

RUTHENIUM PHENOLATES. SYNTHESIS, CHARACTERIZATION AND ELECTRON-TRANSFER PROPERTIES OF SOME SALICYLALDIMINATO AND 2-(ARYLAZO)PHENOLATO COMPLEXES OF RUTHENIUM

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Abstract—Eleven mixed-ligand ruthenium(II) complexes of the general formula $[Ru(bpy)_2]$ (L)]ClO₄ [bpy = 2,2'-bipyridine, L = salicylaldiminate or 2-(arylazo) phenolate anion] have been synthesized and characterized. The complexes are diamagnetic (low-spin d^6 , S = 0) and in solution show intense MLCT transitions in the visible region. In acetonitrile solution they all show a reversible ruthenium(II)-ruthenium(III) oxidation in the range 0.5–0.9 V versus SCE and an irreversible ruthenium(III)-ruthenium(IV) oxidation near 1.6 V versus SCE. The potential of the ruthenium(II)-ruthenium(III) couple is sensitive to the nature of substituents on the ligand L. Two successive one-electron reductions of the coordinated bpy are also observed near -1.5 and -1.8 V versus SCE. Two representative $[Ru^{III}(bpy)_2(L)]^{2+}$ complexes have been synthesized by chemical oxidation of their ruthenium(II) precursors by aqueous ceric solution and isolated as perchlorate salts. These oxidized complexes are paramagnetic (low-spin d^5 , S = 1/2) and show rhombic ESR spectra at 77 K. They show intense LMCT transitions in the visible region in acetonitrile solution together with weak ligand-field transitions at lower energies. Chemical reduction of these ruthenium(III) complexes by hydrazine gives back the parent ruthenium(II) complexes. In acetonitrile solution the $[Ru^{III}(bpy)_2(L)]^{2+}$ complexes oxidize N,N-dimethyl aniline, 1,2-napthoquinone-1-oxime, [Ru^{II}(bpy)₂Cl₂] and [Fe^{II}(C₅H₅)₂] to produce N,N,N',N'tetramethylbenzidine, 1,2-napthoquinone-1-iminoxy radical, [Ru^{III}(bpy)₂Cl₂]⁺ and $[Fe^{III}(C_5H_5)_2]^+$, respectively, which have been characterized by spectroscopic and electrochemical techniques.

The interest in the chemistry of ruthenium¹ is largely due to the versatile electron-transfer properties exhibited by its complexes, which are again due to the wide range of oxidation states offered by this metal. The coordination environment around ruthenium plays the key role in stabilizing its different oxidation states and hence dictates the redox properties of the complexes. The chemistry

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tate N,O-coordinators forming stable six-membered chelate rings. The phenolate oxygen in L is a hard donor and hence stabilizes metals in their

of ruthenium in various coordination spheres, with

special reference to redox properties, is therefore of

significant importance and we have been active in

this area.² In the present study, we have used a

group of ligands which are abbreviated in general

as HL, where H is the dissociable phenolic hydro-

gen. The two types of ligand, viz. salicylaldimines

and 2-(arylazo)phenols, bind metal ions as biden-

higher oxidation states,³ while the imine (C==N) and azo (N==N) functions, due to their π -acid character, stabilize the lower oxidation states.⁴ Therefore, we have over here two donor sites with opposite nature in the same ligand. It may be noted here that the ruthenium chemistry of these two types of ligands appears to have received relatively less attention.^{5.6} In this paper we have restricted our study to ruthenium complexes incorporating only one L. To satisfy the remaining four coordination sites of this RuL moiety, we have used 2,2'-bipyridine(bpy) as the coligand. The synthesis, characterization and electron-transfer properties of a group of [Ru(bpy)₂(L)]ⁿ⁺ (n = 1,2) complexes are reported in this paper.

