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SYNTHESIS, CHARACTERIZATION AND ELECTRON TRANSFER PROPERTIES OF SOME PICOLINATE COMPLEXES OF RUTHENIUM

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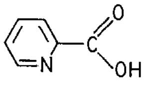
Abstract—In aqueous solution ruthenium trichloride reacted with picolinic acid (Hpic) in the presence of a base to afford $[Ru(pic)_3]$. In solution it shows intense ligand-to-metal charge transfer transitions near 310 and 370 nm, together with a low-intensity absorption near 2000 nm. $[Ru(pic)_3]$ is one-electron paramagnetic and shows a rhombic ESR spectrum in 1 : 1 dimethylsulphoxide–methanol solution at 77 K. The distortions from octahedral symmetry have been calculated by ESR data analysis. The axial distortion is larger than the rhombic one. In acetonitrile solution it shows a reversible ruthenium(III)–ruthenium(II) reduction at −0.09 V vs. SCE and a reversible ruthenium(III)–ruthenium(IV) oxidation at 1.52 V vs. SCE. Chemical or electrochemical reduction of $[Ru^{III}(pic)_3]$ gives $[Ru^{II}(pic)_3]^-$, which in solution shows intense MLCT transitions near 360, 410 and 490 nm, and is converted back to $[Ru(pic)_3]$ by exposure to air. Reaction of $[Ru(pic)_3]$ with 8-quinolinol (HQ) in dimethylsulphoxide solution affords $[RuQ_3]$. $[Ru(bpy)(pic)_2]$ (bpy = 2,2′-bipyridine) has been prepared by the reaction of Hpic with $[Ru(bpy)(acac)_2]Cl$ (acac = acetylacetonate ion) in ethyleneglycol. It is diamagnetic and in solution shows intense MLCT transitions near 370, 410 and 530 nm. In acetonitrile solution it shows a reversible ruthenium(II)–ruthenium(III) oxidation at 0.44 V vs. SCE and a reversible one-electron reduction of bpy at −1.64 V vs. SCE.

There is considerable interest in the chemistry of ruthenium,[1] due in part to the versatile electron transfer properties exhibited by the complexes of this metal. Variation of the coordination environment around ruthenium plays the key role in modulating the redox properties of its complexes. Hence, the coordination of ruthenium by ligands of different types has been a worthwhile exercise.[1] In this present work, which has emerged from our interest in the chemistry of ruthenium in various coordination spheres,[2] we have used picolinic acid (Hpic, **1**; H stands for the dissociable acidic hydrogen) as the principal ligand. The picolinate ion (pic) binds metal ions as bidentate N,O-donors forming a five-membered chelate ring (**2**). It is interesting to note that the chemistry of ruthenium picolinates has received relatively little attention.[2d,e,3] The present work deals with tris- and bis-picolinate complexes of ruthenium. In the case of the bis-picolinate complex, 2,2′-bipyridine has been used as the coligand to satisfy the remaining two coordination sites of the $Ru(pic)_2$ moiety. The synthesis, characterization and electron transfer properties of these


Picolinic acid
(Hpic)
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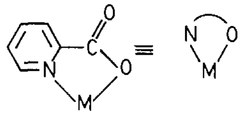
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two picolinate complexes of ruthenium are reported in this paper.

EXPERIMENTAL

Materials

Commercial ruthenium trichloride (Arora Matthey, Calcutta, India) was converted to $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. Picolinic acid was obtained from Spectrochem (Bombay, India). Hydrazine hydrate (80%, AR), dimethylsulphoxide (AR) and acetylacetone were purchased from S.D. Fine-Chemicals (Bombay, India). 2,2′-Bipyridine (bpy) and 8-quinolinol (HQ) were purchased from Loba Chemie (Bombay, India). $[Ru(bpy)Cl_3]$ and $[Ru(bpy)(acac)_2]Cl$ (acac = acetylacetonate) were prepared by following published procedures.[4,5] Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.[6,7] Dinitrogen gas for electrochemical work was purified by successively bubbling it through alkaline dithionite and concentrated sulphuric acid. All other chemicals and solvents were reagent grade commercial materials and were used as received.

Preparation of complexes

$[Ru(pic)_3]$. $RuCl_3 \cdot 3H_2O$ (200 mg, 0.76 mmol) was added to a solution of picolinic acid (800 mg, 6.50 mmol) in water (20 cm^3). The solution was stirred and a solution of anhydrous sodium carbonate (300 mg, 2.83 mmol) in water (20 cm^3) was added dropwise over a period of 30 min. The resulting solution was then refluxed for 2 h. Upon cooling, $[Ru(pic)_3]$ separated as a golden yellow crystalline solid, which was collected by filtration, washed with water followed by ethanol, and dried in air. The yield was 220 mg (62%).

