Pergamon

PII: S0277-5387(97)00028-4

Polyhedron Vol. 16, No. 17, pp. 3047–3053, 1997

0277-5387/97 $17.00+0.00

Chemistry of 2-(arylazo)phenolate complexes of ruthenium. Synthesis, characterization and redox properties

Nimai Chand Pramanik and Samaresh Bhattacharya*

Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Calcutta 700 032, India

(Received 7 October 1996; accepted 14 January 1997)

Abstract—A family of five 2-(arylazo)phenolate (ap-R) complexes of ruthenium of type [Ru^{II}(bpy)(ap-R)$_2$] (bpy = 2,2′-bipyridine) has been synthesized and characterized. The complexes are diamagnetic (low-spin d^6, S = 0) and in acetonitrile solution show intense MLCT transitions in the visible region. Cyclic voltammetry of the complexes in acetonitrile solution shows a reversible ruthenium(II)–ruthenium(III) oxidation in the range 0.04–0.26 V *vs* SCE followed by an irreversible ruthenium(III)–ruthenium(IV) oxidation in the range 1.18-1.32 V *vs* SCE. The potential of these two oxidations is sensitive to the nature of substituent R in the ap-R ligand. A one-electron reduction of the coordinated bpy is also observed near −1.6 V *vs* SCE. The five [Ru^{III}(bpy)(ap-R)$_2$]$^+$ complexes have been synthesized by chemical oxidation of their respective ruthenium(II) precursors by iodine and isolated as the iodide salts. These oxidized complexes are one-electron paramagnetic (low-spin, d^5, S = 1/2) and show rhombic ESR spectra at 77 K. In acetonitrile solution they show intense LMCT transitions in the visible region 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. © 1997 Elsevier Science Ltd

Keywords: ruthenium 2-(arylazo)phenolates; synthesis; characterization; redox properties.

The present work has emerged from our interest in the chemistry of ruthenium phenolates [1] of type **1** where X is a second donor atom linked to the ortho carbon directly or *via* one intervening atom forming a five- or six-membered chelate ring. Coordination by phenolate oxygen is known to stabilize the higher oxidation states of ruthenium [1,2]. However, the nature of X also plays an important role in the redox stability of the metal. The phenolic ligand used in this work is 2-(arylazo)phenol (**2**), abbreviated in general as Hap-R where H stands for the dissociable phenolic hydrogen. The azo-group is a recognized stabilizer of the lower oxidation states of ruthenium [3]. Therefore we have two donor sites with opposite natures in this 2-(arylazo)phenolate ligand. It may be noted here that the chemistry of 2-(arylazo)phenolate complexes of ruthenium, Ru(ap-R)$_n$, (**3**); (n = 1, 2, 3) has not received much attention [1(d),4]. We have recently reported our studies on a series of mono 2-(arylazo)phenolate complexes of ruthenium [1(d)], which has led us to explore the chemistry of the bis complexes. To satisfy the remaining two coordination sites of this Ru(ap-R)$_2$ moiety, 2,2′-bipyridine (bpy) has been used as the coligand. The synthesis of a group of [Ru(bpy)(ap-R)$_2$] complexes, their characterization and spectroscopic and redox properties 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. 2,2′-bipyridine was purchased from Loba, Bombay, India. [Ru(bpy)Cl$_3$] was synthesized following a reported procedure [5]. The 2-(arylazo)phenol ligands were prepared by coupling diazotized anilines with p-cresol. Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were

---

* Author to whom correspondence should be addressed.

performed as reported in the literature [6]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

Preparations

The [Ru^{II}(bpy)(ap-R)$_2$] and [Ru^{III}(bpy)(ap-R)$_2$]I complexes were synthesized by following two general methods. Details are given for two respective cases only.