EXPERIMENTAL

Materials

Commercial ruthenium trichloride, purchased from Arora Matthey, Calcutta, India, was converted to $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. cis- $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ and methylsalicylaldehyde were synthesized using reported procedures.^{7,8} The salicylaldimine ligands were prepared by reacting equimolar amounts of salicylaldehyde and the respective amine in hot ethanol. The 2-(arylazo)phenol ligands were prepared by coupling diazotized aniline with p-cresol. Ferrocene was purchased from Aldrich. All other chemicals and solvents were reagent-grade commercial materials and were used as received. Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.9,10

Preparations

The complexes reported in this work were prepared by following two general methods. Details are given for two respective cases only.

 $[Ru^{II}(bpy)_2(sal-H)]ClO_4$. Ru $(bpy)_2Cl_2$ (100 mg, 0.19 mmol) was dissolved in ethanol (40 cm³) and AgNO₃ (65 mg, 0.38 mmol) was added. The mixture was stirred for 30 min. The deposited AgCl was separated by filtration and to the filtrate was added Hsal-H (38 mg, 0.19 mmol) and NaOAc (16 mg, 0.19 mmol). The resulting red solution was refluxed for 1 h on a water bath. The solution was then cooled to room temperature and a saturated aqueous solution of NaClO₄ (10 cm³) was added. [Ru (bpy)₂(sal-H)]ClO₄ precipitated as a deep brownish-red crystalline solid, which was collected by

filtration, washed with cold water and dried *in vacuo* over P_4O_{10} . Recrystallization from 1 : 1 acetonitrile– benzene gave dark red crystals of $[Ru(bpy)_2(sal-H)]ClO_4$; yield 105 mg (78%).

 $[Ru^{III}(bpy)_2(sal-H)](ClO_4)_2$. To a solution of $[Ru^{II}(bpy)_2(sal-H)]ClO_4$ (100 mg, 0.14 mmol) in acetonitrile was added an aqueous solution of ammonium ceric sulphate (100 mg, 0.16 mmol). The resulting solution was stirred for 10 min upon which the colour of the solution changed from red to deep green. The green solution was then filtered to remove any insoluble material. A saturated aqueous solution of NaClO₄ (10 cm³) was then added to the filtrate. Upon partial evaporation of the solvents, a dark crystalline product separated out which was collected by filtration, washed with cold water and dried *in vacuo* over P₄O₁₀; yield 95 mg (84%).

Physical measurements

Microanalyses (C,H,N) were performed using a Perkin-Elmer 240C elemental analyser. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Hitachi U-3400 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. ¹H NMR spectra were obtained on a Bruker AC-200 NMR spectrometer using TMS as the internal standard. X-band ESR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen) and the spectra were calibrated with DPPH (g = 2.0037). Solution electrical conductivity was measured using a Philips PR 9500 bridge with a solute concentration of 10^{-3} M. Electrochemical measurements were made using a PAR model 370-4 electrochemistry system as before.² A saturated calomel reference electrode (SCE) was used as the reference electrode. All electrochemical data are collected at 298 K and are uncorrected for junction potentials.

RESULTS AND DISCUSSION

Synthesis and characterization

Six salicylaldimines and five 2-(arylazo)phenols have been used in the present study. Individual ligands and their abbreviations are shown in struc-



tures 1 and 2. The HMe-sal-H ligand, which is structurally similar to the Hap-H ligand, has been used in particular to compare the effect of HC=N versus N=N on the redox properties of the complexes. The *para*-substituents (R') have been chosen so that a gradual variation in their inductive effect is maintained in order to study their influence on the metal-centred redox potentials. Eleven complexes of ruthenium(II) of the type [Ru(bpy)₂(L)] ClO₄ have been synthesized in good yields by following a general route as shown in eq. (1). The two chloride ligands of [Ru(bpy)₂Cl₂] are displaced in ethanol by Ag⁺ to produce [Ru(bpy)₂(EtOH)₂]²⁺

