectroscopic properties of a series of heterochelates $[Ru(bpy)_2(L\text{–}X)](ClO_4)$ derived from the Schiff bases of *o*-aminophenol and *p*-substituted (X) benzaldehydes, HL-X (X = NO_2, Cl, F, Me, OMe and NMe_2).

EXPERIMENTAL

Physical measurements

FT-IR spectra were recorded on a MAGNA-IR750 spectrometer series III using KBr discs and electronic spectra on a Shimadzu UV-160 spectrophotometer. Luminescence measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer. The electrochemical data were obtained with a BAS100B

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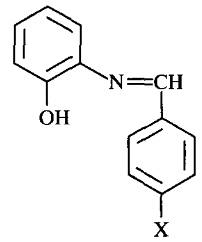
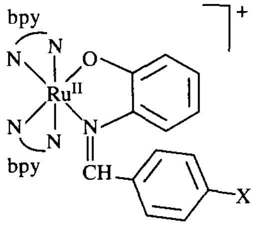


HL–X (X = NO_2, Cl, F, Me, OMe or NMe_2)



X	Compound
NO_2	1
Cl	2
F	3
Me	4
OMe	5
NMe_2	6

electrochemistry system. A three-electrode assembly (BAS) comprising a glassy carbon or Pt working electrode, Pt auxiliary electrode and an aqueous Ag–AgCl reference electrode were used. The electrochemical measurements were carried out in acetonitrile solution of the complexes (1 mmol dm^{-3}) and the concentration of the supporting electrolyte tetraethylammonium perchlorate (TEAP) was maintained to 0.1 mol dm^{-3}. All the potentials reported in this study were referenced against aqueous Ag–AgCl electrode, which under similar experimental conditions gave a value of 0.36 V for the ferrocene/ferrocenium couple. Carbon, hydrogen and nitrogen analyses were carried on a Perkin–Elmer 240C elemental analyzer.

Materials

All reagents and solvents were purchased from commercial sources and used as received. $Ru(bpy)_2Cl_2 \cdot 2H_2O$ was prepared by the known methods [11]. Silver perchlorate was prepared from silver carbonate and perchloric acid, and recrystallized from C_6H_6.

Preparation of the ligands

The Schiff base ligands were prepared by refluxing equimolar (10 mmol) quantities of *o*-aminophenol and *p*-substituted benzaldehyde in methanol (50 cm^3) for 5 h. Concentration of the solution gave yellow to orange crystals, which were filtered off and recrystallized from ethanol; yield 70–80%, m.p. 160°C (NO_2), 115°C (Cl), 110°C (F), 105°C (Me), 112°C (OMe) and 116°C (NMe_2).

Preparation of the complexes

$[Ru(bpy)_2(L\text{-}X)](ClO_4)$ (**1**–**6**). All the complexes were prepared under nitrogen atmosphere in the same way as described below for **1**.

To a suspension of *cis*-$[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (0.52 g, 1 mmol) in ethanol (80 cm^3) at room temperature was added $AgClO_4$ (0.42 g, 2 mmol) and stirred for 2 h. AgCl precipitated was removed by filtration through a glass frit (F-grade). The filtrate was treated with a solution of HL–NO_2 (0.26 g, 1 mmol) dissolved in ethanol (20 cm^3), followed by triethylamine (0.1 g, 1 mmol). The resulting solution was stirred at room temperature for 10 h, during which time it became dark red–orange. The solution was filtered to remove any solid deposited and the filtrate was evaporated to dryness on a rotary evaporator, when a red–orange microcrystalline solid deposited. This was collected by filtration, recrystallized from methanol–ethanol (1 : 1) mixture; yield 0.52 g (65%).

CAUTION! Silver perchlorate and other perchlorate salts described above are potentially explosive. Although $AgClO_4$ was recrystallized in gram quantities without any difficulty, extreme caution should be exercised in handling these compounds.