[Ru^{II}(bpy)(ap-H)$_2$]. [Ru(bpy)Cl$_3$] (200 mg, 0.55 mmol) was taken in ethanol (40 cm^3) and Hap-H (290 mg, 1.37 mmol) was added to it followed by an ethanolic solution (5 cm^3) of NaOH (55 mg, 1.37 mmol). The mixture was refluxed for 3 h under nitrogen. The solution was then cooled to room temperature and the solvent was evaporated under reduced pressure. The solid mass thus obtained was washed thoroughly with water followed by hexane and dried *in vacuo* over P_4O_{10}. Recrystallization from 1 : 1 dichloromethane–hexane solution gave [Ru(bpy)(ap-H)$_2$] as a reddish brown crystalline solid. The yield was 280 mg, 75%.

[Ru^{III}(bpy)(ap-H)$_2$]I. To a solution of [Ru(bpy)(ap-H)$_2$] (200 mg, 0.295 mmol) in acetonitrile (30 cm^3) was added a solution of iodine (75 mg, 0.295 mmol) in acetonitrile (10 cm^3), followed by stirring for 30 min. The initial reddish brown colour turned to brownish green within 10 min. A saturated aqueous solution of KI (10 cm^3) was then added to it and the solution was kept in a refrigerator for 24 h. [Ru(bpy)(ap-H)$_2$]I precipitated as a brownish green microcrystalline solid which was collected by filtration, washed with cold water and dried *in vacuo* over P_4O_{10}. The yield was 195 mg, 82%.

Physical measurements

^{1}H NMR spectra were obtained on a JEOL JNM FX 100 NMR spectrometer using TMS as the internal standard. All electrochemical measurements were made using the PAR model 273 electrochemistry system. All electrochemical experiments were performed under a dinitrogen atmosphere. A planar Beckman 39273 platinum inlay working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A platinum-wire gauge working electrode was used in the coulometric experiments. All electrochemical data are collected at 298 K and are uncorrected for junction potentials. All other physical measurements were made as described before [1(e)].

RESULTS AND DISCUSSION

Synthesis and characterization

The reaction of [Ru(bpy)Cl$_3$] with 2-(arylazo)phenol in refluxing ethanol in the presence of NaOH afforded [Ru(bpy)(ap-R)$_2$] in good yield [eq. (1)]. During the course of this synthesis ruthenium undergoes a one-electron reduction.

$$[\mathrm{Ru(bpy)Cl_3}] \xrightarrow[\text{EtoH}]{\text{Hap-R, NaOH}} [\mathrm{Ru(bpy)(ap\text{-}R)_2}] \qquad (1)$$

Though it is not known when this reduction is actually taking place and the reaction proceeds without any familiar reducing agent, it appears that ethanol may serve as the reductant. Using five different 2-(arylazo)phenol ligands five such complexes have been synthesized and their compositions have been confirmed by elemental (C,H,N) analytical data (Table 1). 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.

As the 2-(arylazo)phenolate ion is an unsymmetrical bidentate ligand, [Ru(bpy)(ap-R)$_2$] complexes may exist in three geometrical isomeric forms **4**, **5**, **6**. Both **4** and **5** have a C_2 axis indicating that the two 2-(arylazo)phenolate ligands are magnetically equivalent and so are the two pyridine rings of bpy, while in **6** there is no such C_2 axis. Hence the number of ^{1}H NMR signals in **6** is expected to be twice the number expected in **4** or **5** (provided no overlap of signals occur). The ^{1}H NMR spectrum of [Ru(bpy)(ap-H)$_2$] has been recorded in CDCl$_3$ solution. The phenyl region of this spectrum is rather complicated. However it shows two methyl signals of equal intensity at 2.16 and 2.36 ppm. This clearly indicates the non-equivalence of the two ap-H ligands and hence structure **6** is assigned to this complex. Similarly in the ^{1}H NMR spectra of both [Ru(bpy)(ap-Me)$_2$] and [Ru(bpy)(ap-OMe)$_2$], four methyl signals are observed which correspond only to structure **6**. Therefore we assume structure **6** for all five [Ru(bpy)(ap-R)$_2$] complexes. It may be mentioned here that similar complexes of type [Ru^{II}(bpy)(N-O)$_2$] are found to have the same geometry (**6**) [1(g),7].