$[Ru(bpy)(pic)_2]$. Picolinic acid (150 mg, 1.22 mmol) was added to a solution of $[Ru(bpy)(acac)_2]Cl$ (200 mg, 0.41 mmol) in ethyleneglycol (40 cm^3). The solution was then refluxed for 2 h with a slow stream of nitrogen gas flowing through it. Ethyleneglycol was evaporated from the resulting red–brown solution under reduced pressure. The solid residue thus obtained was dissolved in a small volume of acetonitrile and was chromatographed through a silica gel (60–120 mesh) column. With acetonitrile as the eluant, a light yellow band came out and was rejected. With 1 : 1 acetonitrile–methanol as the next eluant, a deep red–brown band separated which was collected. Evaporation of the solvents from the eluate gave a red–brown solid. This was recrystallized from 1 : 1 dichloromethane–hexane solution to afford $[Ru(bpy)(pic)_2]$ as a dark crystalline solid. The yield was 130 mg (64%).

$[RuQ_3]$. To a solution of $[Ru(pic)_3]$ (100 mg, 0.21 mmol) in dimethylsulphoxide (40 cm^3) was added 8-quinolinol (HQ; 200 mg, 1.38 mmol) and the solution was refluxed for 1 h to produce a greenish brown solution. Evaporation of the solvent gave an amorphous solid which was thoroughly washed with hot water and dried *in vacuo* over P_4O_{10}. Recrystallization from 1 : 1 dichloromethane–hexane solution gave $[RuQ_3]$ as a dark crystalline solid. The yield was 90 mg (79%).

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 Hitachi U-3400 and Shimadzu MPS-2000 spectrophotometers. 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 about 10^{-3} M. Electrochemical measurements were made using the PAR model 370-4 electrochemistry system incorporating the following components: 174A polarographic analyser, 175 universal programmer, RE 0074 X–Y recorder, 173 potentiostat, 179 digital coulometer, 377 cell system. All electrochemical experiments were performed under dinitrogen. 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 were collected at 298 K and are uncorrected for junction potentials.

RESULTS AND DISCUSSION

Tris(picolinato)ruthenium(III)

$[Ru(pic)_3]$ was synthesized in reasonable yield by the smooth reaction of ruthenium trichloride with picolinic acid [eq. (1)] in aqueous solution in the presence of a base. The composition of this complex

$$RuCl_3 + 3Hpic \longrightarrow [Ru(pic)_3] + 3HCl \quad (1)$$

has been confirmed by the excellent agreement of observed elemental (C, H, N) analytical data with the calculated values (Table 1). It may be noted here that synthesis of $[Ru(pic)_3]$ from two other ruthenium-containing starting materials, namely $K_2[RuCl_5(H_2O)]$ and $[Ru_2(CH_3COO)_4Cl]$, has been reported in the literature.[3d,e] Our synthetic method uses the most common source of ruthenium as the starting material and is much less complicated than the other reported routes. As picolinate ion is an unsymmetrical bidentate ligand, $[Ru(pic)_3]$ may exist in *meridional* and *facial* isomeric forms, and $[Ru(pic)_3]$ synthesized from $[Ru_2(CH_3COO)_4Cl]$ is reported to have the *meridional* structure.[3e] $[Ru(pic)_3]$, synthesized by us, showed no sign of being a mixture of isomers, and we assume the same *meridional* structure for the $[Ru(pic)_3]$ synthesized by our method.

The IR spectrum of $[Ru(pic)_3]$ shows many vibrations of different intensities. Some sharp and strong vibrations are observed at 1674, 1459, 1318, 1285, 1246, 1142, 1043, 856, 762, 689 and 466 cm^{-1}. Assignment of each individual band has not been attempted. However, the band at 1674 cm^{-1} is assigned to the carbonyl stretching vibration of the carboxylate group in the picolinate ligand. In picolinic acid the same vibration is observed at 1720 cm^{-1}. The decrease in frequency is due to complexation. $[Ru(pic)_3]$ is soluble in dimethylsulphoxide, acetonitrile, methanol and water, producing light yellow solutions. Conductivity measurements show that in solution it is a non-electrolyte, as expected. Electronic spectra of $[Ru(pic)_3]$ have been recorded both in dimethylsulphoxide and acetonitrile solutions. Spectral data are given in Table 1. The electronic spectral behaviour in the two solutions is almost identical, indicating that the composition of the complex remains intact in both solutions. Each solution shows two intense absorptions, one with a maximum at 310 nm and the other appearing as a shoulder near 370 nm. Picolinic acid or the picolinate ion does not show any absorption in this region. Hence, these absorptions are assigned to ligand-to-metal charge transfer transitions. A third absorption with low intensity is observed near 2000 nm in both solutions and is discussed below.