RESULTS AND DISCUSSION

The ruthenium(II) mixed-chelates **1**–**6** have been straightforwardly prepared in fairly good yields (60–70%) by reacting solvated $[Ru(bpy)_2(S)_2]^{2+}$ species with the Schiff bases. The substituents in the *p*-position of the phenyl ring has been varied with an aim to maximize the σ-donor ability of the ligands on going from **1** to **6**. The analytical data of the complexes are given in Table 1, which also include the characteristic $\nu(C{=}N)$ vibration of the compounds. Relative to the free ligands, the $\nu(C{=}N)$ frequency in the complexes are shifted to lower energy by 20–25 cm^{-1}. The ionic nature of the perchlorate in all the complexes are evident due to the presence of ν_3 and ν_4 bands at 1090 and 622 cm^{-1}, respectively.

The redox properties of the mixed-ligand complexes were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and the relevant electrochemical data are given in Table 2. Cyclic voltammograms of all the complexes, except **6**, exhibit a reversible Ru^{II}/Ru^{III} and an irreversible Ru^{III}/Ru^{IV} metal-centred oxidation processes in the positive potential region up to 2.0 V. In the case of **6**, as shown in Fig. 1, both the oxidation processes take place reversibly. The criteria of reversibility were checked by observing constancy of peak to peak separation

Table 1. Analytical data[a] and characteristic ν(C=N)(cm^{-1}) vibration of the complexes

	Analysis (%)			
Complex	C	H	N	ν(C=N)
1	52.97(53.22)	3.64(3.49)	11.23(11.29)	1585
2	53.42(53.22)	3.45(3.36)	9.52(9.40)	1590
3	53.57(54.43)	3.67(3.57)	9.86(9.62)	1590
4	56.35(56.39)	4.09(4.01)	9.84(9.67)	1592
5	55.86(55.17)	4.00(3.92)	9.77(9.66)	1595
6	56.62(55.91)	4.37(4.25)	11.51(11.36)	1600

[a] Calculated values are given in parentheses.

Table 2. Electrochemical data for ruthenium(II) complexes in MeCN

	Oxidation[a]							
Complex	$E^1_{1/2}$ (V)	ΔE_p (mV)	$E^2_{1/2}$	E^{2c} (V)	Reduction[b]			
1	0.58	59	—	1.44	−0.876(66)[d]	−1.131(62)	−1.676(68)	−1.93(96)
2	0.541	60	—	1.416	−1.68(78)	−1.93(80)		
3	0.534	60	—	1.38	−1.68(72)	−1.932(85)		
4	0.512	61	—	1.336	−1.69(69)	−1.94(84)		
5	0.496	60	—	1.216	−1.70(82)	−1.94(94)		
6	0.430	59	0.735(61)	0.716	−1.71(65)	−1.95(88)		

[a] AgCl (Pt electrode).

[b] In volts vs. Ag–AgCl (glassy carbon electrode).

[c] Irreversible peak potential from DPV.

[d] The values in parentheses are peak separations in mV.

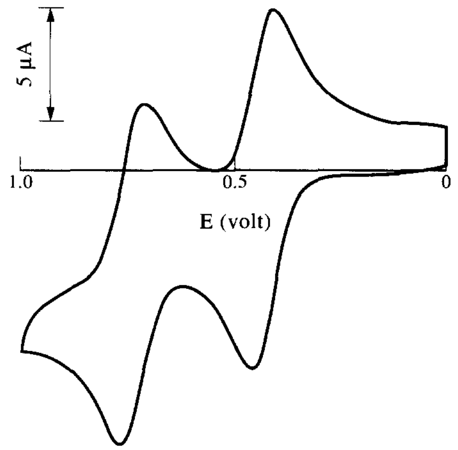


Fig. 1. Cyclic voltammogram of **6** in CH_3CN with a platinum electrode at a scan rate of 100 mVs^{-1}.