$$[\operatorname{Ru}(\operatorname{bpy})_{2}\operatorname{Cl}_{2}] \xrightarrow{\operatorname{Ag^{+},EtOH}}_{-2\operatorname{AgCl}} [\operatorname{Ru}(\operatorname{bpy})_{2}(\operatorname{EtOH})_{2}]^{2+}$$
$$\xrightarrow{\operatorname{HL}}_{\operatorname{NaOAC}} [\operatorname{Ru}(\operatorname{bpy})_{2}(L)]^{+} \quad (1)$$

in situ, which upon further reaction with HL in the presence of sodium acetate affords the desired complex cations which have been isolated as perchlorate salts in the solid state. It may be noted here that synthesis of the $[Ru(bpy)_2(ap-H)]^+$ complex has been reported earlier.⁶ As bpy is a symmetric bidentate ligand and L is a chelating bidentate ligand, $[Ru(bpy)_2(L)]^+$ may exist in only



one isomeric form, **3**. Hence, the synthesis of $[Ru(bpy)_2(L)]^+$ from *cis*- $[Ru(bpy)_2Cl_2]$ is stereoretentive.

Characterization data of the complexes are given in Table 1. Elemental (C,H,N) analytical data are in excellent agreement with the compositions of the complexes. Magnetic susceptibility measurements show that all these complexes are diamagnetic, which corresponds to the +2 state of ruthenium (low-spin d^6 , S = 0) in these complexes. IR spectra of $[Ru(bpy)_2(L)]ClO_4$ are complex in nature due to vibrations arising from bpy, L and the ClO_4^- ion. Assignment of all bands has not been attempted. However, some useful information is obtained by careful examination of the spectra and also by comparison with the spectrum of cis-[Ru(bpy)₂Cl₂]. For example, the v(Ru-Cl) stretch observed at 335 cm^{-1} in [Ru(bpy)₂Cl₂] is absent in all [Ru(bpy)₂ (L)]ClO₄ complexes, as expected. A broad and very intense band near 1100 cm⁻¹, together with a sharp and intense band near 625 cm⁻¹ are observed in all the 11 complexes due to the presence of the perchlorate ion. Several new bands are observed in the $[Ru(bpy)_2(L)]^+$ complexes, which are obviously due to the coordinated L. The IR spectral data are therefore in good agreement with the compositions of these complexes.

The $[Ru(bpy)_2(L)]ClO_4$ complexes are readily soluble in acetonitrile and much less soluble in dichloromethane and chloroform producing intense pinkish-red solutions. Molar conductivity data (Table 1) show that in acetonitrile solution these complexes behave as 1:1 electrolytes, as expected. Electronic spectra recorded in acetonitrile solutions show several intense absorptions in the visible region (Table 1). Selected spectra are shown in Fig. 1. The electronic spectral properties displayed by the six salicylaldiminato complexes are very similar. Each shows four intense absorptions in the visible region, which are probably due to allowed metal-to-ligand charge-transfer transitions. Three of the five 2-(arylazo)phenolato complexes show four absorptions in the visible region while the remaining two show three absorptions. These absorptions are also assigned to metal-toligand charge-transfer transitions. Multiple chargetransfer transitions in these complexes may result from lower symmetry splitting of the metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling.11 Multiple charge-transfer transitions have been observed before in similar mixed-ligand complexes.^{2a,e}

[']H NMR spectra recorded in CDCl₃ solution on two representative complexes, viz. [Ru(bpy)₂(sal-Me)]⁺ and [Ru(bpy)₂(ap-H)]⁺, show many sharp signals due to all the protons present in these complexes. In the sal-Me complex the methyl signal of the sal-Me ligand is observed at 2.08 ppm. The eight aromatic protons on the sal-Me ligand and 16 protons on the two bpy ligands show signals in the