Magnetic susceptibility measurement shows that $[Ru(pic)_3]$ is one-electron paramagnetic ($\mu_{eff} = 1.95$ B.M.), which corresponds to the +3 state of ruthenium (low-spin d^5, $S = 1/2$) in this complex. The ESR spectrum of $[Ru(pic)_3]$, recorded in 1 : 1

Table 1. Microanalytical, electronic spectral and cyclic voltammetric data

Compound	Analytical data[a] (%)			Solvent	Electronic spectral data	Cyclic voltammetric data[c] E°_{298}, V (ΔE_p, mV)	
	C	H	N		λ_{max}, nm (ε^b, $M^{-1}\,cm^{-1}$)	$Ru^{II/III}$	Others
$[Ru(pic)_3]$	46.1 (46.2)	2.5 (2.6)	8.9 (9.0)	dimethylsulphoxide	1980 (25), 370[d](4400), 310 (9900)	0.00 (80)	—
				acetonitrile	2000 (30), 367[d](4200), 310 (9800)	−0.09 (80)	1.52 (80)
$[Ru(bpy)(pic)_2]$	52.6 (52.7)	3.2 (3.2)	11.2 (11.2)	dichloromethane	540 (3400), 410 (5500), 375[d](4300)	0.44 (80)	—
				acetonitrile	527 (3300), 405 (5200), 360[d](3900)	0.44 (80)	−1.64 (80)

[a] Calculated values are given in parentheses.

[b] Extinction coefficient.

[c] Supporting electrolyte, TEAP (0.1 M); reference electrode, SCE; $E^\circ_{298} = 0.5(E_{pa}+E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials; $\Delta E_p = E_{pa} - E_{pc}$; scan rate, 50 mV s^{-1}.

[d] Shoulder.

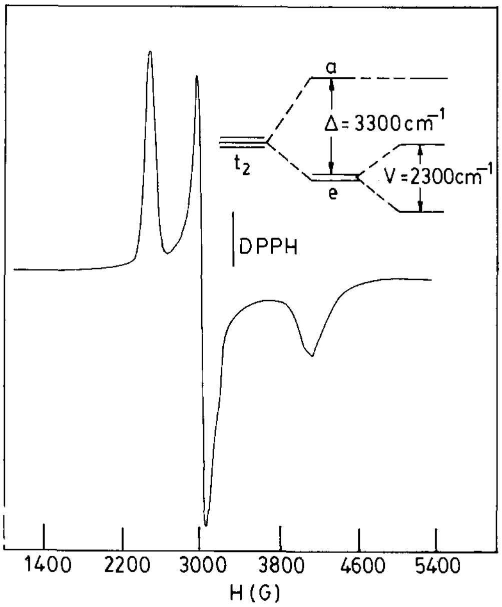


Fig. 1. ESR spectrum in 1 : 1 dimethylsulphoxide–methanol solution at 77 K and computed t_2 splittings of $[Ru(pic)_3]$.

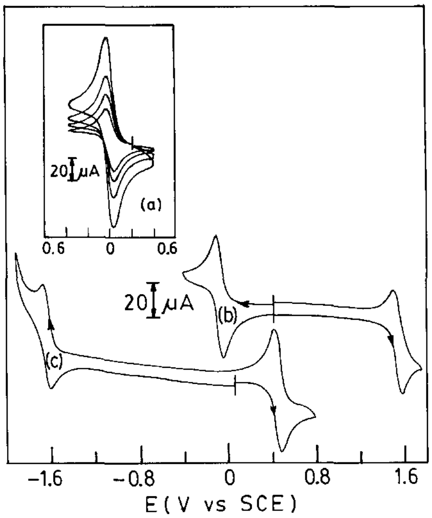


Fig. 2. Cyclic voltammograms of: (a) $[Ru(pic)_3]$ in dimethylsulphoxide solution (0.1 M TEAP) at scan rates of 50, 100, 200 and 500 mV s^{-1}; (b) $[Ru(pic)_3]$ in acetonitrile solution (0.1 M TEAP) at scan rate of 50 mV s^{-1}; (c) $[Ru(bpy)(pic)_2]$ in acetonitrile solution (0.1 M TEAP) at scan rate of 50 mV s^{-1}. Sample concentration was about 10^{-3} M in each case.

