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Synthesis, structure and electrochemical properties of a group of ruthenium(III) complexes of *N*-(aryl)picolinamide

Anindya Das,[a] Shie-Ming Peng,[b] Gene-Hsiang Lee[b] and Samaresh Bhattacharya*[a]

[a] *Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032, India. E-mail: samaresh_b@hotmail.com*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC*

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Reaction of *N*-(aryl)picolinamide (HL–R; R = OCH_3, CH_3, H, Cl and NO_2) with ruthenium trichloride or $[Ru(DMSO)_4Cl_2]$ in refluxing 2-methoxyethanol in the presence of a base (NEt_3) affords tris complexes of the type $[Ru(L–R)_3]$. The structure of the $[Ru(L–OCH_3)_3]$ complex has been determined by X-ray crystallography. In these complexes the amide ligands are coordinated to the metal center as monoanionic bidentate N,N-donors. All the $[Ru(L–R)_3]$ complexes are one-electron paramagnetic and show rhombic ESR spectra at 77 K. They also show intense LMCT transitions in the visible region. Cyclic voltammetry on all the complexes shows a ruthenium(III)/ruthenium(IV) oxidation within the range of 0.89 to 1.21 V *vs.* SCE and a ruthenium(III)/ruthenium(II) reduction within the range of −0.22 to −0.41 V *vs.* SCE. Representative one-electron oxidized and reduced complexes, *viz.* $[Ru^{IV}(L–H)_3]^+$ and $[Ru^{II}(L–H)_3]^-$, respectively, have also been generated in solution and characterized spectroscopically as well as electrochemically.

Introduction

There has been considerable current interest in the chemistry of ruthenium,[1] which is primarily due to its fascinating redox, photophysical and photochemical properties. As all these properties are directed by the coordination environment around the central metal ion, complexation of ruthenium by ligands of selected types is of significant importance. In the present study, which has originated from our interest in the chemistry of ruthenium in different coordination environments,[2] we have selected a group of amide ligands (**1**) derived from picolinic acid and para-substituted anilines. The chemistry of ruthenium complexes of amide ligands has been receiving serious attention largely because of their relevance to peptide chemistry.[3] The selected ligands (**1**) are referred to as *N*-(aryl)picolinamides and abbreviated in general as HL–R, where H stands for the potentially dissociable N–H proton and R for the para substituent. Such ligands are known to bind to metal ions either as neutral N,O-donors (as in **2**) or as monoanionic N,N-donors (as in **3**) *via* loss of the amide proton.[3] Though the ability to display these two different coordination modes has been incorrectly referred to as linkage isomerism by some authors,[3l,3m] this property is of particular interest.

The primary objective of the present study has been to synthesize homoleptic tris complexes of these *N*-(aryl)picolinamide ligands (**1**). Reaction of these ligands with two different ruthenium starting materials, *viz.* ruthenium trichloride and $[Ru(DMSO)_4Cl_2]$, has been found to successfully afford the targeted tris $[Ru(L–R)_3]$ complexes. It may be noted here that though there are some reports on ruthenium complexes of different amide ligands,[3] the chemistry of such tris-amide complexes of ruthenium appears to have remained unexplored. An account of the chemistry of these $[Ru(L–R)_3]$ complexes is reported in this paper with special reference to their synthesis, characterization and redox properties.

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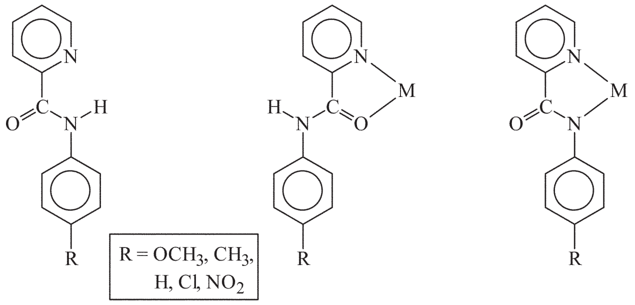


1 **2** **3**

Experimental

Materials and physical measurements

Commercial ruthenium trichloride (Arora Matthey, Kolkata, India) was converted to $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. $[Ru(DMSO)_4Cl_2]$ and the *N*-(aryl)picolinamides were prepared by following reported procedures.[4,3k] All other chemicals and solvents were reagent grade commercial materials and were used as received. Purification of acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature.[5]