Compound	C	Analysis" (%) H	Z	$\frac{\Lambda_{M}^{h}}{\mathrm{cm}^{2}}\mathrm{M}^{-1})$	Electronic spectral data ^b λ_{max} (nm) $(\varepsilon/M^{-1} m^{-1})$	Cyclic voltammetri $Ru^{II}-Ru^{III}$ E_{298}^{0} (V $\Delta E_{p}/mV$)	c data ^c $Ru^{III}-Ru^{IV}$ E_{pa} (V)
[Ru(bpy) ₂ (sal-OMe)]ClO4	55.4 (55.2)	3.8 (3.8)	9.4 (9.5)	140	$5.40^{d}(6400), 485(8400), 410^{d}(6800), 350(11200)$	0.56(70)	1.58
[Ru(bpy) ₂ (sal-Me)]ClO ₄	56.3 (56.5)	3.8 (3.9)	9.6 (9.7)	155	$550^d(6700), 490(10\ 100)$ $410^d(8000), 360(10\ 200)$	0.60(60)	1.58
[Ru(bpy) ₂ (sal-H)]ClO ₄	55.5 (55.9)	3.7 (3.7)	9.7 (9.9)	134	$570^{d}(7200), 510(11600)$ $425^{d}(9200), 375(11300)$	0.63(70)	1.60
[Ru(bpy)2(sal-Cl)]CIO4	53.0 (53.3)	3.5 (3.4)	9.2 (9.4)	148	$545^d(7000), 480(10\ 300)$ $400^d(8100), 350(10\ 300)$	0.67(60)	1.62
[Ru(bpy) ₂ (sal-NO ₂)]ClO ₄	52.8 (52.6)	3.3 (3.3)	11.0	136	$560^{d}(5600), 485(9000)$ $405^{d}(7000), 360(9000)$	0.79(70)	1.64
[Ru(bpy) ₂ (Me-sal-H)]ClO ₄	56.2 (56.5)	3.7 (3.9)	9.8 (9.7)	150	$550^{d}(6000), 484(10\ 800)$ $410^{d}(8500), 365(10\ 000)$	0.59(60)	1.58
$[Ru(bpy)_2(ap-OMe)]CIO_4$	54.3 (54.1)	3.8 (3.8)	11.2 (11.1)	142	$540^d(6000), 475(11500), 385(8000), 340(9600)$	0.60(70)	1.56
[Ru(bpy) ₂ (ap-Me)]ClO ₄	55.5 (55.3)	3.8 (3.9)	11.4 (11.4)	138	$545^{d}(4600), 465(10\ 200), 330^{d}(7000), 335^{d}(7800)$	0.64(60)	1.56
[Ru(bpy) ₂ (ap-H)]ClO ₄	54.7 (54.7)	3.6 (3.7)	11.8 (11.6)	152	$550^{d}(3100), 470(7200), 380(4600), 340(5400)$	0.68(60)	1.60
[Ru(bpy)2(ap-Cl)]ClO4	52.5 (52.2)	3.4 (3.4)	11.0 (11.1)	140	$560^d(2800), 475^d(6500), 435(7700)$	0.72(70)	1.62
[Ru(bpy) ₂ (ap-NO ₂)]ClO ₄	51.6 (51.5)	3.4 (3.4)	12.6 (12.7)	144	$650^{4}(2400), 470(9800), 435^{4}(7300)$	0.84(70)	1.64
"Calculated values in parenthe	ses.						

^b In CH₃CN. ^c Conditions: solvent, acetonitrile; supporting electrolyte, TEAP(0.1M); working electrode, platinum; reference electrode, SCE; solute concentration, $10^{-3}M$; $E_{298}^{0.8} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials; $\Delta E_{p} = E_{pa} - E_{pc}$; scan rate, 50 m s⁻¹. ^d Shoulder.

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Table 1. Characterization data of the $[Ru^{ff}(bpy)_2(L)]ClO_4$ complexes

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Fig. 1. Electronic spectra of [Ru^{II}(bpy)₂(sal-H)]ClO₄
 (----) and [Ru^{II}(bpy)₂ (ap-OMe)]ClO₄ (---) in acetonitrile solution.

range 6.4–9.2 ppm. No attempt has been made to assign the signals to individual protons. The azomethine proton shows a distinct resonance at 9.00 ppm. In the ap-H complex, the methyl signal of the ap-H ligand appears at 2.26 ppm and the aromatic protons are observed in the expected region (6.1–9.0 ppm).