dimethylsulphoxide–methanol solution at 77 K, is shown in Fig. 1. A rhombic ESR spectrum, characteristic of ruthenium(III) in a *meridional* N_3O_3 coordination sphere,[8] is observed with three distinct g-values. The rhombicity of the spectrum indicates the asymmetry of the electronic environment around ruthenium in $[Ru(pic)_3]$. This spectrum may be considered as pseudo-axial, consisting of a rather isolated signal at 1.627 ($g_{\parallel}$ in the axial case) and two relatively close signals at 2.217 and 2.690 (rhombic components 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. 1). 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 using the observed g-values, the g-tensor theory of low-spin d^5 complexes[9] and a reported method.[8,10] The axial distortion ($\Delta = 3300$ cm^{-1}) is indeed stronger than the rhombic one ($V = 2300$ cm^{-1}). The calculated values of ΔE_1 and ΔE_2 are 2400 and 4800 cm^{-1} (2080 nm), respectively. The ΔE_2 transition is observed in the spectra of $[Ru(pic)_3]$ in both dimethylsulphoxide and acetonitrile solutions (Table 1). The ΔE_1 transition, which extends into the IR region, could not be detected.

Cyclic voltammograms of $[Ru(pic)_3]$ have been recorded in dimethylsulphoxide and acetonitrile solutions. Voltammetric data are presented in Table 1 and voltammograms are shown in Fig. 2. In dimethylsulphoxide solution, $[Ru(pic)_3]$ shows a reversible one-electron reduction at 0.00 V (all potentials are referenced to SCE), which is assigned to the ruthenium(III)–ruthenium(II) reduction [eq. (2)].

$$[Ru^{III}(pic)_3] + e^- \rightleftharpoons [Ru^{II}(pic)_3]^- \qquad (2)$$

The one-electron nature of this couple has been confirmed by coulometric experiments (see below). The cathodic and anodic peak currents for this couple are almost equal, as expected for reversible processes. The observed peak-to-peak separation (ΔE_p) is slightly larger (80 mV) than that expected for ideal reversible couples, but they do not change with change in scan rates (Fig. 2), supporting the reversibility of this reduction. In acetonitrile solution, $[Ru(pic)_3]$ shows two voltammetric responses, one reversible ruthenium(III)–ruthenium(II) reduction [eq. (2)] at −0.09 V and a second reversible one-electron oxidation at 1.52 V, which is assigned to the ruthenium(III)–ruthenium(IV) oxidation [eq. (3)]. The one-electron stoichiometry of

$$[Ru^{III}(pic)_3] \rightleftharpoons Ru^{IV}(pic)_3]^+ + e^- \qquad (3)$$

these couples has been established by comparing their current heights with those of a standard ferrocene–ferrocenium couple ($\Delta E_p = 80$ mV) under identical experimental conditions. For both couples the ΔE_p values are 80 mV and the peak currents are almost equal, as expected. The ruthenium(III)–ruthenium(IV) oxidation is not observed in dimethylsulphoxide solution because solvent oxidation precedes metal oxidation. Complexes of ruthenium, in an N_3O_3 coordination sphere, are known to display both ruthenium(III)–ruthenium(II) and ruthenium(III)–ruthenium(IV) couples,[8,11] the potentials of which depend on the nature of the ligands. In RuQ_3 (Q = 8-quinolinolate anion), for example, the above couples occur at -0.70 and 0.66 V, respectively.[8] Both potentials are approximately 750 mV lower than those in $[Ru(pic)_3]$, which indicates that the higher oxidation states ($+3$ and $+4$) of ruthenium are better stabilized in the 8-quinolinolate complex. The 8-quinolinolate anion is also an N,O-donor like the picolinate anion. Both ligands have nitrogen incorporated in a pyridine ring, but the oxygen is phenolate in 8-quinolinolate, whereas it is carboxylate in the picolinate anion. Therefore, it is evident that coordination by phenolate oxygen stabilizes the higher oxidation states of ruthenium better than that by carboxylate oxygen.