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Perkin–Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. ESR spectra were recorded with a Varian E-109C X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All ESR spectra were calibrated with the aid of DPPH ($g = 2.0037$). Electrochemical measurements were made using a CH Instruments model 600 A electrochemical analyzer. A platinum disc working electrode (area = 0.02 cm^2), a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. With this experimental setup the ferrocene/ferrocenium couple appeared at 0.20 V with $\Delta E_p = 70$ mV. A platinum wire gauge working electrode was used in the coulometric experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Synthetic procedures

The [Ru(L–R)$_3$] (R = OCH$_3$, CH$_3$, H, Cl and NO$_2$) complexes were synthesized by following two general procedures. Yields varied in the range of 60–75%. Specific details are given for one complex.

[Ru(L–H)$_3$]. *Method A. N*-(Phenyl)picolinamide (227 mg, 1.15 mmol) was dissolved in 2-methoxyethanol (40 mL) and to it was added triethylamine (116 mg, 1.15 mmol). Then RuCl$_3$·3H$_2$O (100 mg, 0.38 mmol) was added to the solution. The solution was heated at reflux for 4 h to produce a brownish-violet solution. After being cooled to room temperature, [Ru(L–H)$_3$] precipitated as a brownish-violet solid and was collected by filtration, washed thoroughly with ethanol and dried in air. Purification of the product was done by thin layer chromatography on a silica gel plate, using 1:1 benzene–acetonitrile as the eluant. A dark brownish-violet band separated and was extracted with acetonitrile. On evaporation of the acetonitrile extract [Ru(L–H)$_3$] was obtained as a dark microcrystalline solid. Yield: 73%.
Method B. N-(Phenyl)picolinamide (123 mg, 0.62 mmol) was dissolved in 2-methoxyethanol (40 mL) and to it was added triethylamine (63 mg, 0.62 mmol). Then [Ru(DMSO)$_4$Cl$_2$] (100 mg, 0.21 mmol) was added to the solution. The solution was heated at reflux for 4 h to produce a brownish-violet solution. Isolation of the purified [Ru(L–H)$_3$] complex was done as in Method A. Yield: 62%. Anal. calcd: C, 63.75; H, 4.50; N, 11.44; found: C, 64.04; H, 4.54; N, 11.34.

[Ru(L–OCH$_3$)$_3$]. Anal. calcd: C, 62.42; H, 3.90; N, 12.14; found: C, 62.14; H, 3.93; N, 12.11.

[Ru(L–CH$_3$)$_3$]. Anal. calcd: C, 59.84; H, 4.22; N, 10.74; found: C, 59.80; H, 4.20; N, 10.77.

[Ru(L–Cl)$_3$]. Anal. calcd: C, 54.30; H, 3.02; N, 10.56; found: C, 54.54; H, 2.97; N, 10.57.

[Ru(L–NO$_2$)$_3$]. Anal. calcd: C, 52.23; H, 2.90; N, 15.23; found: C, 52.09; H, 2.93; N, 15.20.

X-Ray crystallography

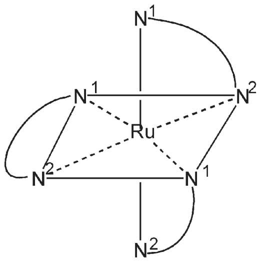
Single crystals of [Ru(L–OCH$_3$)$_3$] were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker Smart CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) by ω scans. X-Ray data reduction and the structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs.[6] The structure was solved by direct methods.†

Table 1 Crystallographic data for [Ru(L–OCH$_3$)$_3$]

Formula	$C_{39}H_{33}N_6O_6Ru$
Formula weight	782.78
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.5172(5)
b/Å	13.5574(6)
c/Å	14.6025(7)
α/deg	117.086(1)
β/deg	95.729(1)
γ/deg	103.286(1)
U/Å^3	1753.19(14)
Z	2
T/K	295(2)
μ/mm^{-1}	0.504
Reflections collected	23 191
Independent reflections	8042
R_{int}	0.0269
R_1	0.0323
wR_2	0.0820