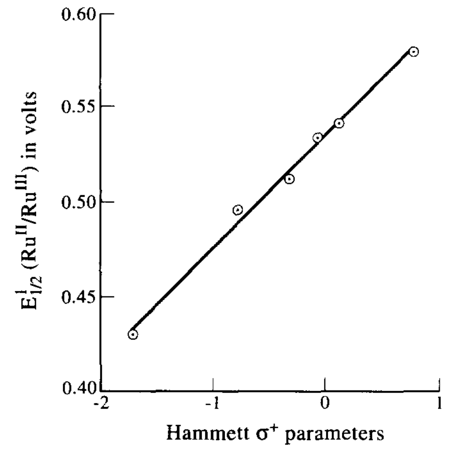


Fig. 2. Plot of $E^1_{1/2}$ (Ru^{II}/Ru^{III} couple) *vs* the Hammett σ^+ parameters with a linear least-squares fit to the data.

($\Delta E_p = E_{pa} - E_{pc} = 60$–65 mV) and ratio of peak heights (${}^iP_a/{}^iP_c \approx 1$) with the variation of scan rates. The potential of the Ru^{II}/Ru^{III} couple can be tuned from 0.43 V (*vs* Ag–AgCl) for **6** to 0.58 V for **1**, a range of 0.15 V, whereas Ru^{III}/Ru^{IV} couple can be varied from 0.735 V (**6**) to 1.44 V (**1**), a range of 0.7 V. A comparison of the electrochemical data (Table 2), reveals that the complexes with electron-donating substituents on the Schiff base ligands get most easily oxidized relative to those containing the electron-accepting substituents. It is possible to make a more detailed analysis of the redox data in terms of quantifying the substituent effects. The simplest way to do this is to consider a Hammett type relationship. Recently, Constable *et al.* [12] reported a plot of Ru^{II}/Ru^{III} potential against Hammett σ^+ parameters (σ^+, an electrophilic substitution constant) rather than σ parameters. They pointed out it is more appropriate to use Hammett σ^+ parameters rather than σ parameters as the oxidation processes deal with reactions which involve the development of positive charge (albeit on the metal centre rather than on the organic ligand). As shown in Fig. 2, a linear correlation is obtained by plotting the redox potentials ($E^1_{1/2}$) of Ru^{II}/Ru^{III} couple against the Hammett σ^+ parameters (NO_2, +0.79; Cl, +0.11; F, −0.07; Me, −0.31; OMe, −0.78; NMe_2, −1.7) [13]. It is interesting to note that the introduction of a strongly electron-releasing substituent like NMe_2 in the Schiff base of **6** has not only shifted the potential of the Ru^{II}/Ru^{III} couple to the lowest value (0.43 V) of the series but also has facilitated the removal of an electron from the Ru^{III} centre to such an extent that the oxidation to Ru^{IV} occurs reversibly at a potential as low as 0.735 V. The oxidation potential of Ru(bpy)$_3^{2+}$ (1.25 V) [14,15] gets drastically reduced on replacement of a bpy ligand with a L–X anion and in the case of **6** the reduction is by 0.82 V. Thus, HL–NMe_2 should form a very stable *tris*-complex with ruthenium(III) and perhaps will be a good candidate even for the facile synthesis of corresponding ruthenium(IV) species. While comparing the redox potentials of these complexes with that of Ru(bpy)$_3^{2+}$ it should be noted, however, that the single biggest effect is the overall +1 charge on the complexes compared to +2, which will electrostatically make the oxidation easier irrespective of the donor set about the metal ion. Similar studies of the role of substituents or donor sets in ruthenium complexes have been reported by others [16–18]. For example, Chakravorty *et al.* [16] have studied the electrochemical behaviour of *tris*(N-aryl-salicylaldimine) Ru^{III} complexes and have shown that the potentials of both Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} couples increase systematically with increasing electron-withdrawing character of the ligands. On the other hand, Ward *et al.* [17,18] have investigated substantial lowering of redox potentials on substituting a pyridine ring in a polypyridine Ru^{II} complexes by a phenolic moiety.

In the negative potential region, all the complexes undergo two quasi-reversible reduction processes around −1.68 and −1.94 V *vs* Ag–AgCl (glassy carbon electrode), which are due to the reduction of the bpy ligands. On the other hand, with a Pt electrode the reduction events have been found to occur irreversibly. Since each bpy can accept two electrons in its lowest unoccupied molecular orbitals [19,20], one should except to observe four such reduction steps in the series. The observation of only two couples up to −2.2 V was limited by the cut-off potential of the supporting electrolyte in acetonitrile.