Infrared spectra of these complexes show many vibrations of different intensities and no attempt has been made to assign each individual band. However, comparison with the spectrum of [Ru(bpy)Cl$_3$] shows that besides a few common vibrations which are due to the bpy ligand, some additional bands are observed beyond 1600 cm^{-1} which must be due to the coordinated 2-(arylazo)phenolate ligands. The ν(Ru—Cl) stretch, observed at 330 cm^{-1} in [Ru(bpy)Cl$_3$], is absent in the spectra of all these complexes, as expected.

The [Ru(bpy)(ap-R)$_2$] complexes are soluble in common organic solvents like acetonitrile, dichloromethane, chloroform *etc.*, producing intense reddish brown solutions. All these complexes behave as non-electrolytes in solution, as expected. Electronic spectra of these complexes, recorded in acetonitrile solution, show several intense absorptions in the visible region (Table 1) which are probably due to

Table 1. Characterization data of the $[Ru^{II}(bpy)(ap\text{-}R)_2]$ complexes

Compound	Microanalytical data[a]			Electronic spectral data[b]	Cyclic voltammetric data[c]		Coulometric
					Ru^{II}–Ru^{III}	Ru^{III}–Ru^{IV}	
	%C	%H	*N	λ_{max}(nm)(ε/M^{-1} cm^{-1})	E^0_{298}(VΔE_p/mV)	E_{pa}(V)	n-values[e]
$[Ru(bpy)(ap\text{-}OMe)_2]$	61.5	4.7	11.2	500(9900); 390[d](16300)	0.04(70)	1.18	0.96
	(61.7)	(4.6)	(11.4)	350(19100)			
$[Ru(bpy)(ap\text{-}Me)_2]$	64.4	4.5	11.7	510(11100); 395(12100);	0.05(60)	1.20	0.96
	(64.5)	(4.8)	(11.9)	340(14800)			
$[Ru(bpy)(ap\text{-}H)_2]$	63.3	4.7	12.0	500(10000); 390(11900);	0.08(70)	1.23	0.98
	(63.6)	(4.4)	(12.4)	320[d](19300)			
$[Ru(bpy)(ap\text{-}Cl)_2]$	57.6	3.9	11.0	510(12100); 400[d](10100);	0.14(70)	1.25	0.95
	(57.8)	(3.7)	(11.2)	350(11200)			
$[Ru(bpy)(ap\text{-}NO_2)_2]$	55.9	3.7	14.4	500(14400); 390(14800);	0.26(60)	1.32	0.97
	(56.2)	(3.6)	(14.6)	320[d](18700)			

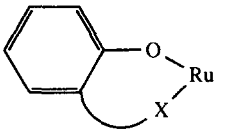
[a] Calculated values are in parantheses.

[b] In acetonitrile solution.

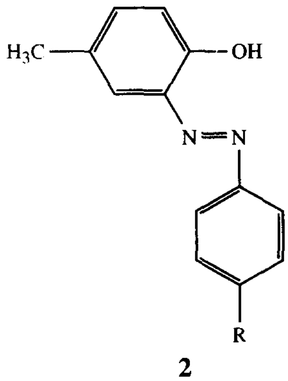
[c] Conditions: solvent, acetonitrile; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration 10^{-3}M; $E^0_{298} = (E_{pa}+E_{pc})/2$; where E_{pa} and E_{pc} are anodic and cathodic peak potentials; $\Delta E_p = E_{pa}-E_{pc}$; scan rate, 50 mV s^{-1}.

[d] Shoulder.

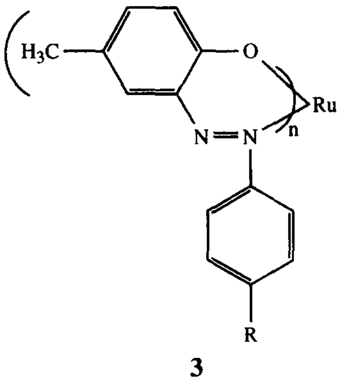
[e] n, number of electron-transfer.