Cyclic voltammetric studies

The electron-transfer properties of all the [Ru $(bpy)_2(L)$]ClO₄ complexes have been studied in



Fig. 2. Cyclic voltammograms of (a) $[Ru(bpy)_2(Me-sal-H)]ClO_4$ and (b) $[Ru(bpy)_2(ap-H)]ClO_4$ in acetonitrile solution (0.1 M TEAP) at a scan rate of 50 mV s⁻¹. The solute concentration in each case was 10^{-3} M.

acetonitrile solution by cyclic voltammetry. Voltammetric data are presented in Table 1 and selected voltammograms are shown in Fig. 2. All the complexes show two metal-centred oxidations and two ligand(bpy)-based reductions. We shall first consider the ligand-based reductions. Two successive reversible one-electron reductions near -1.50 and -1.75 V (all potentials are referenced to SCE) are displayed by all these complexes which are assigned to the reductions of the two bpy ligands,^{2a} as shown in eqs (2) and (3). The one-electron nature of these couples has been established by comparing

$$[Ru^{II}(bpy)_{2}(L)]^{+} + e^{-} \Longrightarrow$$

$$[Ru^{II}(bpy)(bpy^{-})(L)] - (2)$$

$$[Ru^{II}(bpy)(bpy^{-})(L)] + e^{-} \Longrightarrow$$

$$[Ru^{II}(bpy^{-})_2(L)]^-$$
 (3)

their current heights with those of the standard ferrocene–ferroceniun couple under identical experimental conditions. The ΔE_p values lie within the range 60–70 mV and do not change with changes in scan rates, supporting the reversibility of these ligand-based reductions. It is well known¹² that each bpy can successively accept two electrons in the lowest unoccupied molecular orbital. Hence, in these [Ru(bpy)₂(L)]⁺ complexes, four successive reductions are expected. Only two of these have been experimentally observed. The remaining two reductions are not observed due to solvent cut-off. The two reduction potentials in these [Ru(bpy)₂(L)]⁺ complexes compare well with those observed in similar complexes.^{2a.e}

We shall now consider the metal-centred oxidations. All these complexes show a reversible one-electron oxidation in the potential range 0.56-0.84 V, which is assigned to the ruthenium(II)-ruthenium(III) oxidation [eq. (4)]. The one-electron nature of this couple has been

$$[\operatorname{Ru}^{II}(\operatorname{bpy})_2(L)]^+ \Longrightarrow [\operatorname{Ru}^{III}(\operatorname{bpy})_2(L)]^{2+} + e^{-}$$
(4)

confirmed by coulometric experiments (*vide infra*). In $[Ru(bpy)_3]^{2+}$, the ruthenium(II)-ruthenium(III) oxidation occurs at 1.30 V.¹³ Therefore, replacement of only one bpy by L has caused a negative shift of *ca* 700 mV. In spite of the presence of one π -acid function in L, this large shift in oxidation potential shows the ability of phenolate oxygen to stabilize the higher oxidation states of ruthenium. In $[Ru(bpy)_2(Me-sal-H)]^+$, the ruthenium(II)ruthenium(III) oxidation occurs at 0.59 V, while in

