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Ruthenium(II/III) bipyridine complexes incorporating thiol-based imine functions

Synthesis, spectroscopic and redox properties

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Abstract

A group of five new ruthenium(II) bipyridine heterochelates of the type $[Ru^{II}(bpy)_2L]^+$ **1a–1e** have been synthesized (bpy=2,2′-bipyridine; L=anionic form of the thiol-based imine ligands, $HS–C_6H_4N=C(H)C_6H_4(R)$ (R=OMe, Me, H, Cl, NO_2). The complexes **1a**−**1e** are 1:1 conducting and diamagnetic. The complexes **1a**−**1e** exhibit strong MLCT transitions in the visible region and intra-ligand transitions in the UV region. In acetonitrile solvent complexes show a reversible ruthenium(III)–ruthenium(II) couple in the range 0.2–0.4 V and irreversible ruthenium(III)→ruthenium(IV) oxidation in the range 1.15–1.73 V vs. SCE. Two successive bipyridine reductions are observed in the ranges −1.43 to −1.57 and −1.67 to −1.78 V vs. SCE. The complexes are susceptible to undergo stereoretentive oxidations to the trivalent ruthenium(III) congeners. The isolated one-electron paramagnetic ruthenium(III) complex, $\mathbf{1c}^+$ exhibits weak rhombic EPR spectrum at 77 K ($g_1=2.106$, $g_2=2.093$, $g_3=1.966$) in 1:1 chloroform–toluene. The EPR spectrum of $\mathbf{1c}^+$ has been analyzed to furnish values of distortion parameters ($\Delta=8988$ cm^{-1}; $V=0.8833$ cm^{-1}) and energy of the expected ligand field transitions ($\nu_1=1028$ nm and $\nu_2=1186$ nm) within the t_2 shell. One of the ligand field transitions has been experimentally observed at 1265 nm.

Keywords: Ruthenium(II/III) bipyridine complexes; Schiff base ligand; Spectroscopic and electrochemical properties

1. Introduction

Since the discovery of important photo-redox activities of ruthenium complexes incorporating 2,2′-bipyridine ligand, there has been continuous research activity in the direction of developing new ruthenium–bipyridine complexes with the perspective of tuning the redox and photophysical functions of this class of complexes [1–16]. Basic strategies behind all these activities are either to introduce selective groups within the bipyridine moiety itself or use other types of donor sites along with the ruthenium–bipyridine core to generate new mononuclear or polynuclear mixed ligand complexes to modulate the photo-redox activities [17–33]. The present work originates from our interest in developing new hetero ruthenium–bipyridine tris complexes of the type $[Ru^{II/III}(byp)_2L]^{1+/2+}$ where L is an electron-rich thiol-based anionic Schiff-base ligand. The ligand L can act as both a σ- and a π-donor in contrast to the σ-donor but π-acceptor nature of bipyridine molecule. Herein we report the synthesis of a group of new ruthenium–bipyridine complexes having a RuN_5S chromophore, their spectroscopic and electrochemical properties and the electronic structure of the trivalent congener. To the best of our knowledge this work demonstrates the first example of $[Ru^{II/III}(byp)_2L]^{1+/2+}$ complexes where L is a thiol-based Schiff base ligand.

2. Experimental

2.1. Materials

Commercially available ruthenium trichloride (S.D. Fine Chemicals, Bombay, India) was converted to $RuCl_3–3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. The starting complex $[Ru^{II}(bpy)_2Cl_2]\cdot 2H_2O$ was prepared according to the reported procedure

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[34]. The compounds 2-amino thiophenol and *p*-substituted benzaldehydes were obtained from Fluka, Switzerland. Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) used for the column chromatography was purchased from S.D. Fine Chemicals, Bombay, India. For spectroscopic and electrochemical studies HPLC-grade solvents were used. Commercial tetraethyl ammonium bromide was converted to pure tetraethyl ammonium perchlorate (TEAP) by following an available procedure [35].