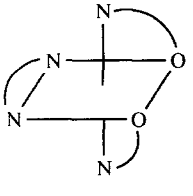
1



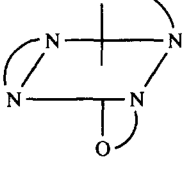
2



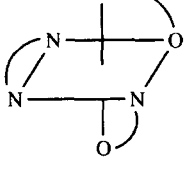
3



4



5



6

allowed metal-to-ligand charge-transfer transitions. Multiple charge transfer transitions in such 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 [8]. Such spectral behaviour has been observed before in similar [Ru(bpy)(N-O)$_2$] type complexes [1(g),7].

Cyclic voltammetric studies

The electron transfer properties of the [Ru(bpy)(ap-R)$_2$] complexes have been studied in acetonitrile solution by cyclic voltammetry. Voltammetric data are presented in Table 1. All these complexes show three voltammetric responses, two metal-centered oxidations and one ligand based reduction, which are separately discussed below.

A reversible one-electron process in the range 0.04–0.25 V (all potentials are referenced to SCE) was observed in all complexes, which is assigned to the ruthenium(II)–ruthenium(III) oxidation [eq. (2)]. The peak-to-peak separation (ΔE_p) for this couple lies in the range 60–70 mV (Table 1) and it remains unchanged upon changing the scan rates, indicating the reversible nature of this oxidation. The peak currents (i_{pa} and i_{pc}) of this couple are almost equal which further supports the reversibility. The one-electron stoichiometry of this reaction [eq. (2)] has been confirmed by constant potential coulometry (Table 1).

$$[\mathrm{Ru^{II}(bpy)(ap\text{-}R)_2}] \rightleftharpoons [\mathrm{Ru^{III}(bpy)(ap\text{-}R)_2}]^+ + e^- \qquad (2)$$

The potentials of the ruthenium(II)–ruthenium(III) couple in these complexes are lower than those in [Ru^{II}(bpy)$_2$(ap-R)]$^+$ complexes [1(d)] by ~600 mV. This shows the ability of the 2-(arylazo)phenolate ligand to stabilize the higher oxidation states of ruthenium. In the 2-(arylazo)phenolate ligand the azo group is a recognized stabilizer of ruthenium(II) while the phenolate oxygen is known to stabilize the higher oxidation states of this metal. The observed lowering of the ruthenium(II)–ruthenium(III) oxidation potential upon replacing the bpy by ap-R reflects that the effect of phenolate oxygen coordination is greater than the effect of azo-nitrogen coordination. It may be noted here that a gradual decrease in the potential of the ruthenium(II)–ruthenium(III) couple is observed in the series: [Ru(bpy)$_3$]$^{2+}$, 1.30 V [9]; [Ru(bpy)$_2$(ap-H)]$^+$, 0.68 [1(d)]; [Ru(bpy)(ap-R)$_2$], 0.08 V. From this observed trend, the potential of the ruthenium(II)–ruthenium(III) couple in [Ru(ap-R)$_3$] is expected to occur near -0.6 V, which indicates that in the tris complex the $+3$ state of ruthenium will be very stable.

The potential of the ruthenium(II)–ruthenium(III) couple in these [Ru(bpy)(ap-R)$_2$] complexes is found to be sensitive to the nature of the substituent R in the 2-(arylazo)phenolate ligand. With increasing electron withdrawing character of R the formal potential (E^0_{298}) increases. The plot of E^0_{298} *vs* 2σ [σ = Hammett constant of R [10]; OMe = -0.27, Me = -0.17, H = 0.00, Cl = 0.23 and NO$_2$ = 0.78] is linear (Fig. 1) with $\rho = 0.108$ V (ρ = reaction constant of this couple [11]). It is clear from this plot that a single substituent on the ap-R ligand, which is six bonds away from the electro-active metal centre, can influence the metal oxidation potential in a predictable manner.