 $[Ru(bpy)_2(ap-H)]^+$ the same occurs at 0.68 V. The Me-sal-H and ap-H ligands are very similar (see structures 1 and 2), except that the former has an imine (HC==N) function while the latter has an azo (N=N) function. The observed difference of 90 mV in the oxidation potential is therefore attributable to the difference in the π -acidity of these two functions. It is well documented in the literature that the azo function is a stronger π -acid than the imine function and hence is a better stabilizer of ruthenium(II).¹⁴ For both the salicylaldiminato and 2-(arylazo)phenolato complexes, the potential of the ruthenium(II)-ruthenium(III) couple is found to be sensitive to the nature of the substituents R and R' in ligand L. In the two salicylaldiminato complexes with R' = H and R = H and Me, viz. $[Ru(bpy)_2(sal-H)]^+$ and $[Ru(bpy)_2(Me-sal-H)]^+$, the ruthenium(II)-ruthenium(III) oxidation occurs at 0.63 and 0.59 V, respectively (Table 1). The lower potential in the Me-sal-H complex is therefore attributable to the electron-donating nature of $R(CH_3)$ in this complex. Such a comparison has not been possible in the 2-(arylazo) phenolato complexes, where R is CH₃ uniformly. For the five salicylaldiminato complexes with R = H and the five 2-(arylazo)phenolato complexes with $R = CH_3$, the formal potential (E_{298}^0) increases with increasing electron-withdrawing character of R'. The plot of E_{298}^0 versus σ [σ = Hammett constant of R';¹⁵ OMe = -0.27, Me = -0.17, H = 0.0, Cl = 0.23and NO₂ = 0.78] is linear (Fig. 3) with $\rho = 0.21$ V for the salicylaldiminato complexes and $\rho = 0.22$ V for the 2-(arylazo)phenolato complexes. (ρ = reac-



Fig. 3. Least-squares plot of E_{298}^0 values of the Ru^{II}/Ru^{III} couple versus σ .

tion constant of this couple¹⁶). From this linear correlation with a reasonable slope it is clear that a single substituent on the phenolate ligand can influence the metal oxidation potential in a predictable manner.

All the 11 $[Ru(bpy)_2(L)]ClO_4$ complexes show a second irreversible one-electron oxidation near 1.6 V, which is assigned to the ruthenium(III)-ruthenium(IV) oxidation [eq. (5)]. The one-electron nature of this oxidation

$$[Ru^{III}(bpy)_2(L)]^{2+} \longrightarrow [Ru^{IV}(bpy)_2(L)]^{3+} + e^{-}$$
(5)

has been established from current height measurements. The irreversibility of this oxidation indicates that $[Ru^{IV}(bpy)_2(L)]^{3+}$, generated during the anodic scan, is not stable in solution, even on cyclic voltammetric time scale. This instability of $[Ru^{IV}(bpy)_2(L)]^{3+}$ may be attributed to its high reduction potential (~1.6 V) which makes it a potential oxidant. The formal potential of this oxidation appears to be much less sensitive to the nature of substituents on the ligand L (Table 1).

 $[Ru^{III}(bpy)_2(L)]^{2+}$ species. The reversibility of the ruthenium(II)-ruthenium(III) couple, together with its relatively low positive potentials in these complexes point to the possibility of the ruthenium-(III) species, $[Ru^{III}(bpy)_2(L)]^{2+}$, being stable. To investigate this, two representative complexes, viz. $[Ru^{II}(bpy)_2(sal-H)]^+$ and $[Ru^{II}(bpy)_2(ap-OMe)]^+$, have been oxidized in acetonitrile solution (0.1 M TEAP) by constant potential coulometry at 0.90 V. The oxidations have been smooth and quantitative affording deep green solutions, which show almost identical voltammetric responses as their respective precursors. The green solutions of [Ru^{III}(bpy)₂ (L)²⁺ are converted back to the pinkish-red solutions of $[Ru^{II}(bpy)_2(L)]^+$ upon coulometric reduction at 0.3 V. This indicates that the redox reaction [eq. (4)] takes place without any gross change in stereochemistry. The same two ruthenium(III) complexes have also been synthesized by chemical oxidation of their ruthenium(II) precursors by aqueous ceric solution. The same green solution as before is produced, from which the cationic complexes have been isolated in the solid state as dark crystalline perchlorate salts. The compositions of these complexes have been confirmed by their elemental analytical data (Table 2). Besides small shifts in the band positions, the IR spectra of these complexes are almost identical to those of their precursors, as expected. The observed magnetic moments of these complexes