The electrochemical responses of the Schiff base HL–NO_2 and corresponding complex (**1**) show (Fig. 3) interesting features. In the free ligand, two suc-

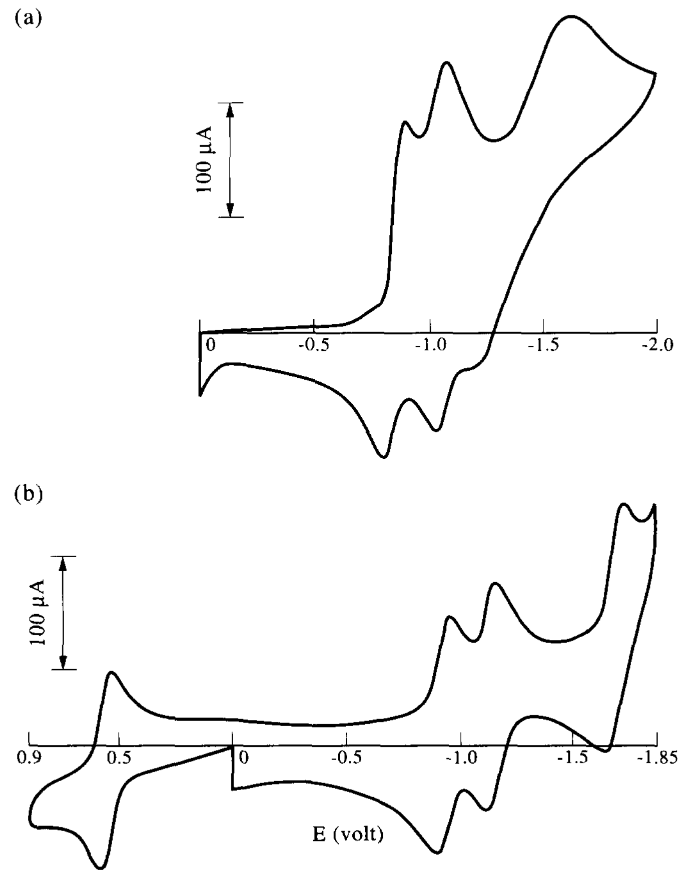


Fig. 3. Cyclic voltammograms of HL–NO_2 (a) and its complexes **1** (b) in CH_3CN with a glassy carbon electrode at a scan rate of 100 mVs^{-1}.

cessive reversible couples are observed at −0.86 and −1.06 V which are nominally shifted in the complex at −0.88 and −1.13 V. These ligand-centred electron transfer processes are characteristic of the electron-seeking property of the nitro group. The fact that the two electron transfer processes in the complex is slightly but definitely more difficult relative to those of the free ligand can be attributed to the enhanced electron density of L–NO_2 anion in the complex.

The UV–vis spectral data of the complexes are given in Table 3. The absorption spectra of all the complexes are similar showing two very intense bands in the UV region and two moderately intense bands in the visible regions. The lowest energy band observed between 501 nm (for **1**) and 517 nm (for **6**) can be attributed to metal ($d\pi$)–π^* (bpy) MLCT transition. The next higher energy band located between 353 nm (for **1**) and 359 nm (for **6**) is due to the Schiff base n–π^* transition because similar bands are also observed in the free ligands in the same energy region. The absorptions below 300 nm are due to π–π^* ligand centred transitions. It may be mentioned that the MLCT transition of $[Ru(bpy)_3](ClO_4)_2$ occurring at 452 nm [21] gets substantially displaced to a lower energy on substituting one bpy with a Schiff base ligand, which is in consonance with greater σ-donor and weaker π-acceptor property of the Schiff bases relative to bpy. It is interesting to note that the peak position of the MLCT band in the complexes undergoes blue-shift with the increase in electron-withdrawing ability of the substituent X. In fact a linear correlation [$\bar{\nu}_{max} = 260\sigma^+ + 19{,}750$] can be obtained by plotting the energies of the lowest MLCT band maxima vs the Hammett σ^+ parameters. The effect of substituents on the energy of MLCT transition is similar to that observed in the redox potential of Ru^{II}/Ru^{III} couple. As shown in Fig. 4, a linear correlation is obtained for $\bar{\nu}_{max}$ (MLCT) vs $\Delta E^1_{1/2}$ plot. It should be noted that although the MLCT transition involves the promotion of an electron from a metal-centred $d\pi$ orbital to the lowest antibonding bpy-centred π^* orbital, in the mixed-chelates the HOMO–LUMO energy gap of the system is considerably reduced by increasing electron density of the metal centred by a Schiff base.