The [Ru(bpy)(ap-R)$_2$] complexes show a second one-electron irreversible oxidation in the range 1.18–1.32 V which is assigned to the ruthenium(III)–ruthenium(IV) oxidation [eq. (3)]. The one-electron nature of this oxidation is established by comparing its current height (i_{pa}) with that of the ruthenium(II)–ruthenium(III) oxidation.

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

The irreversible nature of this oxidation indicates the [Ru^{IV}(bpy)(apr-R)$_2$]$^{2+}$, formed during the anodic scan, is very unstable and undergoes very fast chemical transformation. The potential of this oxidation (E_{pa}) also correlates linearly with the Hammett constant (σ) of R (Fig. 1). The slope in this case is $\rho = 0.064$ V, which indicates that this ruthenium(III)–ruthenium(IV) oxidation potential is relatively less sensitive to the nature of R than the ruthenium(II)–ruthenium(III) oxidation potential.

A reversible one-electron reduction near -1.6 V is displayed by all these complexes which is assigned to the reduction of the coordinated bpy [eq. (4)]. The one-electron nature of this couple has been established by comparing its current heights with those

$$[\mathrm{Ru(bpy)(ap\text{-}R)_2}] + e^- \rightleftharpoons [\mathrm{Ru}(\overset{\cdot}{\overline{\mathrm{bpy}}})\mathrm{(ap\text{-}R)_2}]^- \qquad (4)$$

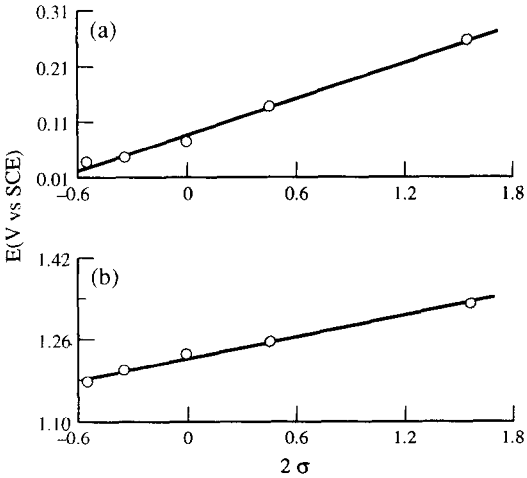


Fig. 1. Least-squares plot of (a) E^0_{298} values of Ru^{II}/Ru^{III} couples *vs* 2σ and (b) E_{pa} values of Ru^{III}/Ru^{IV} couples *vs* 2σ.

of the ruthenium(II)–ruthenium(III) couple. It is well known [12] that each bpy can successively accept two electrons in its lowest unoccupied molecular orbital. Hence in these $[Ru(bpy)(ap\text{-}R)_2]$ complexes two successive one-electron reductions are expected, of which only one reduction is observed. The second reduction, which is expected to occur at much more negative potential, is not observed due to solvent cut-off.