Results and discussion

Reaction of the amide ligands (HL–R, **1**) with ruthenium trichloride in the presence of a base (NEt$_3$) has afforded the tris [Ru(L–R)$_3$] complexes in decent yields. The same tris complexes have also been synthesized, in slightly lower yields, using [Ru(DMSO)$_4$Cl$_2$] as the ruthenium starting material instead of ruthenium trichloride. It may be noted here that ruthenium undergoes a one-electron oxidation during the course of this second reaction and in view of the ruthenium(III)/ruthenium(II) reduction potential displayed by these complexes (*vide infra*), aerial oxygen appears to have served as the oxidant. The observed elemental (C, H, N) analytical data of the [Ru(L–R)$_3$] complexes agree well with their compositions. The formulation of these complexes indicates that the amide ligands are coordinated to the metal center as monoanionic bidentate N,N-donors (**3**). As the deprotonated amide ligand in **3** is unsymmetrically bidentate in nature, the [Ru(L–R)$_3$] complexes may exist, in principle, in two different isomeric forms, *viz.* meridional (**4**) and facial (**5**). To determine the stereochemistry of these complexes, as well as to verify the coordination mode of the amide ligands in them, the structure of a representative member of this family, *viz.* [Ru(L–OCH$_3$)$_3$], has been determined by X-ray crystallography. The structure is shown in Fig. 1 and some selected bond parameters are listed in Table 2. The structure shows that each amide ligand is coordinated to ruthenium through the pyridine and amide nitrogens, as envisaged above, forming a five-membered chelate ring (**3**) with a bite angle of ~80°. Ruthenium is thus sitting in an N$_6$ coordination sphere, which is distorted from the ideal octahedral geometry as reflected in all the bond parameters around ruthenium. The relative disposition of the pyridine and amide nitrogens shows that the complex has the meridional stereochemistry (**4**), which is quite common in tris-chelates of ruthenium(III).[7] The Ru–N distances are all quite normal



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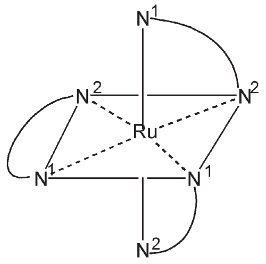

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† CCDC reference number 231953. See http://www.rsc.org/suppdata/nj/b3/b317018g/ for crystallographic data in .cif or other electronic format.

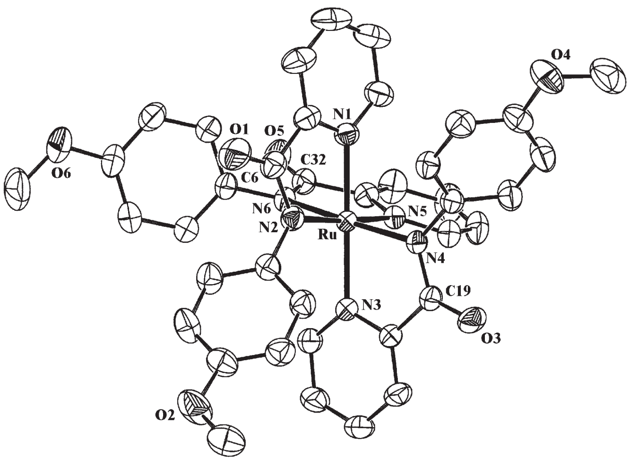

Fig. 1 View of the [Ru(L–OCH_3)$_3$] complex.

and so are the C–O and C–N distances in the amide fragment.[3] As all the five [Ru(L–R)$_3$] complexes have been synthesized similarly and they show similar properties (*vide infra*), the other four [Ru(L–R)$_3$] ($R \neq OCH_3$) complexes are assumed to have a similar structure as [Ru(L–OCH_3)$_3$].