2.2. Physical measurements

Solution electrical conductivity was checked using a Systronic conductivity bridge, 305. Electronic spectra (900–200 nm) were recorded using a Shimadzu UV 160 spectrophotometer. The near-IR spectrum was recorded by using a Hitachi 330 spectrophotometer. Infrared spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility was checked with a PAR vibrating-sample magnetometer. ^{1}H NMR spectra were obtained using a 300 MHz Varian FT-NMR spectrometer. Cyclic voltammetry and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum-wire working electrode, a platinum-wire auxiliary electrode and an SCE reference electrode were used in a three-electrode configuration. TEAP was the supporting electrolyte and the solution concentration was ~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}. A platinum-wire gauze working electrode was used in coulometric experiments. All electrochemical experiments were carried out under a dinitrogen atmosphere and are uncorrected for junction potentials. EPR measurements were made using 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, $g=2.0023$). The elemental analyses were carried out with a Carlo Erba (Italy) elemental analyzer. The following Hammett σ values for *p*-substituents were used: H, 0.00; Me, −0.17; OMe, −0.27; Cl, +0.23; NO_2, +0.78 [36].

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

2.3. Treatment of EPR data

An outline of the procedure can be found in our recent publications [37,38]. We would like to note that a second solution also exists that is different from the chosen one, having small Δ, ν_1 and ν_2 values. The experimentally observed near-IR result clearly eliminates this solution as unacceptable.

2.4. Synthesis of ligands (HL^1–HL^5) and complexes **1a–1e**

The ligands HL^{1-5} were prepared by condensing 2-aminothiophenol with the appropriate benzaldehyde in dry ethanol under ice-cold conditions. The use of dry ethanol is absolutely essential to get the desired ligands in the pure solid state.

The complexes **1a**–**1e** were synthesized using a general method. Yields varied in the range 55–60%. Specific details are given for one representative case, **1c**.

2.4.1. Bis(2,2′-bipyridine)(N-phenylthiosalicylaldimine) ruthenium(II) perchlorate dihydrate $[Ru^{II}(bpy)_2L^3]ClO_4\cdot 2H_2O$ (**1c**)

The starting complex $Ru^{II}(bpy)_2Cl_2\cdot 2H_2O$ (300 mg, 0.57 mmol) was dissolved in absolute ethanol (20 cm^3) and to this 468 mg (2.28 mmol) of $AgClO_4$ was added and the mixture was refluxed for 30 min. It was then cooled and filtered through a sintered glass crucible. To this filtrate 240 mg (1.13 mmol) of HL^3 and 93 mg (1.13 mmol) of anhydrous sodium acetate were added and the resulting mixture was stirred under a nitrogen atmosphere. The stirring was continued overnight and the resultant product was cooled for about 4 h and then filtered. The solid product thus obtained was washed thoroughly with ice-cold water and dried in a vacuum desiccator over P_4O_{10}. The crude product was purified by column chromatography using a silica-gel column. The excess ligand was initially eluted with benzene. The desired deep brown colored complex **1c** was then eluted using a 3:1 dichloromethane–acetonitrile mixture. On removal of the solvent under reduced pressure the complex **1c** was obtained in the solid state. The product was then further purified by recrystallization from dichloromethane–hexane (1: 4). The yield was 58%.

2.4.2. Bis(2,2′-bipyridine)(N-phenylthiosalicylaldimine) ruthenium(III) diperchlorate dihydrate $[Ru^{III}(bpy)_2L^3](ClO_4)_2\cdot 2H_2O$ ($\mathbf{1c}^+$)

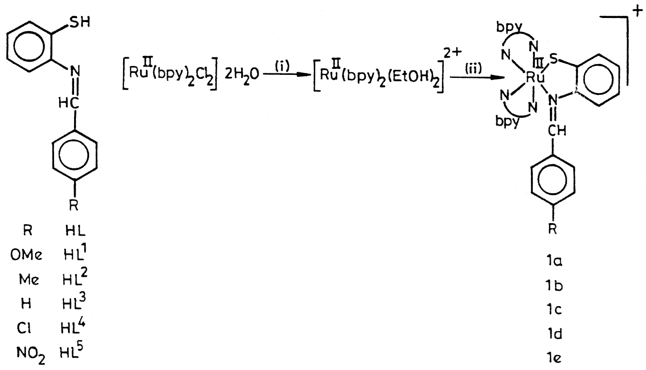
$[Ru^{II}(bpy)_2L^3]ClO_4\cdot 2H_2O$ (100 mg) was dissolved in acetonitrile (25 cm^3) and excess aqueous ceric ammonium sulfate solution was added to it. The mixture was stirred vigorously for 2 h. The color changed from deep brown to bluish green. The volume of the oxidized solution was reduced under vacuum. An aqueous solution of saturated sodium perchlorate was added to the concentrated solution and the mixture was kept in the refrigerator for 2 h. The solid compound thus obtained was filtered under high vacuum and washed with ice-cold water followed by cold methanol. The solid mass was finally dried in vacuo over P_4O_{10}. Yield: 95 mg (85%).