(Table 2) correspond to the +3 oxidation state of ruthenium (low-spin d^5 , S = 1/2) in these complexes. These complexes are highly soluble in acetonitrile, producing green solutions. Conductivity measurements show that in solution these complexes behave as 1:2 electrolytes, as expected. Electronic spectra recorded in acetonitrile solution show several intense absorptions in the visible region, together with a low intensity absorption at lower energy. Spectra are shown in Fig. 4 and spectral data are given in Table 2. The intense absorptions in the visible region are probably due to allowed ligand-to-metal charge-transfer transitions. The absorption at lower energy will be discussed below.

ESR spectra of the two $[Ru^{III}(bpy)_2(L)]^{2+}$ complexes have been recorded in 1:1 acetonitrile-toluene solution at 77 K. Both complexes show rhombic ESR spectra with three distinct g values (Fig. 5, Table 2). The rhombicity of the spectra indicates the asymmetry of electronic environments around ruthenium in these complexes. Under the combined influence of this low-symmetry and spin-orbit coupling, the three t_2 -levels become well separated and hence two electronic transitions (transition energies ΔE_1 and ΔE_2 ; $\Delta E_1 < \Delta E_2$) are probable within these three levels. These transition energies have been computed (Table 2) using the observed gvalues, the g-tensor theory of low-spin d^5 complexes¹⁷ and a reported method.¹⁸ The ΔE_2 transition in the sal-H complex has indeed been observed at 1180 nm (8475 cm⁻¹), while the ΔE_1 transition could not be observed because the solvent itself is not transparent in this region. Similarly in



Fig. 4. Electronic spectra of [Ru^{III}(bpy)₂(sal-H)](ClO₄)₂
(----) and [Ru^{III}(bpy)₂(ap-OMe)](ClO₄)₂ (---) in acetonitrile solution.



Fig. 5. ESR spectra of (a) $[Ru^{III}(bpy)_2(sal-H)](ClO_4)_2$ and (b) $[Ru^{III}(bpy)_2 (ap-OMe)](ClO_4)_2$ in 1:1 acetonitrile– toluene solution at 77 K.

the ap-OMe complex, the ΔE_2 transition has been observed at 950 nm (10526 cm⁻¹), which is very close to the theoretically predicted value. The ΔE_1 transition, which extends into the IR region in this complex, could not be detected.

Redox Reactions

The stability of the $[Ru^{III}(bpy)_2(L)]^{2+}$ complexes and their reduction potentials suggest that they might behave as mild one-electron oxidants. The two ruthenium(III) complexes have indeed been successfully applied as oxidants in a few redox reactions, which are individually discussed below.

Addition of a few drops of hydrazine hydrate to the deep green solution of $[Ru^{III}(bpy)_2(L)]^{2+}$ in acetonitrile solution brings about an instantaneous colour change to pinkish-red. Spectrophotometric examination of this pinkish-red solution confirms the quantitative reduction of the ruthenium(III) complexes to the corresponding $[Ru^{II}(bpy)_2(L)]^+$ complexes. No attempt has been made to detect the oxidation products of hydrazine. Similar smooth reduction has been achieved by the addition of N,N-dimethyl aniline (DMA) to a solution of $[Ru^{III}(bpy)_2(L)]^{2+}$ in acetonitrile. Cyclic voltammetry on the resultant solution shows a new response at 0.42 V, which is characteristic of N,N,N',N'-tetramethylbenzidine (TMB, 4).¹⁹ Evi-