Magnetic susceptibility measurements show that the [Ru(L–R)$_3$] complexes are one-electron paramagnetic (μ_{eff} = 1.87–1.92 μ_B), which corresponds to the +3 state of ruthenium (low-spin d^5, $S = \frac{1}{2}$) in these complexes. ESR spectra of the [Ru(L–R)$_3$] complexes have been recorded in 1:1 dichloromethane–toluene solution at 77 K. Each complex shows a rhombic ESR spectrum with three distinct signals (g_1, g_2 and g_3; in the order of decreasing magnitude). A selected spectrum is shown in Fig. 2 and the spectral data for all complexes are given in Table 3. The rhombicity of the spectra reflects the asymmetry of the electronic environment around ruthenium in these [Ru(L–R)$_3$] complexes. The spectra may be considered as pseudo-axial, consisting of a rather isolated signal (g_3; $g_\parallel$ 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, two electronic transitions (transition energies ΔE_1 and ΔE_2; $\Delta E_1 < \Delta E_2$) are probable 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,[8] and a reported method.[9] The axial distortion is indeed observed to be stronger than the rhombic one for all the complexes.[10] The calculated values of ΔE_1 (~4500 cm^{-1}) and ΔE_2 (~6700 cm^{-1}) indicate that two ligand-field transitions should take place around 2200 and 1500 nm, respectively. Both of these expected transitions have indeed been observed in the spectra of all these complexes (*vide infra*). The ESR spectral data thus show that these [Ru(L–R)$_3$] complexes are significantly distorted from the ideal octahedral geometry, as was also indicated by the structure determination of one complex.

Table 2 Selected bond parameters (distances in Å, angles in °) for [Ru(L–OCH_3)$_3$]

Ru–N(1)	2.0481(17)	C(6)–O(1)	1.219(3)
Ru–N(2)	1.9945(17)	C(19)–O(3)	1.238(2)
Ru–N(3)	2.0561(16)	C(32)–O(5)	1.236(3)
Ru–N(4)	2.0214(16)	C(6)–N(2)	1.364(3)
Ru–N(5)	2.1067(16)	C(19)–N(4)	1.345(3)
Ru–N(6)	2.1226(16)	C(32)–N(6)	1.330(3)
N(1)–Ru–N(3)	176.41(6)	N(1)–Ru–N(2)	80.00(7)
N(2)–Ru–N(5)	170.94(6)	N(3)–Ru–N(4)	79.94(7)
N(4)–Ru–N(6)	168.72(6)	N(5)–Ru–N(6)	76.43(6)

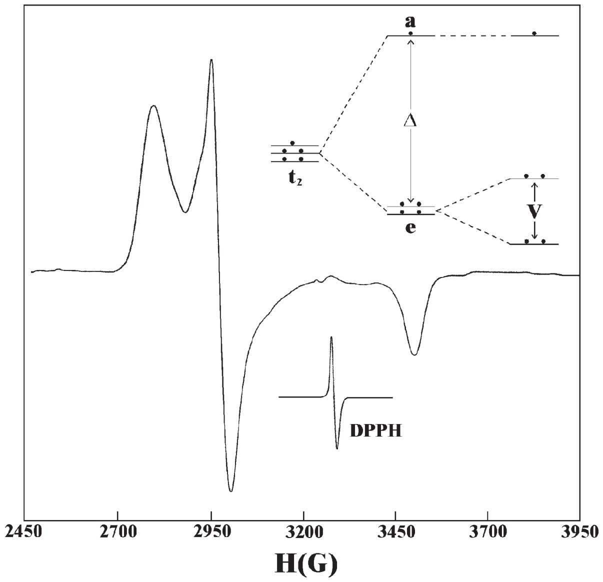

Fig. 2 ESR spectrum of [Ru(L–Cl)$_3$] in 1:1 dichloromethane–toluene solution at 77 K.

Infrared spectra of the [Ru(L–R)$_3$] complexes show several bands of different intensities in the 1700–400 cm^{-1} region. No attempts have been made to assign each individual band to a specific vibration. However, comparison with the spectra of the corresponding uncoordinated ligands shows that the N–H stretch, observed near 3140 cm^{-1} in the uncoordinated ligand, is absent in the complexes and the C=O stretch, observed at around 1680 cm^{-1} in the uncoordinated ligand, is shifted to ~1620 cm^{-1} in the complexes. These differences are in accordance with the observed coordination mode (**3**) of the amide ligands.[11]

The [Ru(L–R)$_3$] complexes are soluble in dichloromethane, chloroform, acetone, acetonitrile, *etc.*, producing intense brownish-violet solutions. Electronic spectra of these complexes have been recorded in acetonitrile solution. A selected spectrum is shown in Fig. 3 and full spectral data are presented in Table 4. Each complex shows several intense absorptions in the ultraviolet and visible region and two relatively weak absorptions in the near-infrared region. The intense absorptions in the ultraviolet region are attributable to transitions within the ligand orbitals and those in the visible region are probably due to ligand-to-metal charge-transfer transitions. To have a better insight into the nature of the absorptions in the visible region, qualitative EHMO calculations have been performed[12] on a computer-generated model of the [Ru(L–H)$_3$)] complex. A partial MO diagram is shown in Fig. 4. The highest singly-occupied molecular orbital (HOMO) and the next two filled orbitals (HOMO-1 and HOMO-2) are relatively close in energy and have major (> 70%) contributions from the ruthenium d_{xy}, d_{yz} and d_{zx} orbitals, and hence they may be regarded as the ruthenium t_2 orbitals. The next occupied orbital (HOMO-3) is rather isolated and is localized