3. Results and discussion

3.1. Synthesis and characterization

A group of five substituted thiol-based Schiff base ligands used are abbreviated as HL^1–HL^5. The deprotonated form of HL binds to the metal ion in a bidentate S, N manner forming a five-membered chelate ring. The complexes **1** have been synthesized from $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ following the synthetic route shown in Scheme 1.

The complex cations (**1a**–**1e**) were precipitated directly from the reaction mixture as their dihydrated perchlorate salts and the crude products were purified by column chromatography using a silica-gel column.



Scheme 1. (i) $AgClO_4$, EtOH, heat, stirring; (ii) HL, NaO_2CMe, N_2, stirring.

The use of an inert atmosphere during the synthesis of the complexes (**1a**–**1e**) is found to be essential as the presence of atmospheric oxygen facilitates the formation of the oxidized trivalent congener of **1**.

The microanalytical data of the complexes (Table 1) are in good agreement with the calculated values, thus confirming the gross composition of the mixed tris chelates $[Ru(byp)_2L]ClO_4\cdot 2H_2O$ (**1a**−**1e**). The complexes exhibit 1:1 conductivity in acetonitrile solution (Table 1) and all the monocations are essentially diamagnetic.

3.2. Spectra

The ν(C=N) stretching frequency of the free ligands (HL) appears near 1620 cm^{-1} which has been shifted to 1590 cm^{-1} (Table 1) in accordance with the coordination of the azomethine function to the metal ion [39]. 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 (Table 1) due to the presence of ionic perchlorate.

The ^1H NMR spectra of the complexes were recorded in $(CD_3)_2$ SO solvent using a 300 MHz instrument. The spectra of one representative complex (**1d**) is shown in

Table 1
Microanalytical[a], conductivity[b], infrared[c] and electronic[b] spectral data

Compound	Elemental analysis (%)			Λ_M/Ω^{-1} (cm^2 mol^{-1})	IR (cm^{-1})		UV–Vis λ_{max} (nm) (ε[d], M^{-1} cm^{-1})
	C	H	N		ν(C=N)	$\nu(ClO_4^-)$	
1a	64.51 (64.39)	5.17 (5.08)	2.13 (2.20)	145	1593	1100, 610	618(1603)[e], 498(4800), 428(4800), 335(25000), 318(37200)[e], 296(58400), 250(34600), 217(50000)
1b	66.18 (66.06)	5.31 (5.22)	2.39 (2.27)	150	1594	1100, 620	625(1100)[e], 483(3330), 430(4798), 331(7450), 285(12998), 246(7598), 208(17066)
1c	65.50 (65.61)	5.10 (5.00)	2.42 (2.32)	147	1595	1097, 621	630(2000)[e], 490(5340), 430(5330), 350(7400)[e], 290(33800), 240(30100), 220(41400)
1d	62.21 (62.07)	4.51 (4.57)	2.32 (2.19)	155	1591	1091, 623	687(4233)[e], 491(7102), 432(7170), 330(13387), 280(46000), 243(41280), 205(46000)
1e	61.19 (61.06)	4.57 (4.50)	4.45 (4.31)	145	1595	1095, 620	696(1980)[e], 535(2795), 441(4283), 364(5125), 287(38279), 252(27544), 213(32150)
1c$^+$	56.44 (56.34)	4.34 (4.29)	2.16 (1.99)	235	1590	1110, 625	605(6270), 415(15026), 305(35030), 220(35110)