The position of the MLCT absorptions are also affected by solvents (MeCN, MeOH, $MeNO_2$, DMF, Me_2CO, CH_2Cl_2 and H_2O), albeit to a small extent (Table 4). The band maximum shifts to higher energy with the increase in polarity of the solvent. Again linear correlations have been obtained by plotting $\bar{\nu}_{max}$(MLCT) against Kosower's **Z** [22] [$\bar{\nu}_{max} = 17{,}560 + 29.8$ **Z**] and Reichardt's $\mathbf{E_T}$ [23] [$\bar{\nu}_{max} = 17{,}805 + 40.1$ $\mathbf{E_T}$] solvent scale. The observed solvent effect of the complexes is indicative of a dipolar charge distribution in the ground state and a charge-transfer axis that is collinear with the dipole-axis. In other words, the trend observed indicates a

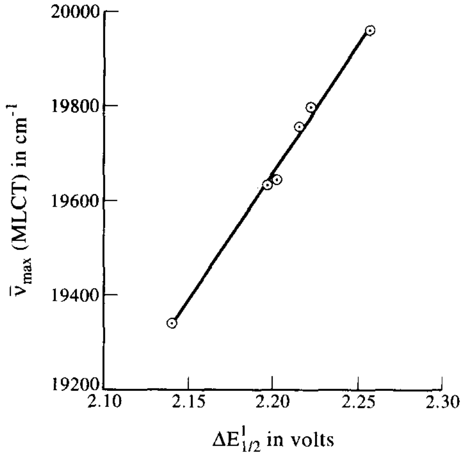


Fig. 4. Correlations between the redox potential, $\Delta E^1_{1/2}$ and the energy of the MLCT band maxima for the complexes listed in Table 1.

Table 4. Spectral data of MLCT transition for complex **4** in various solvents and relevant parameters from various solvent scales

Solvents	λ_{max}, nm (ν_{max}, cm^{-1})	E_T	Z
H_2O	490(20,410)	63.1	94.6
MeOH	499(20,040)	55.5	83.6
$MeNO_2$	509(19,650)	46.3	—
MeCN	510(19,610)	46.0	71.3
Me_2CO	511(19,570)	42.2	65.7
CH_2Cl_2	512(19,530)	41.1	64.2
DMF	511(19,570)	48.3	68.5

Table 3. Electronic spectral data of the complexes

Complex	λ_{max}, nm (ε, mol^{-1}cm^{-1})			
1	501(7600)	353(8200)	293(35,000)	245(22,800)
2	505(8600)	355(11,000)	294(19,800)	244(18,500)
3	506(9960)	356(12,900)	294(48,500)	245(32,000)
4	509(7600)	356(9800)	294(15,800)	245(16,100)
5	513(9300)	358(12,500)	293(18,400)	244(17,300)
6	517(12,400)	359(12,900)	293(45,000)	245(34,000)

polar ground state and nonpolar excited state of the complexes. However, this is in contrast to the small degree of solvatochromism that is observed for the MLCT bands of $Ru(bpy)_3^{2+}$ and related systems [24,25], for which the MLCT band shifts to lower energy with increased solvent polarity [26]. Interestingly, in $[Ru(bpy)_2(L\text{–}X)]^+$ species the n–π^* transition also undergoes blue-shift when polarity of the solvent is increased. Although solvation by a polar solvent stabilizes both the n and π^* orbitals, the stabilization of non-bonding orbitals is more pronounced, particularly with hydrogen-bonding solvents like H_2O, MeOH etc. than π^* orbitals. The net result is the increase in the energy of the n–π^* transition.