Table 3 ESR *g* values[a] and derived parameters

Compound	g_1	g_2	g_3	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
[Ru(L–OCH_3)$_3$]	2.333	2.220	1.898	5.797	1.873	4.905	6.973
[Ru(L–CH_3)$_3$]	2.327	2.203	1.894	5.682	2.056	4.713	6.944
[Ru(L–H)$_3$]	2.327	2.203	1.884	5.408	1.904	4.518	6.608
[Ru(L–Cl)$_3$]	2.356	2.218	1.886	5.537	2.082	4.562	6.814
[Ru(L–NO_2)$_3$]	2.319	2.203	1.884	5.373	1.791	4.534	6.523

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

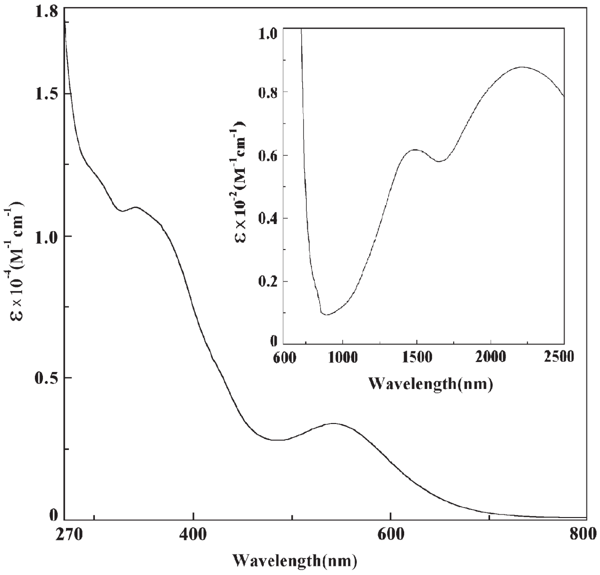

Fig. 3 Electronic spectrum of [Ru(L–H)$_3$] in acetonitrile solution.

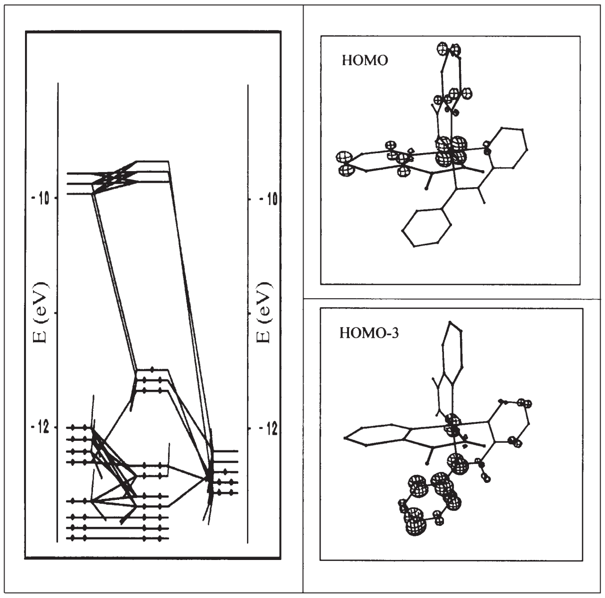

Fig. 4 Partial molecular orbital diagram of [Ru(L–H)$_3$]. Some carbon atoms of the phenyl rings in two amide ligands have been omitted for clarity.

almost entirely ($>90\%$) on the amide ligands. The intense absorption in the 520–570 nm region may therefore be assigned to the charge-transfer transition taking place from the filled ligand (HOMO-3) orbital to the singly-occupied ruthenium t_2 orbital (HOMO). The two weak absorptions in the near-infrared region are assignable to the two ligand-field transitions within the three split t_2 orbitals (*vide supra*).