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

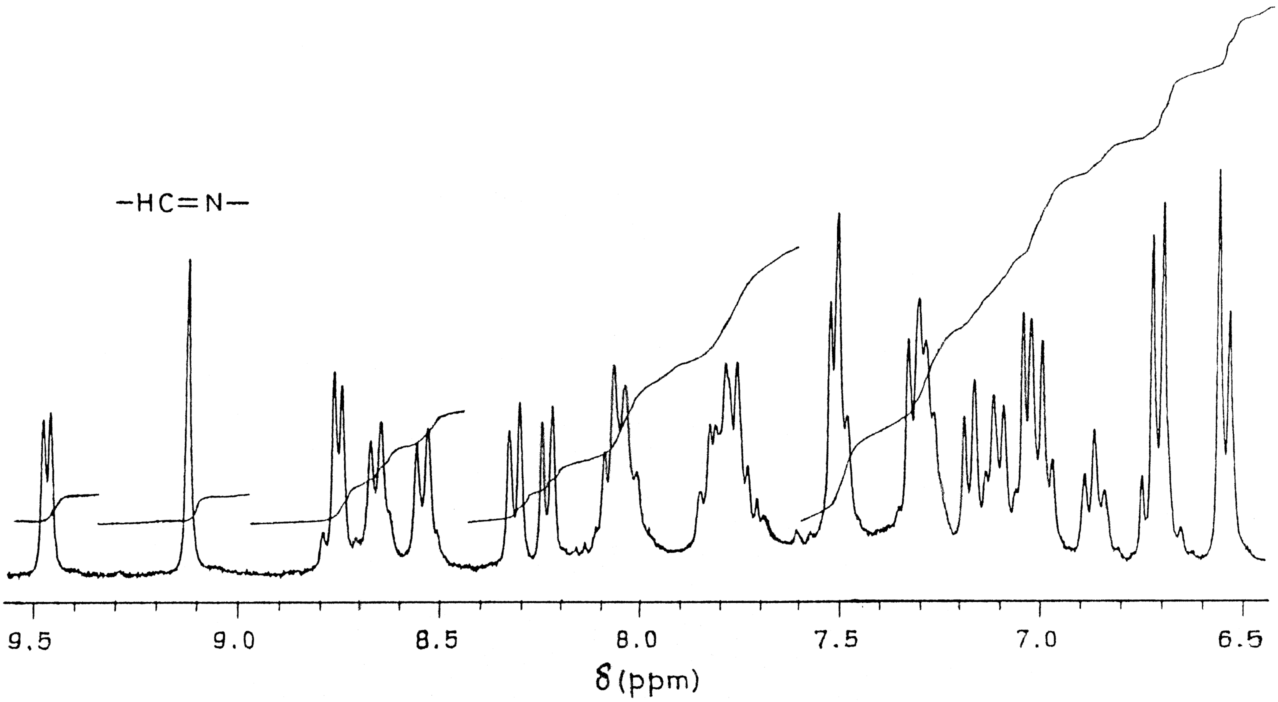


Fig. 1. ^{1}H NMR spectrum of $[Ru(bpy)_2L^4]ClO_4 \cdot 2H_2O$, **1d** in $(CD_3)_2SO$.

Fig. 1. The presence of asymmetric ligand L in the complexes (**1a**–**1e**) makes all the six aromatic rings inequivalent. The complexes **1c** and **1a**, **1b**, **1d**, **1e** thus possess 25 and 24 non-equivalent aromatic protons, respectively. Since the electronic environment of many aromatic hydrogen atoms are similar, their signals appear in a narrow chemical shift range. In fact the aromatic regions of the spectra are complicated due to the overlapping of several signals which have precluded the identification of individual resonances. However, direct comparisons of the intensity of the aromatic region proton signals with that of the clearly observable azomethine proton (–CH=N–) in the downfield region [δ(–CH=N–), ~9.2 ppm] and with the aliphatic protons for the complexes **1a** ($-OCH_3$; δ, 3.32 ppm and **1b** –Me; δ, 2.51 ppm) reveal the presence of the expected number of aromatic protons for all the complexes. The singlet due to the azomethine (–CH=N–) proton in the complexes **1a**–**1e** is found to be considerably deshielded, $\delta > 9$ ppm relative to that of the free ligands, $\delta \sim 8.5$ ppm as a consequence of electron donation to the metal center [40].

The electronic spectra of the complexes (**1a**–**1e**) were recorded in acetonitrile solvent in the region of 200–900 nm. The spectral data are listed in Table 1 and the representative spectrum is shown in Fig. 2. The complexes exhibiting multiple absorptions in the UV–visible region. In the visible region the complexes primarily display two moderately intense transitions near 500 and 430 nm. The lowest energy band is associated with a shoulder near 600 nm. The bands near 500 nm and 430 nm can be assigned to $d\pi(Ru) \rightarrow \pi^*(bpy)$ (symmetric) and $d\pi(Ru^{II}) \rightarrow \pi^*(bpy)$ (antisymmetric) MLCT (metal-to-ligand charge-transfer) transitions [41–44]. The next highest energy band near 350 nm may be due to the $d\pi(Ru^{II}) \rightarrow L$ MLCT transition. 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).

It may be noted that for the $Ru(bpy)_3^{2+}$ complex the lowest energy MLCT transition takes place at 450 nm in acetonitrile solution [45], which has reasonably red shifted (~500 nm) on substitution of one bipyridine ligand by the L. This is possibly due to the greater σ-donor and weaker π-acceptor properties of L^- compared to bpy.