The reversibility of the ruthenium(III)–ruthenium(II) couple in $[Ru(pic)_3]$, together with its low potential, suggest that the reduced complex may be stable. To investigate this, $[Ru^{II}(pic)_3]^-$ was generated by coulometric reduction of $[Ru(pic)_3]$ in dimethylsulphoxide solution (0.1 M TEAP) at -0.25 V. The reduction was smooth and quantitative, and the colour of the solution changed from light yellow to dark red. The electronic spectrum of this red solution showed intense absorptions at 490 nm ($\varepsilon = 13{,}500$ M^{-1} cm^{-1}), 410 nm (shoulder, $\varepsilon = 7400$ M^{-1} cm^{-1}) and 360 nm (shoulder, $\varepsilon = 4900$ M^{-1} cm^{-1}), which are assigned to metal-to-ligand charge transfer transitions. $[Ru^{II}(pic)_3]^-$ was also generated by chemical reduction of $[Ru(pic)_3]$ in dimethylsulphoxide solution by hydrazine hydrate. The same dark red solution of $[Ru^{II}(pic)_3]^-$ was obtained, which showed a spectrum almost identical to that shown by the coulometrically reduced solution, as expected. Upon long exposure to air, this dark red solution regained the light yellow colour of the parent complex. The electronic spectrum of this solution confirmed the presence of $[Ru(pic)_3]$ in it. However, intensity measurements of the spectral bands indicated that about 60% of $[Ru(pic)_3]$ was regenerated. The conversion of $[Ru^{II}(pic)_3]^-$ to $[Ru(pic)_3]$ became considerably faster when air was drawn through the solution of $[Ru^{II}(pic)_3]^-$ with the help of a water-suction pump. These results indicate that $[Ru(pic)_3]$ may be used as a catalyst in similar redox reactions.

All the three picolinate ligands can be replaced from $[Ru(pic)_3]$ by three 8-quinolinolate ligands by reacting it with 8-quinolinol in refluxing dimethylsulphoxide (see Experimental section). The product has been identified by its characteristic spectral and cyclic voltammetric properties.[8] This indicates that under appropriate conditions, $[Ru(pic)_3]$ can be used as a starting material to form other tris-chelated complexes.

(2,2′-Bipyridine)bis(picolinato)ruthenium(II)

From the foregoing discussion on the electron transfer properties of $[Ru(pic)_3]$, it is clear that chelation of ruthenium by three picolinate ligands stabilizes the $+3$ state of this metal, whereas the $+2$ state is not so stable in this N_3O_3 coordination sphere. This indicates that, to obtain a stable picolinate complex of ruthenium(II), at least one of the three picolinate ligands of $[Ru(pic)_3]$ needs to be replaced by a strong π-acid ligand. This strategy has prompted us to choose 2,2′-bipyridine (bpy), which is a familiar stabilizer of ruthenium(II), as the co-ligand. The targeted mixed-ligand complex, $[Ru^{II}(bpy)(pic)_2]$, was prepared by the smooth displacement of acetylacetonate ligands (acac) from $[Ru(bpy)(acac)_2]Cl$ by picolinate ions in refluxing ethyleneglycol [eq. (4)]. It may be noted here that

$$[Ru^{III}(bpy)(acac)_2]Cl + 2Hpic + e^- \longrightarrow [Ru^{II}(bpy)(pic)_2] + 2Hacac + Cl^- \quad (4)$$

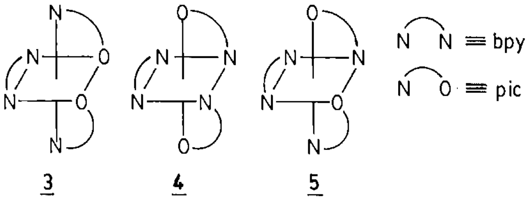
during the course of this synthetic reaction, ruthenium undergoes a one-electron reduction. With reference to the potential of the ruthenium(II)–ruthenium(III) couple in $[Ru(bpy)(pic)_2]$ (see below), it appears that the solvent may serve as the reductant.

Elemental analysis data (Table 1) agree well with the composition of this complex. Magnetic susceptibility measurements show that $[Ru(bpy)(pic)_2]$ is diamagnetic, as expected for complexes of ruthenium(II) (low-spin d^6, $S = 0$). The IR spectrum of $[Ru(bpy)(pic)_2]$ shows many vibrations of different intensities and is therefore complex in nature. Comparison with the spectrum of $[Ru(pic)_3]$ shows that some vibrations (e.g. 1635, 855, 698, 545, 460 cm^{-1}) are very similar to those observed in $[Ru(pic)_3]$ and hence are probably due to the coordinated picolinate ligands. Some other vibrations (e.g. 1600, 1485, 1466, 1445, 1420, 1025 cm^{-1}), which are absent in $[Ru(pic)_3]$, are due to the bound bpy. Vibrations similar to these are observed in Ru–bpy complexes.