Redox properties of the [Ru(L–R)$_3$] complexes have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBAP). A representative voltammogram is shown in Fig. 5 and voltammetric data are given in Table 4. Each complex shows an oxidative response on the positive side of SCE and a reductive response on the negative side. In view of the results of the EHMO calculations (*vide supra*), these responses are respectively assigned to the ruthenium(III)/ruthenium(IV) oxidation and ruthenium(III)/ruthenium(II) reduction. Both the redox responses are reversible, as reflected in the equality of the anodic peak current (i_{pa}) with the cathodic peak current (i_{pc}). Though the peak-to-peak separation (ΔE_p) is slightly larger (~80 mV) than ideally expected for a reversible electron-transfer process, it remains unchanged upon changing the scan rate and thus supports the reversibility. The potentials of both the ruthenium(III)/ruthenium(IV) oxidation and ruthenium(III)/ruthenium(II) reduction have been found to be sensitive to the nature of the substituent R in the amide ligand. The potentials increase with increasing electron-withdrawing character of the substituent R and plots of the redox potential *versus* 3σ [σ = Hammett constant of R:[13] $OCH_3 = -0.27$, $CH_3 = -0.17$, $H = 0.00$, $Cl = 0.23$ and $NO_2 = 0.78$] is linear for both couples (Fig. 6) with slopes (ρ = reaction constant of the couple[14]) of 0.10 V (for the ruthenium(III)/ruthenium(IV) oxidation) and 0.06 V (for the ruthenium(III)/ruthenium(II) reduction). This linear correlation of the redox potentials with the electronic nature (3σ) of the substituents with reasonable slopes (ρ) clearly shows that a single substituent on the amide ligand, which is six bonds away from the metal center, can still

Table 4 Electronic spectral and cyclic voltammetric data

		$E_{1/2}$/V (ΔE_p/mV)^b	
Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})^a	Ox	Red
[Ru(L–OCH$_3$)$_3$]	2183 (75), 1481 (53), 566 (2100), 358^c (9200), 314^c (10 800), 246 (29 000)	0.89 (80)	−0.41 (80)
[Ru(L–CH$_3$)$_3$]	2119 (61), 1567 (49), 550 (2400), 366^c (8600), 310^c (10 200), 246^c (29 800)	0.93 (78)	−0.40 (78)
[Ru(L–H)$_3$]	2209 (90), 1475 (62), 540 (3400), 368^c (10 300), 302^c (11 600), 248^c (32 100)	1.01 (80)	−0.38 (80)
[Ru(L–Cl)$_3$]	2174 (67), 1572 (48), 542 (2600), 362^c (8700), 304^c (11 100), 246^c (34 500)	1.10 (78)	−0.29 (78)
[Ru(L–NO$_2$)$_3$]	2067 (77), 1350 (98), 526 (2000), 320 (18 400), 264 (14 400), 214 (21 300)	1.21 (80)	−0.22 (80)
[Ru^{IV}(L–H)$_3$]$^+$	1300 (400), 704 (5200), 558^c (4200)		
[Ru^{II}(L–H)$_3$]$^-$	498 (4500), 412 (3800), 304^c (5200)		

^{a} In acetonitrile ^{b} Solvent, acetonitrile; supporting electrolyte, TBAP; scan rate 50 mV s^{-1}. ^{c} Shoulder.

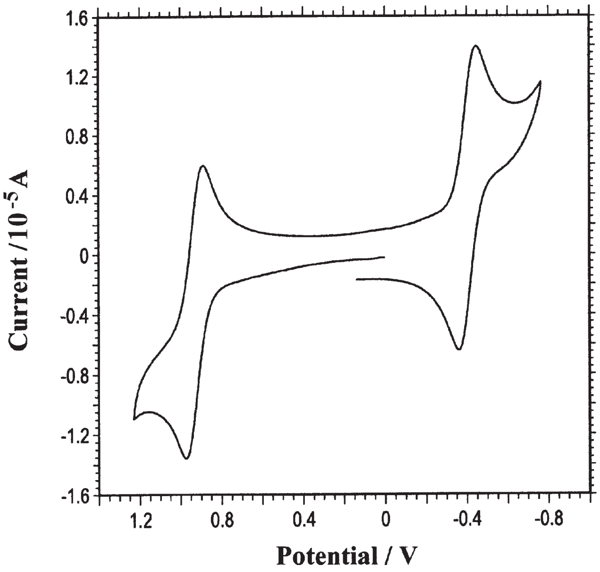

Fig. 5 Cyclic voltammogram of [Ru(L–CH$_3$)$_3$] in acetonitrile solution (0.1 M TBAP) at a scan rate of 50 mV s^{-1}.