3.3. Electron transfer properties

The electron transfer properties of the complexes have been studied by cyclic voltammetry and differential pulse voltammetry using a platinum-wire working electrode. All complexes systematically display four redox processes in the potential range of ±2 V vs. the saturated calomel electrode (SCE). Representative voltammograms are displayed in Fig. 3 and the reduction potentials data are shown in Table 2.

3.3.1. Metal redox

The complexes (**1a**–**1e**) display one reversible couple in the range 0.26–0.4 V vs. SCE (Fig. 3) which is assigned to the ruthenium(III)–ruthenium(II) process Eq. (1). The one-electron nature of the couple is

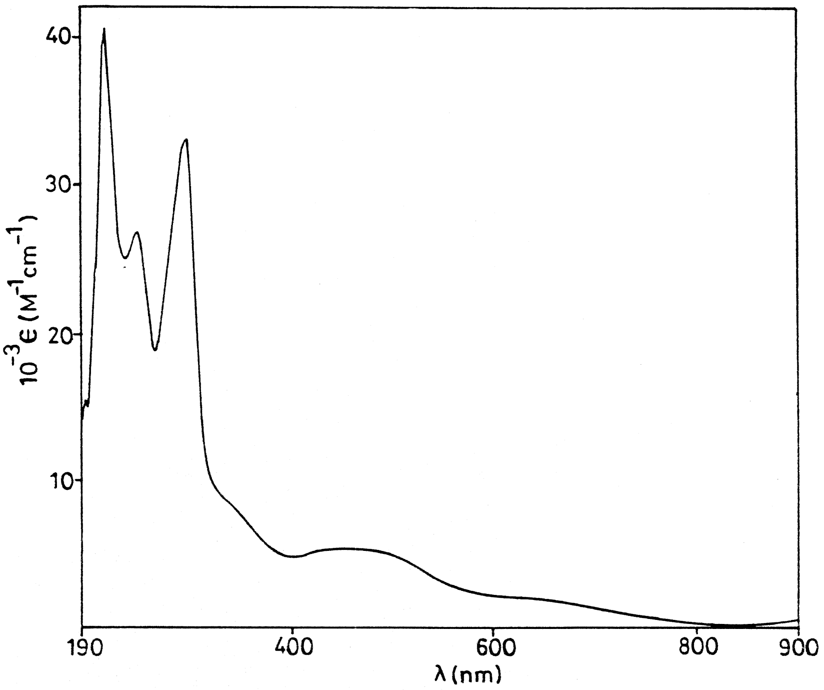


Fig. 2. Electronic spectrum of $[Ru(bpy)_2L^3]ClO_4 \cdot 2H_2O$, **1c** in acetonitrile.

$$[Ru^{III}(bpy)_2(L)]^{2+} + e^- \rightleftharpoons [Ru^{II}(bpy)_2(L)]^{1+} \quad (1)$$

confirmed by constant potential coulometry (Table 2). The presence of trivalent ruthenium in the oxidized solution is established by the characteristic EPR spectrum of the ruthenium(III) congener (see later). The formal potential of the couple (Eq. 1) varies depending on the electronic nature of the substituents present in the ligand frame, as expected (Table 2), and a plot of $E_{1/2}$ vs. σ_R is linear (Fig. 3) [46], where σ_R is the Hammett constant of the substituent R. Under identical experimental conditions, the ruthenium(III)–ruthenium(II) couple of $Ru(bpy)_3^{2+}$ ap-