Compound C H N (B.M.) $(\Omega^{-1} \text{ cm}^2 \text{ M}^{-1})$ λ_{\max} (r [Ru(bpy)_2(sal-H)](CIO_1) 49.2 3.2 8.7 1.82 242 1180 (Ru(bpy)_2(sal-H)](CIO_1) 49.0 (3.2) (8.7) 1.82 242 180'	$\frac{1}{2}$ $M = 1$ $\frac{1}{2}$
[Ru(bpy) ₂ (sal-H)](CIO ₄) ₂ 49.2 3.2 8.7 1.82 242 1180 (49.0) (3.2) (8.7) 4.42 48.7	A = A = A = A = A = A = A = A = A = A =
	42 1180(850), 770(2330), 2.5008 2.2239 1.88 480 ⁴ (2190), 360(3120)
[Ru(bpy) ₂ (ap-OMe)](ClO ₄) ₂ 48.0 3.4 9.7 1.85 240 950((47.8) (3.4) (9.8) 4.75(5)	40 950(250), 575(2550), 2.2439 2.0098 1.89 475(2990), 410(3920)

In 1:1 acetonitrile-toluene solution at 77 K

Shoulder

Table 2. Characterization data of the [Ru^{III} (bpy)₂(L)](ClO₄)₂ complexes

Me N N N N M

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dently TMB has been produced by one electron oxidation of DMA, followed by a

$$2DMA + 2[Ru^{III}(bpy)_2(L)]^{2+} \longrightarrow$$
$$TMB + 2[Ru^{II}(bpy)_2(L)]^{+} + 2H^{+} \qquad (6)$$

coupling reaction [eq. (6)]. It appears from the current height measurement of the TMB response that about 45% of the oxidant has been utilized in the coupling reaction. The remainder has probably been wasted in the side reactions.²⁰

Another organic compound, 1,2-napthoquinone-



1-oxime (HnqO, 5), has been used as a reductant, which upon oxidation affords a stable free radical [eq. (7)]. Addition of HnqO to the acetonitrile solution of $[Ru^{III}(bpy)_2(L)]^{2+}$

$$[Ru^{III}(bpy)_{2}(L)]^{2+} + HnqO \longrightarrow$$

$$nqO' + H^{+} + [Ru^{II}(bpy)_{2}(L)]^{+} \quad (7)$$

causes the expected colour change from green to pinkish-red and the ESR spectrum recorded on the pinkish-red solution at 77 K shows an intense sharp signal at g = 2.005 with three nitrogen hypertine lines ($A_N = 20$ G), characteristic of the iminoxy radical nqO^{.21}

Two transition metal complexes, *viz*. $[Ru^{II}(bpy)_2]$ Cl_2] and $[Fe^{II}(C_5H_5)_2]$, have also been used as reducing agents. Equimolar solutions of [Ru(bpy)₂Cl₂] and [Ru^{III}(bpy)₂(L)]²⁺ are mixed and cyclic voltammetry on the resultant solution confirms that the expected redox reaction has indeed taken place. A reversible one-electron reduction at 0.30V characteristic of [Ru^{III}(bpy)₂Cl₂]⁺²² is observed together with the reversible one-electron oxidation of $[Ru^{II}(bpy)_{2}(L)]^{+}$ near 0.6V. Similarly cyclic voltammetry on the solution obtained by mixing equimolar solutions of $[Ru^{III}(bpy)_2(L)]^{2+}$ and $[Fe^{II}(C_5H_5)_2]$ shows the reversible reduction of $[Fe^{III}(C_5H_5)_2]^+$ at 0.18 V, in addition to the reversible oxidation of $[Ru^{II}(bpy)_2(L)]^+$. These redox reactions show that the $[Ru^{III}(bpy)_2(L)]^{2+}$ complexes can function as efficient one-electron oxidants in acetonitrile solution.

CONCLUSION

This study on the salicylaldiminato and 2-(arylazo)phenolato complexes of the type $[Ru^{II}(bpy)_2(L)]^+$ reveals that coordination by phenolate oxygen favours higher oxidation states of ruthenium and the metal-centred redox potentials are tunable in a desired direction by the correct choice of substituent on the phenolate ligand (L). The oxidized complexes, $[Ru^{III}(bpy)_2(L)]^{2+}$, are stable enough to be isolated as salts and they can act as efficient oneelectron oxidants to bring about oxidations of both organic molecules and transition metal complexes in non-aqueous medium.

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