Bis(quinolin-8-olato) Complexes of Ruthenium. Synthesis, Characterization and Cyclic Voltammetric Studies†

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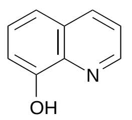
Nimai Chand Pramanik and Samaresh Bhattacharya*

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

Reaction of quinolin-8-ol (HQ) with [Ru(bpy)Cl$_3$] (bpy = 2,2′-bipyridine) in the presence of NEt$_3$ affords [Ru^{II}(bpy)(Q)$_2$] which shows a Ru^{II}–Ru^{III} oxidation at −0.16 V *vs.* SCE and a Ru^{III}–Ru^{IV} oxidation at 1.06 V *vs.* SCE; its oxidation by Ce^{4+} gives [Ru^{III}(bpy)(Q)$_2$]$^+$ which has been isolated and characterized as the perchlorate salt.

There is continuing interest in the chemistry of ruthenium,[1] primarily due to the fascinating electron-transfer properties exhibited by complexes of this metal. Variation of the coordination environment around ruthenium plays a key role in modulating the redox properties of its complexes. Complexation of ruthenium by ligands of different types is of particular interest in this respect and we have been active in this area.[2] In the present work we have used quinolin-8-ol (HQ, **1**; H stands for the dissociable phenolic hydrogen) as the principal ligand. The quinolin-8-olate anion (Q$^-$) binds metal ions as a didentate N,O-coordinator forming a five-membered chelate ring (**2**). It may be noted here that the chemistry of ruthenium quinolin-8-olates appears to have received relatively less attention.[3] Herein we report our studies on two bis(quinolin-8-olato) complexes of ruthenium. To satisfy the remaining two coordination sites of the Ru(Q)$_2$ moiety, 2,2′-bipyridine (bpy) has been used as the co-ligand. The synthesis, characterization and redox properties of the [Ru^{II}(bpy)(Q)$_2$] (**3**) and [Ru^{III}(bpy)(Q)$_2$]$^+$ (**4**) complexes are described.



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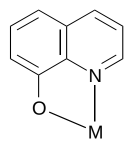

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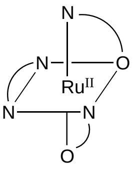

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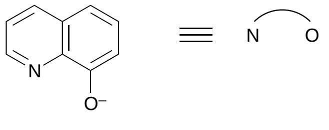

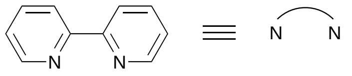

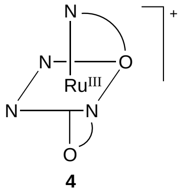

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[Ru(bpy)(Q)$_2$] was synthesized in good yield from the reaction of [Ru(bpy)Cl$_3$] with HQ in refluxing ethanol in the presence of NEt$_3$. The composition of the complex was confirmed by microanalysis. Magnetic susceptibility measurements showed that it is diamagnetic, as expected for complexes of ruthenium(II) (low-spin, d^6, $S = 0$). Out of three possible geometric isomers of [Ru(bpy)(Q)$_2$], we assign structure **3** to it in analogy with the stereochemistry of other [Ru^{II}(bpy)(N—O)$_2$] complexes.[2f,4] Comparison of the IR spectrum of [Ru(bpy)(Q)$_2$] with that of [Ru(bpy)Cl$_3$] shows that in the former complex the ν(Ru—Cl) stretch near 330 cm^{-1} is absent and many new vibrations are present in the fingerprint region due to coordinated Q$^-$ ligands. The electronic spectrum of [Ru(bpy)(Q)$_2$] in acetonitrile solution showed three intense absorptions in the visible region at 570 (ε = 8000), 450 (ε = 12 000) and 370 (ε = 9300 dm^3 mol^{-1} cm^{-1}) which are probably due to allowed metal-to-ligand change-transfer transitions. Similar spectral behaviour has been observed previously for other [Ru(bpy)(N—O)$_2$] complexes.[2f,4]

A cyclic voltammogram of [Ru(bpy)(Q)$_2$], recorded in acetonitrile (Fig. 1, Table 1), showed one reversible oxidation at −0.16 V which is assigned to the [Ru^{II}(bpy)(Q)$_2$]–[Ru^{III}(bpy)(Q)$_2$]$^+$ couple, followed by an irreversible oxidation at 1.06 V due to the [Ru^{III}(bpy)(Q)$_2$]$^+$–[Ru^{IV}(bpy)(Q)$_2$]$^{2+}$ couple. A reduction response, observed at −1.92 V, is assigned to the [Ru^{II}(bpy)(Q)$_2$]–[Ru^{II}(bpy$^{\bullet -}$)(Q)$_2$]$^-$ couple. It is interesting to note here that a gradual decrease in the potential of the ruthenium(II)–ruthenium(III) couple was observed in the series [Ru(bpy)$_3$]$^{2+}$, 1.30 V; [Ru(bpy)$_2$(Q)]$^+$, 0.48 V; [Ru(bpy)(q)$_2$], −0.16 V; [Ru(Q)$_3$],

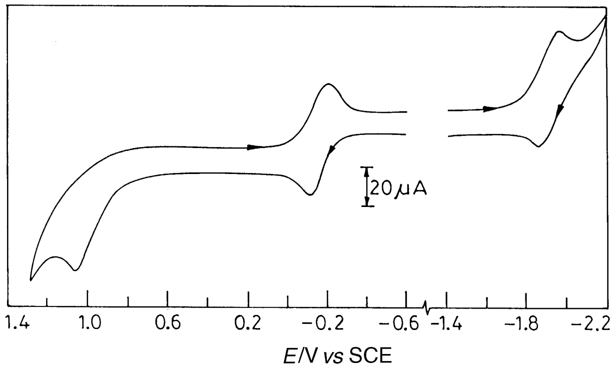

Fig. 1 Cyclic voltammogram (scan rate 50 mV s^{-1}) of [Ru(bpy)(Q)$_2$] in CH$_3$CN (0.1 mol dm^{-3} TEAP) at a platinum electrode (298 K)