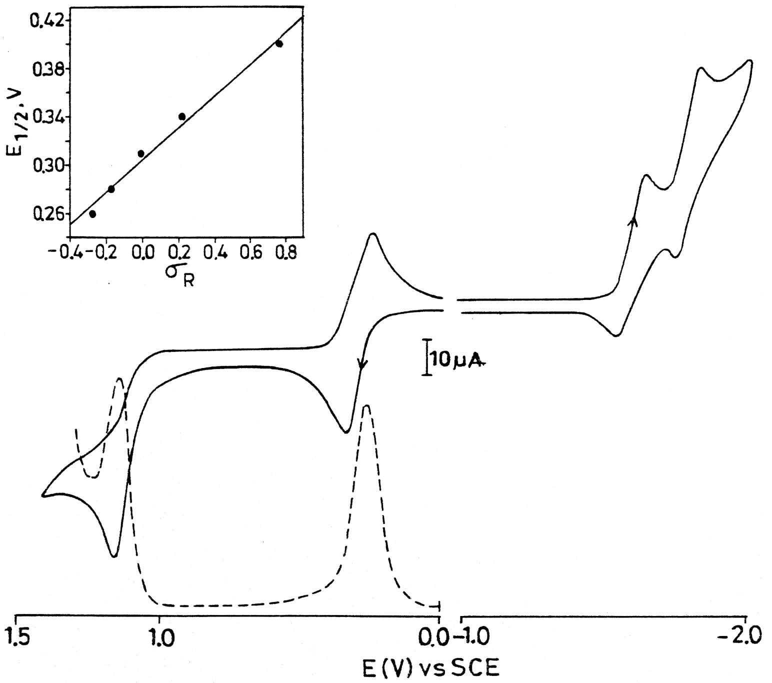


Fig. 3. Cyclic voltammograms of ~10^{-3} M solution of $[Ru(bpy)_2L^1]ClO_4 \cdot 2H_2O$, **1a** in acetonitrile at 298 K (——). Differential pulse voltammograms are shown for the oxidation processes only (--------). Inset shows the least-squares fit of $E_{1/2}$ of the Ru^{III}–Ru^{II} couple vs. σ_R.

Table 2
Electrochemical data at 298 K[a]

Compound	$\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ couple, E^0_{298} (V) [ΔE_p (mv)]	n[b]	$\mathrm{Ru^{III}}$–$\mathrm{Ru^{IV}}$ E_{pa}[c] (V)	Ligand reduction E^0_{298}(V) [ΔE_p(mv)]	
1a	0.26 (60)	1.09	1.15	−1.57(100)	−1.78(110)
1b	0.28 (70)	1.11	1.41	−1.54 (95)	−1.74(100)
1c	0.31 (70)	0.95	1.54	−1.51(90)	−1.72(110)
1d	0.34 (65)	1.07	1.64	−1.45(100)	−1.71(120)
1e	0.40 (65)	1.10	1.73	−1.43(100)	−1.67(120)

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

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

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

pears at 1.29 V [43]. Thus, replacement of one π-acidic bpy ligand from the $\mathrm{Ru(bpy)_3^{2+}}$ core by one σ-donating anionic thiolato ligand $\mathrm{L^-}$ results in a decrease of the ruthenium(III)–ruthenium(II) potential by 0.9–1.0 V depending on the nature of the R group in the ligand frame (L). The reduction of the overall charge of the complex cation from +2 in $\mathrm{Ru(bpy)_3^{2+}}$to +1 in the present set of complexes (**1a**–**1e**) provides further electrostatic stabilization of the oxidized trivalent ruthenium(III) congener which has possibly originated from the better σ-donor and weaker π-acceptor character of $\mathrm{L^-}$ [47].

The low ruthenium(II)–ruthenium(III) oxidation potential in the complexes (**1a**–**1e**) might be responsible for the preferential stabilization of the complexes in the trivalent ruthenium(III) oxidation state if the reaction is carried out under atmospheric conditions as stated before [48].

The complexes exhibit a second irreversible oxidation process in the range 1.15–1.73 V vs. SCE (Fig. 3). Although the current height of this process is found to be ~1.6 times more than that of the previous ruthenium(III)–ruthenium(II) couple, the one-electron nature of the second irreversible oxidation process has been established by differential pulse voltammetry (Fig. 3). The second oxidation process might be due to either $\mathrm{Ru^{III}}\rightarrow\mathrm{Ru^{IV}}$ oxidation or oxidation of the coordinated thiolato function. Since the observed potential difference between the two successive oxidation processes ($\mathrm{Ru^{II/III}}$, second irreversible oxidation process) in the complexes (**1a**–**1e**) (0.9–1.3 V, Table 2) compares well with the reported $\mathrm{Ru^{II/III}}$–$\mathrm{Ru^{III/IV}}$ potential difference in many mononuclear complexes [49,50], it may be reasonable to consider the second oxidation process as ruthenium(III)→ruthenium(IV) oxidation, Eq. (2). However, the possibility of the oxidation of coordinated

$$[\mathrm{Ru^{III}(bpy)_2(L)}]^{2+} - e^- \rightarrow [\mathrm{Ru^{IV}(bpy)_2(L)}]^{3+} \qquad (2)$$

thiol function cannot be ruled out. The irreversible nature of the oxidation process in the cyclic voltammetric timescale has precluded its isolation and further characterization.