$[Ru^{III}(bpy)(ap\text{-}R)_2]^+$ complexes

The reversibility of the ruthenium(II)–ruthenium(III) oxidation in $[Ru(bpy)(ap\text{-}R)_2]$ indicates that $[Ru^{III}(bpy)(ap\text{-}R)_2]^+$ is stable on the cyclic voltammetric time scale. The relatively low oxidation potentials further indicate that $[Ru^{III}(bpy)(ap\text{-}R)_2]^+$ is a weak oxidant and hence it could be stable on much longer time scale. To investigate this, the $[Ru(bpy)(ap\text{-}R)_2]$ complexes have been oxidised in acetonitrile solution (0.1 M TEAP) by constant potential coulometry near 0.5 V. The oxidations have been smooth and quantitative (Table 1) affording brownish green solutions of $[Ru^{III}(bpy)(ap\text{-}R)_2]^+$ which shows voltammograms very similar to their respective ruthenium(II) precursors except that the ruthenium(II)–ruthenium(III) couple now appears as a reductive response. Upon coulometric reduction of the brownish green solutions near −0.2 V, deep reddish brown solutions of $[Ru(bpy)(ap\text{-}R)_2]$ are obtained, which have been identified by their characteristic electronic spectra. The $[Ru^{III}(bpy)(ap\text{-}R)_2]^+$ complexes have also been synthesized by chemical oxidation of the respective $[Ru^{II}(bpy)(ap\text{-}R)_2]$ complexes in acetonitrile solution by iodine and the iodide salts of the complex cations have been isolated in the solid state. Microanalytical data (Table 2) agree well with the compositions of these complexes. Besides small shifts in the band positions, the IR spectra of the $[Ru(bpy)(ap\text{-}R)_2]I$ complexes are almost identical to those of their respective precursors. Conductivity measurements in acetonitrile solution show that the $[Ru(bpy)(ap\text{-}R)_2]I$ complexes behave as 1 : 1 electrolytes (Table 2), as expected. Electronic spectra recorded in acetonitrile solutions show many intense absorptions in the visible region together with a weak adsorption at lower energies (Table 2). The intense absorptions in the visible region are probably due to ligand-to-metal charge-transfer transitions. The low-intensity absorption in the near IR region is discussed below. Addition of hydrazine to the brownish green solution of $[Ru(bpy)(ap\text{-}R)_2]I$ in acetonitrile brings about an instantaneous reduction affording deep reddish brown solutions of $[Ru(bpy)(ap\text{-}R)_2]$.

The $[Ru(bpy)(ap\text{-}R)_2]I$ complexes are one-electron paramagnetic species (Table 2) which is in accordance with the trivalent state of ruthenium (low spin d^5, $S = 1/2$) in these complexes. ESR spectra of the $[Ru(bpy)(ap\text{-}R)_2]^+$ complexes have been recorded in 1 : 1 dichloromethane–toluene solution at 77 K. All five complexes show rhombic ESR spectra with three distinct g-values (Table 3). A representative spectrum is shown in Fig. 2. The rhombic nature of the spectra indicates the asymmetry of electronic environment around ruthenium in these complexes. In view of the stereochemistry of these complexes (**6**, *vide supra*) which has no C_2 axis, this asymmetry is quite expected. The observed spectra may be considered as pseudo-axial, consisting of a rather isolated signal g_3 (g in the axial case) and two relatively close signals g_1 and g_2 (rhombic component of $g_\perp$). Accordingly the axial distortion (Δ) that splits the t_2 level into **a** and **e** components is expected to be larger than the rhombic distortion (V), which splits **e** (Fig. 2). Spin-orbit coupling causes further changes in the energy gaps. Thus

Table 2.

Compound	Microanalytical data[a] %C	%H	%N	μ_{eff} (BM)	Molar conductivity values[b] Λ_M	Electronic spectral data[c] $\lambda_{max}(nm)/(\varepsilon/M^{-1}\,cm^{-1})$
$[Ru(bpy)(ap\text{-}OMe)_2]I$	52.5 (52.7)	4.2 (3.9)	9.5 (9.7)	1.88	142	1400[d](90) ; 820(570) ; 600[d](2300) ; 450(14400) ; 350(18000)
$[Ru(bpy)(ap\text{-}Me)_2]I$	54.5 (54.7)	4.3 (4.1)	9.8 (10.1)	1.83	152	1375[d](80) ; 865(700) ; 630(3100) ; 415(15000) ; 320[d](19700)
$[Ru(bpy)(ap\text{-}H)_2]I$	53.8 (53.6)	3.5 (3.7)	10.2 (10.4)	1.85	148	1350[d](60) ; 850(550) ; 650(1400) ; 420[d](10700) ; 350(17300)
$[Ru(bpy)(ap\text{-}Cl)_2]I$	49.1 (49.4)	3.5 (3.2)	9.2 (9.6)	1.85	139	1360(100) ; 770(900) ; 600(3400) ; 420(14500) ; 350[d](13800)
$[Ru(bpy)(ap\text{-}NO_2)_2]I$	48.0 (48.2)	3.5 (3.1)	12.3 (12.5)	1.84	145	1360[d](85) ; 810(950) ; 620(2800) ; 440[d](13300) ; 325(14200)

[a] Calculated values are in parentheses.