Table 5. Luminescence data in MeCN at room temperature

Complex or ligand	Emission maxima (nm)	Excitation wavelength (nm)
HL–NO_2	500(sh), 450	380
HL–Cl	495(sh), 410	352
HL–Me	492(sh), 410	346
HL–OMe	500(sh), 420	353
1	425(sh), 391	353
2	428(sh), 398	355
4	433(sh), 399	356
5	438(sh), 404	358
6	462(sh), 412	359

Luminescence studies showed that all the free Schiff base ligands and their corresponding ruthenium(II) complexes are luminescent at room temperature in dry acetonitrile when irradiated with UV and visible light. The free ligands show substantial luminescence with maxima ranging from 400 to 550 nm but the strong emission peak occurs around 400–450 nm (Table 5). The complexes also have the similar type of luminescence behaviour with the strong emission peak lying between 390 nm (for **1**) and 410 nm (for **6**). Additionally, weak emission occurs around 600 nm. The room temperature luminescence spectra of

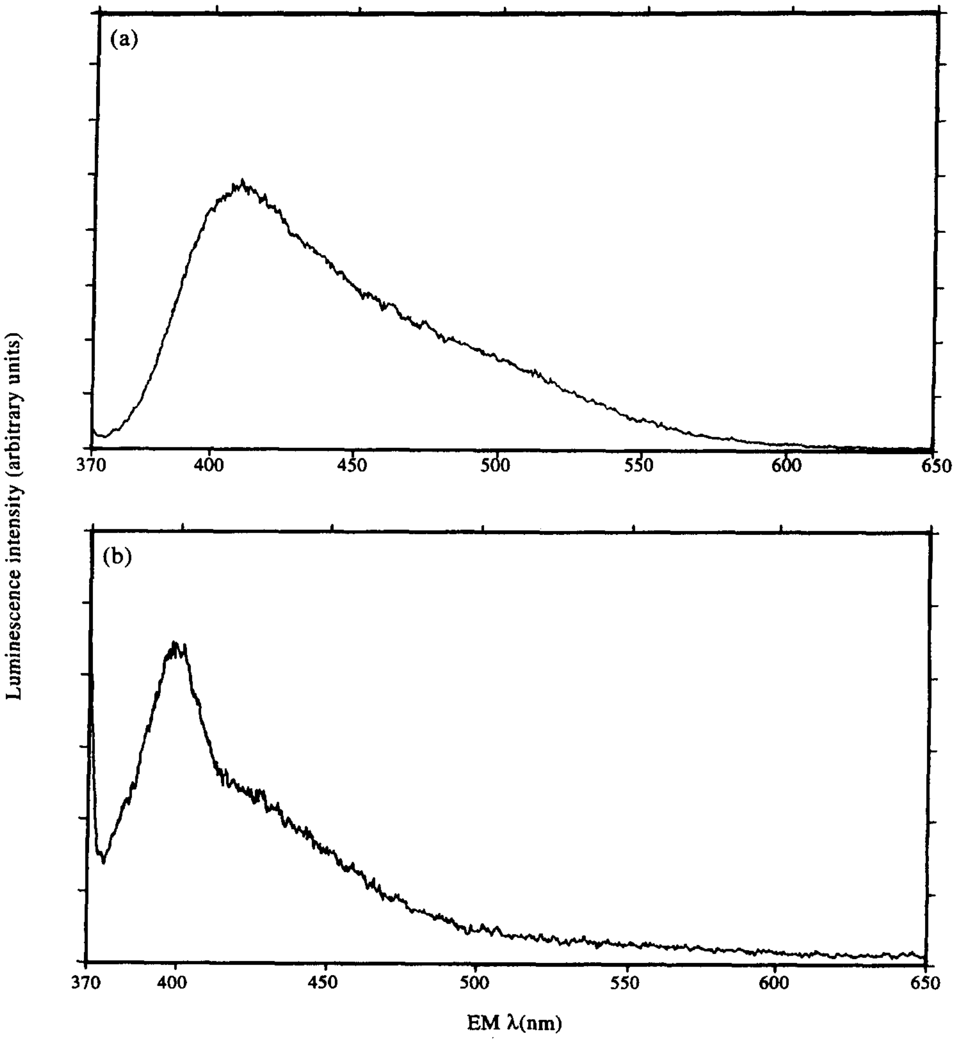


Fig. 5. Luminescence spectra of HL–Me (a) and the complex **4** (b) at room temperature in CH_3CN.

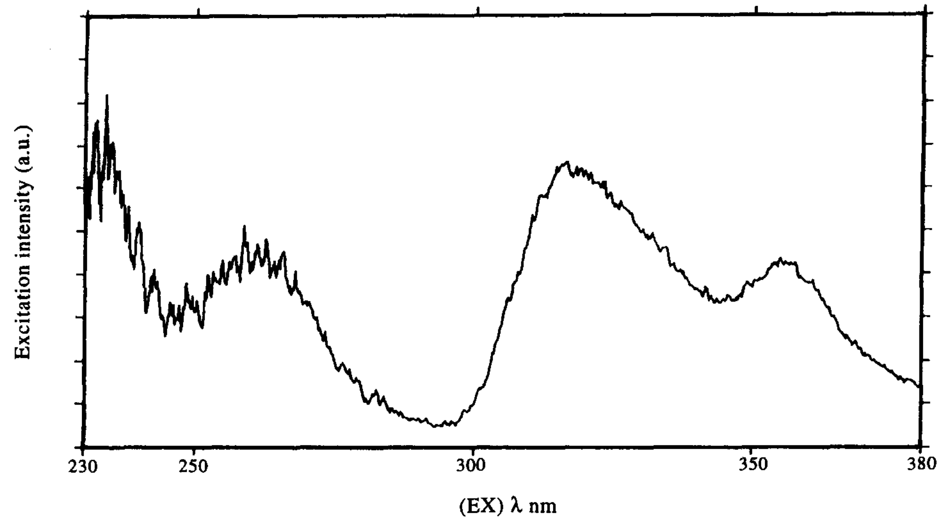


Fig. 6. Excitation spectra of **4** at room temperature in CH_3CN.

HL–Me and its complex (**4**) are shown in Fig. 5. The excitation spectra of **4** shown in Fig. 6 has been found to match closely its absorption spectrum, as is the case with other compounds. Photoluminescence of mononuclear ruthenium(II) complexes usually occurs due to metal-centred (MC), ligand-centred (LC) or charge-transfer (CT) transition [2,27]. For complexes that contain different ligands, excited states of each specific ligand can often be distinguished. In our complexes, the observed bands are probably due to metal-perturbed LC transition because of their similar bands shapes and energies as compared with those observed for the free Schiff bases. In ruthenium(II) polpyridine complexes the lowest energy emission occurs from the ^{3}MLCT excited state and is usually observed in the range 600–700 nm, depending upon the π-acceptor property of the ligand. Thus, while the emission maximum of $Ru(bpy)_3^{2+}$ at 620 mm [28] undergoes red shift on substitution of bpy with more σ-donating ligands [29–31], reversal of trend occurs when bpy is replaced by a more π-acceptor ligand [32–34]. Further, the introduction of σ-donor ligands has also interesting effect on the intensity of the emission spectrum. This occurs because the replacement of a bpy ligand by a Schiff base lowers the energy of the dz^2 and dx^2-y^2 orbitals and thereby shortens the energy gap between the MLCT state and d–d state. The d–d state therefore becomes thermally accessible and decays extremely fast, 'pulling across' an unfavourable equilibrium between the two states. Thus, while the inherent lifetime of the MLCT emission is not affected, the intensity of the emission is decreased as an alternative decay route is available.

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