The effect of the substituents (R) present in the ligand frame (L) is observed to be much more pronounced in the case of the ruthenium(III)–ruthenium(IV) oxidation process compared to the ruthenium(II)–ruthenium(III) oxidation process (Table 2).

3.3.2. Ligand reduction

The complexes display two quasi-reversible reductions in the ranges −1.43 to −1.57 and −1.67 to −1.78 V (Table 2, Fig. 3). The one-electron nature of the couples has been established by the current height considerations. Since the free ligands HL do not exhibit any ligand reductions within the above-mentioned potential range, the observed reductions are therefore considered to be two successive reductions of the coordinated bpy ligands. Since each bpy can accept two electrons in its lowest unoccupied molecular orbitals (LUMO) [51–54], four such reduction steps are expected for each of the complexes (**1a**–**1e**). However, only two reductions corresponding to Eqs. (3) and (4) have been observed within a −2 V potential range.

$$[\mathrm{Ru^{II}(bpy)_2(L)}]^{+} + e^- \rightleftharpoons [\mathrm{Ru^{II}(bpy)(bpy^{\cdot -})(L)}] \qquad (3)$$

$$[\mathrm{Ru^{II}(bpy)(bpy^{\cdot -})(L)}] + e^- \rightleftharpoons [\mathrm{Ru^{II}(bpy^{\cdot -})(bpy^{\cdot -})(L)}]^{-} \qquad (4)$$

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

3.4. Electrogeneration of trivalent ruthenium congeners and distortion parameters

Coulometric oxidations of the complexes in acetonitrile solvent at a potential of 100 mV positive to the corresponding E_{pa} of the $\mathrm{Ru^{III}}$–$\mathrm{Ru^{II}}$ couple produced the deep bluish green colored trivalent-ruthenium(III) complexes. The observed Coulomb count corresponds to 1e^- transfer for all the complexes (Table 2). The oxidized solutions (**1a**$^+$–**1e**$^+$) show the voltammograms which are superimposable on those of the corresponding bivalent complexes (**1a**–**1e**), indicating the stereoretentive nature of the oxidation process [55]. The electrochemical rereductions of the oxidized bluish green solutions (**1**$^+$) at 0.0 V regenerated the corresponding bivalent complexes **1** quantitatively. The

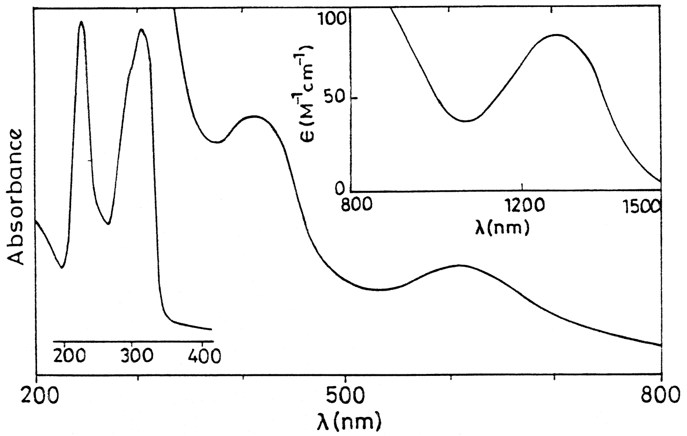


Fig. 4. Electronic spectrum of the oxidized complex $[Ru(bpy)_2L^3](ClO_4)_2\cdot 2H_2O$, **1c**$^+$ in acetonitrile solution. Inset shows the electronic spectrum of **1c**$^+$ in the range 1500–800 nm.

complexes (**1**) can also be oxidized chemically to the same bluish green ruthenium(III) complexes using an aqueous ceric ammonium sulfate solution. Although all the complexes can be oxidized by aqueous ceric solution, only one trivalent complex **1c**$^+$ has been isolated in pure solid state as dihydrated perchlorate salt. The complex **1c**$^+$ is highly soluble in polar solvents such as acetonitrile, dimethylformamide, dimethylsulfoxide and is sparingly soluble in non-polar solvents like chloroform, dichloromethane and benzene. The microanalytical data of the complex (**1c**$^+$) match well with the calculated values (Table 1). In the acetonitrile solution the complex **1c**$^+$ shows 1:2 conductivity (Table 1) and the complex is paramagnetic with a magnetic moment corresponding to one unpaired electron ($\mu = 1.91$ B.M.). In acetonitrile **1c**$^+$ displays two ligand-to-metal charge-transfer (LMCT) transitions in the visible region (Table 1, Fig. 4), as expected for the ruthenium(III) complexes and intraligand transitions in the visible region [56].