[b] In acetonitrile solution.

[c] in acetonitrile solution.

[d] Shoulder.

Table 3. ESR g-values[a] and derived energy parameters[b]

Compound	g_1	g_2	g_3	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
[Ru(bpy)(ap-OMe)$_2$]I	2.147	2.054	1.965	10.32	7.16	6.80	14.00
[Ru(bpy)(ap-Me)$_2$]I	2.142	2.053	1.964	10.04	6.75	6.73	13.53
[Ru(bpy)(ap-H)$_2$]I	2.140	2.054	1.962	9.63	6.18	6.61	12.83
[Ru(bpy)(ap-Cl)$_2$]I	2.109	2.061	1.962	8.76	3.40	7.10	10.61
[Ru(bpy)(ap-NO$_2$)$_2$]I	2.115	2.081	1.963	8.74	2.22	7.63	10.03

[a] In 1 : 1 dichloromethane–toluene solution at 77 K.

[b] Spin-orbit coupling constant (λ) for complexed ruthenium(III) is ~1000 cm^{-1}.

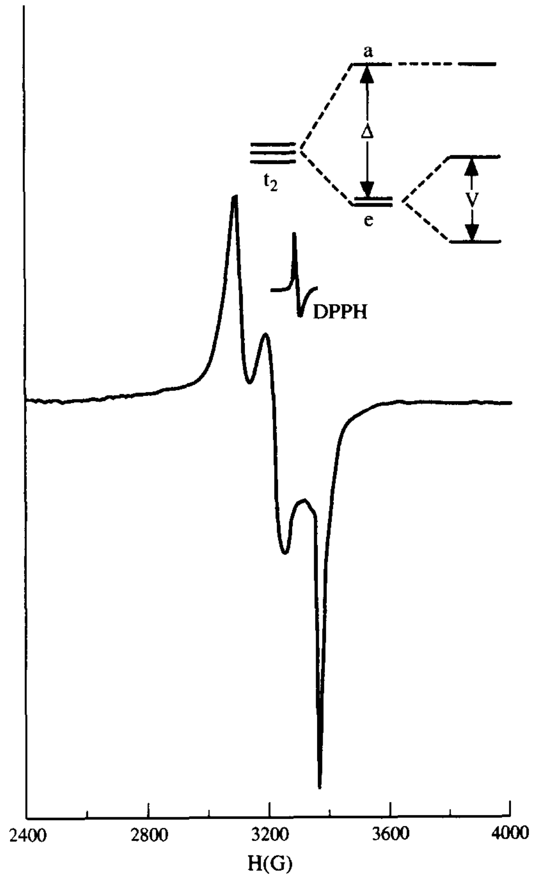


Fig. 2. ESR spectrum in 1 : 1 dichloromethane–toluene solution at 77 K and t_2 splittings of [Ru^{III}(bpy)(ap-H)$_2$]I.

two electronic transitions (transition energies ΔE_1 and ΔE_2; $\Delta E_1 < \Delta E_2$) are possible within these three levels. All these energy parameters have been computed (Table 3) using the observed g-values, the g-tensor theory of low-spin d^5 complexes [13] and a reported method [14]. The axial distortion is indeed larger than the rhombic one. Both the ΔE_1 and ΔE_2 transitions have been observed in the spectra of the [Ru(bpy)(ap-R)$_2$]$^+$ complexes near the predicted energies (Table 2 and Table 3).

Acknowledgements—Financial assistance received from the Department of Science and Technology (SR/OY/C-08/93), New Delhi, is gratefully acknowledged. The authors thank Professor Animesh Chakravorty of the Indian Association for the Cultivation of Science, Calcutta and Professor Ramgopal Bhattacharyya of Jadavpur University, Calcutta, for their help.