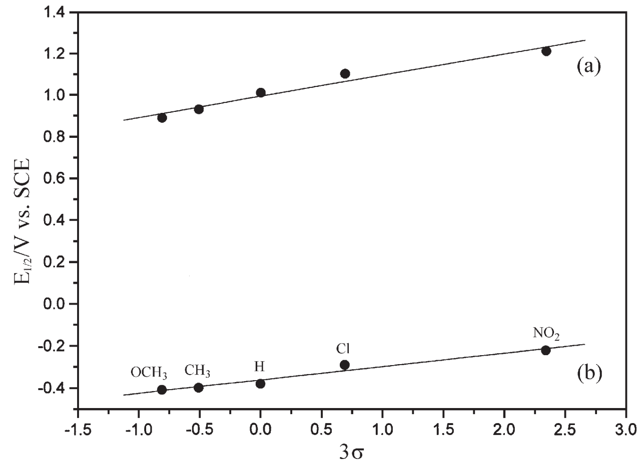

Fig. 6 Least-squares plot of (line a) ruthenium(III)/ruthenium(IV) oxidation potentials and (line b) ruthenium(III)/ruthenium(II) reduction potentials *versus* 3σ.

influence the metal-centered redox potentials in a predictable manner.

The reversibility of the cyclic voltammetric responses in the [Ru(L–R)$_3$] complexes indicate that both the one-electron oxidized and reduced species, *viz.* $[Ru^{IV}(L–R)_3]^+$ and $[Ru^{II}(L–R)_3]^-$, might be stable on a time scale much longer than the cyclic voltammetric time scale. To investigate this, a representative complex, *viz.* [Ru(L–H)$_3$], has been coulometrically oxidized at 1.10 V in acetonitrile solution (0.1 M TBAP). The oxidation was smooth and quantitative (weight of sample = 12 mg, Q_{calcd} = 1.67 Coulomb, Q_{found} = 1.73 Coulomb), associated with a color change from brownish-violet to blue. The electronic spectrum of the blue $[Ru^{IV}(L–H)_3]^+$ complex is found to be significantly different from that of the parent complex (Table 4), the ligand-to-metal charge-transfer transition shifts to lower energy on oxidation. This blue solution has been quantitatively converted back, upon coulometric reduction at 0.8 V, to the brownish-violet solution of $[Ru^{III}(L–H)_3]$, identified by its electronic spectrum. The same reduction can also be brought about chemically by the addition of hyrazine to the blue solution of $[Ru^{IV}(L–H)_3]^+$. Coulometric reduction of the [Ru(L–H)$_3$] complex at −0.66 V has been found to quantitatively generate the $[Ru^{II}(L–H)_3]^-$ species, which is yellowish-brown in color and shows intense absorptions, assignable to metal-to-ligand charge-transfer transition, in the visible region (Table 4). Coulometric oxidation of this yellowish-brown solution of $[Ru^{II}(L–H)_3]^-$ at 0.0 V, as well as chemical oxidation, either by prolonged exposure to aerial oxygen or by addition of hydrogen peroxide, quantitatively regenerates the brownish-violet solution of $[Ru^{III}(L–H)_3]$. The smooth interconversions between the +2, +3 and +4 states of ruthenium in these $[Ru(L–R)_3]^{n+}$ (n = −1, 0 and +1) species indicates that such electron-transfer reactions take place without any gross changes in the stereochemistry of the complexes.

Conclusions

The present study shows that coordination by the amide ligands (HL–R, **1**) in the monoanionic bidentate fashion (**3**) *via* dissociation of the amide proton can successfully stabilize the higher oxidation states of a transition metal. This is manifested in the stabilization of the trivalent state of ruthenium in the [Ru(L–R)$_3$] complexes. The electrochemically generated one-electron oxidized and reduced species, *viz.* $[Ru^{IV}(L–R)_3]^+$ and $[Ru^{II}(L–R)_3]^-$, appear to have the potential to serve as mild oxidant and reductant, respectively, and such possibilities are currently under exploration.

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