$[Ru(bpy)(pic)_2]$ is soluble in common organic solvents like methanol, ethanol, dichloromethane, acetonitrile, etc., producing intense red solutions.

In solution [Ru(bpy)(pic)$_2$] behaves as a non-electrolyte, as expected. Electronic spectra of [Ru(bpy)(pic)$_2$] were recorded in dichloromethane and acetonitrile solutions (Table 1). The similarity in spectral properties in the two solutions indicates that the nature of the solvent has little effect on the spectral transitions. In both solutions, [Ru(bpy)(pic)$_2$] shows three intense absorptions in the visible region, which are probably due to allowed metal-to-ligand charge transfer transitions.

As the picolinate ion is an unsymmetrical bidentate ligand, [Ru(bpy)(pic)$_2$] may exist in three different geometrical isomeric forms, **3**, **4** and **5**. In **3** and **4** there is a C_2 axis, which indicates that the two picolinate ligands and the two pyridine rings of bpy are equivalent. Hence the 16 hydrogens present in this complex are expected to show only eight resonances (four doublets and four triplets) in the ^{1}H NMR spectrum. In the case of **5**, there is no C_2 axis and 16 resonances (eight doublets and eight triplets, provided no overlap of signals occurs) may result. The ^{1}H NMR spectrum of [Ru(bpy)(pic)$_2$], recorded in CDCl$_3$ solution, shows four distinct triplets (1H each), two distinct doublets (1H each), another triplet (4H) and six overlapping doublets (6H). The ^{1}H NMR data thus exclude structures **3** and **4**, and we assign structure **5** to [Ru(bpy)(pic)$_2$].



Cyclic voltammograms of [Ru(bpy)(pic)$_2$] have been recorded in dichloromethane and acetonitrile solutions (Table 1, Fig. 2). In both solutions a reversible oxidation is observed at 0.44 V, which is assigned to the ruthenium(II)–ruthenium(III) oxidation [eq. (5)]. The potential of this couple is about

$$[\mathrm{Ru^{II}(bpy)(pic)_2}] \rightleftharpoons [\mathrm{Ru^{III}(bpy)(pic)_2}]^+ + e^- \qquad (5)$$

500 mV more positive in this complex than in [Ru(pic)$_3$], which indicates that the +2 state of ruthenium is more stable in this mixed-ligand complex. It is interesting to note 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;[12] [Ru(bpy)$_2$(pic)]$^+$, 0.75 V;[2e] [Ru(bpy)(pic)$_2$], 0.44 V; [Ru(pic)$_3$], −0.09 V. This reflects the ability of the picolinate ligand to stabilize ruthenium(III) better than bpy. The ruthenium(III)–ruthenium(IV) couple in [Ru(bpy)(pic)$_2$], which is expected to occur at a much higher potential than in [Ru(pic)$_3$], is not observed due to solvent cut-off. In acetonitrile solution, [Ru(bpy)(pic)$_2$] displays a reversible one-electron reduction at −1.64 V, which is assigned to reduction of the coordinated bpy[2a] [eq. (6)]. In

$$[\mathrm{Ru^{II}(bpy)(pic)_2}] + e^- \rightleftharpoons [\mathrm{Ru^{II}(bpy^{-})(pic)_2}]^- \qquad (6)$$

dichloromethane solution this reduction is not observed due to solvent cut-off.

CONCLUDING REMARKS

Two stable ruthenium–picolinate complexes, [Ru^{III}(pic)$_3$] and [Ru^{II}(bpy)(pic)$_2$], have been synthesized where the two different oxidation states of the metal have been stabilized by creating two different coordination environments around it. In acetonitrile solution, the ruthenium(II)–ruthenium(III) couple appears at −0.09 V in [Ru(pic)$_3$] and at 0.44 V in [Ru(bpy)(pic)$_2$], showing that the redox potential is adjustable in any desired direction by the proper choice of ligands. Reduction of [Ru(pic)$_3$] affords [Ru^{II}(pic)$_3$]$^-$, which is readily oxidized back to [Ru(pic)$_3$] by exposure to air. This points to the possibility of using [Ru(pic)$_3$] as a catalyst in redox reactions.

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