REFERENCES

1. (a) Bhattacharya, S., *Polyhedron*, 1993, **12,** 235; (b) Bhattacharya, S., *Polyhedron*, 1994, **13,** 451; (c) Chakravarty, J. and Bhattacharya, S., *Polyhedron*, 1996, **15,** 257; (d) Chakravarty, J. and Bhattacharya, S. *Polyhedron*, 1996, **15,** 1047; (e) Sinha, P. K., Chakravarty, J. and Bhattacharya, S., *Polyhedron*, 1996, **15,** 2931; (f) Sinha, P. K., Chakravarty, J. and Bhattacharya, S., *Polyhedron*, 1997, **16,** 81; (g) Pramanik, N. C. and Bhattacharya, S., *Polyhedron*, 1997, **16,** 1755.
2. (a) Lahiri, G. K., Bhattacharya, S., Mukherjee, M., Mukherjee, A. and Chakravorty, A., *Inorg. Chem.*, 1987, **26,** 3359; (b) Bhattacharya, S., Boone, S. R., Fox, G. K. and Pierpont, C. G., *J. Am. Chem. Soc.*, 1990, **112,** 1088; (c) Bardwell, D. A., Black, D., Jeffery, J. C., Schatz, E. and Ward, M. D., *J. Chem. Soc., Dalton Trans.*, 1993, 2321.
3. (a) Krause, R. A. and Krause, K., *Inorg. Chem.* 1980, **19,** 2600; (b) Goswami, S., Chakravarty, A. R. and Chakravorty, A., *Inorg. Chem.*, 1981, **20,** 2246.
4. Bensor, E. P. and Legg, J. I., *Inorg. Chem.*, 1981, **20,** 2504.
5. Anderson, S. and Seddon, K. R., *J. Chem. Res.* (*S*), 1979, 74.
6. Sawyer, D. T. and Roberts, J. L., Jr., *Experimental Electrochemistry for Chemists.* John Wiley, New York, 1974, pp. 167–215; (b)Walter, M. and Ramaley, L., *Anal. Chem.*, 1973, **45,** 165.
7. Ghatak, N., Chakravarty, J. and Bhattacharya, S., *Polyhedron*, 1995, **14,** 3591.
8. (a) Pankuch, B. J., Lacy, D. E. and Grosby, G. A., *J. Phys. Chem.*, 1980, **84,** 2061; (b) Ceulemans, A. and Vanquickenborne, L. G., *J. Am. Chem. Soc.*, 1981, **103,** 2238; (c) Decurtius, S., Felix, F., Ferguson, J., Gudel, H. U. and Ludi, A., *J. Am. Chem. Soc.*, 1980, **102,** 4102; (d) Kober, E. M. and Meyer, T. J., *Inorg. Chem.*, 1982, **21,** 3967.
9. Tokel-Takvorian, N. E., Hemingway, R. E. and Bard, A. J., *J. Am. Chem. Soc.*, 1973, **95,** 6582.

10. Hammett, L. P., *Physical Organic Chemistry*, 2nd edn. McGraw-Hill, New York, 1970.
11. Mukherjee, R. N., Rajan, O. A. and Chakravorty, A., *Inorg. Chem.*, 1982, **21,** 785.
12. (a) Vleck, A. A., *Coord. Chem. Rev.*, 1982, **43,** 39; (b) Kahl, J. L., Hanck, K. W. and DeArmond, K., *J. Phys. Chem.*, 1978, **82,** 540.
13. (a) Bleany, B. and O'Brien, M. C. M., *Proc. Phys. Sci. London, Sect. B.*, 1956, **69,** 1216; (b) Griffith, J. S., *The Theory of Transition Metal Ions.* Cambridge University Press, London, 1961, p. 364.
14. Bhattacharya, S. and Chakravorty, A., *Proc. Ind. Acad. Sci. (Chem. Sci.)*, 1985, **95,** 159.