The EPR spectrum of **1c**$^+$ (in chloroform–toluene 1:1) is compatible with the weak rhombic symmetry ($g_1 = 2.106$, $g_2 = 2.093$, $g_3 = 1.966$; Fig. 5) [57,58]. The spec-

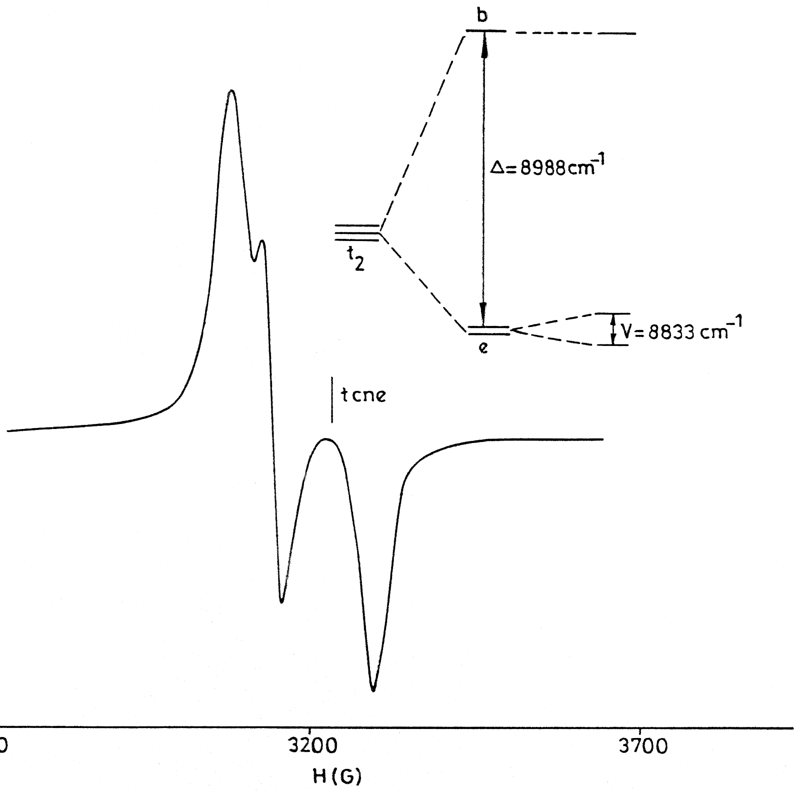


Fig. 5. EPR spectrum of the complex $[Ru(bpy)_2L^3](ClO_4)_2\cdot 2H_2O$, in chloroform–toluene (1:1) glass at 77 K. Inset shows the t_2 splittings.

trum was analyzed using the g-tensor theory for low-spin d^5 ions [59–63]. This yielded the values of axial distortion ($\Delta = 8988\ \mathrm{cm}^{-1}$) which split the $t_2$shell into $e+b$ and the rhombic distortion ($V = 0.8833\ \mathrm{cm}^{-1}$) which further splits into two non-degenerate components (Fig. 5). The value of the orbital reduction factor, k ($0.485\ \mathrm{cm}^{-1}$), is also furnished by the analysis. A pair of optical transitions ν_1 (1028 nm) and ν_2 (1186 nm) among the Kramers doublets are predicted. One weak transition (ν_2) is observed in practice at 1265 nm (Fig. 4). The other expected low-energy transition (ν_1) could not be detected, possibly due to the presence of nearby strong LMCT absorptions. In view of the involved approximations in the theory, the agreement between the experimentally observed ν_2 and the calculated ν_2 value is excellent.

4. Conclusions

We have observed the effect of the thiol-based imine function as a third ligand in the $[\mathrm{Ru(bpy)}_2]$ core with respect to spectroscopic and redox properties. The presence of strong σ-donor and weak π-acceptor thiol-based ligands (L^-) in the complexes (**1a**–**1e**) facilitates the successive reversible $\mathrm{Ru}^{II} \rightleftarrows \mathrm{Ru}^{III}$ and irreversible $\mathrm{Ru}^{III} \rightarrow \mathrm{Ru}^{IV}$ oxidation processes. The low ruthenium(II)–ruthenium(III) oxidation potentials of the complexes (**1**) help to isolate the trivalent congeners ($\mathbf{1}^+$) in the solid state by both electrochemical and chemical means at room temperature. A linear correlationship has been observed between the formal potentials of the ruthenium(II)–ruthenium(III) couple and the Hammett constant (σ) of the substituents (R).

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