Table 1 Cyclic voltammetric data: $E°_{298}$/V(ΔE_p/mV)^a

Compound	Ru^{II}–Ru^{III}	Ru^{III}–Ru^{IV}	bpy reductions
Ru(bpy)(Q)$_2$]	−0.16 (80)	1.06^e	−1.92 (780)
[Ru(bpy)$_2$(Q)]ClO$_4$	0.48 (80)		−1.55 (60) −1.77 (60)
[Ru(bpy)$_3$](ClO$_4$)$_2$^{c}	1.35 (62)		−1.33 (56) −1.52 (70) −1.76 (66)
[Ru(Q$_3$]^d	−0.70 (70)	0.66 (130)	

^{a}Conditions: solvent, acetonitrile; supporting electrolyte, tetramethylammonium perchlorate (TEAP; 0.1 mol dm^{-3}); working electrode, platinum; reference electrode, SCE; solute concentration, 10^{-3} mol dm^{-3}; $E°_{298}$ = 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}. ^{b}Ref. 3*b*. ^{c}Ref. 5. ^{d}Ref. 3*a*. ^{e}E_{pa}.

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*To receive any correspondence.

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-0.70 V (Table 1). This reflects the ability of phenolate oxygen coordination to stabilise ruthenium(III) better than the pyridine nitrogen.

The reversibility of the ruthenium(II)–ruthenium(III) couple in [Ru(bpy)(Q)$_2$] and its low potential indicates that the oxidised species may be stable on a much longer time scale. Chemical oxidation of [Ru(bpy)(Q)$_2$] by aqueous Ce^{4+} solution indeed afforded the stable [Ru(bpy)(Q)$_2$]$^+$, which was isolated and characterized as the perchlorate salt. The IR spectrum of [Ru(bpy)(Q)$_2$]ClO$_4$ is very similar to that of [Ru(bpy)(Q)$_2$], except that intense bands at 1100 and 621 cm^{-1} are displayed by the former, indicating the presence of ClO$_4^-$. [Ru(bpy)(Q)$_2$]ClO$_4$ is one-electron paramagnetic ($\mu_{eff} = 1.88\ \mu_B$) as expected for the $+3$ state of ruthenium (low spin d^5, $S = 1/2$). In 1:1 dichloromethane–toluene solution at 77 K it shows a rhombic EPR spectrum (Fig. 2), with three distinct resonances at $g_1 = 2.403$, $g_2 = 2.153$ and $g_3 = 1.879$. The cyclic voltammogram displayed by the oxidized complex is identical with that of its ruthenium(II) precursor, indicating no gross change in stereochemistry (**4**). In acetonitrile solution [Ru(bpy)(Q)$_2$]ClO$_4$ behaves as a 1:1 electrolyte ($\Lambda_M = 150$ S cm^2 dm^3 mol^{-1}) and shows intense change-transfer transitions at 750 ($\varepsilon = 2600$) 460 (shoulder, $\varepsilon = 8000$) and 410 nm ($\varepsilon = 9700$ dm^3 mol^{-1} cm^{-1}), together with a weak ligand-field transition[6] at 1500 nm ($\varepsilon = 170$ dm^3 mol^{-1} cm^{-1}). Reduction of [Ru^{III}(bpy)(Q)$_2$]$^+$ by hydrazine in acetonitrile solution gave back [Ru^{II}(bpy)(Q)$_2$] quantitatively, which was identified by its characteristic electronic spectrum.

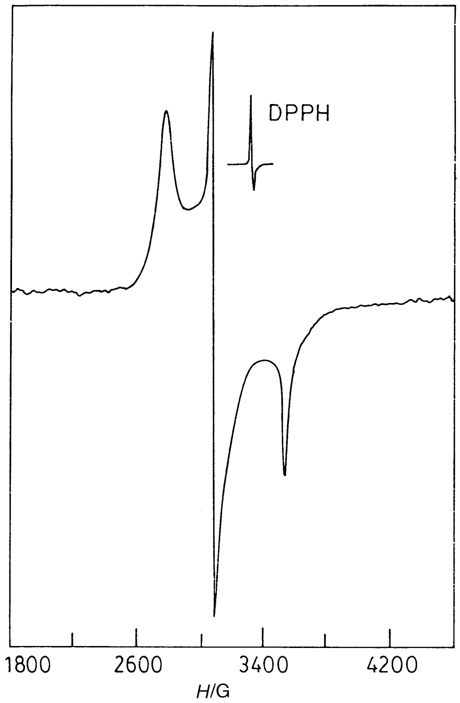

Fig. 2 X-Band EPR spectrum of [Ru(bpy)(Q)$_2$]ClO$_4$ in frozen (77 K) CH$_2$Cl$_2$–PhMe (1:1 v/v)

Experimental

Commercial ruthenium trichloride (Arora Matthey, Calcutta, India) was converted into RuCl$_3$·3H$_2$O by repeated evaporation to dryness with concentrated hydrochloric acid. 2,2′-Bipyridine and quinolin-8-ol were purchased from Loba, Bombay, India. [Ru(bpy)Cl$_3$] was prepared by a published procedure.[7] Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported.[8]

Microanalyses (CHN) 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 330 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. X-band EPR spectroscopy was performed on a Varian E 109C spectrometer fitted with a quartz Dewar for measurement at 77 K (liquid nitrogen) and spectra were calibrated with diphenylpicrylhydrazyl (DPPH) ($g = 2.0037$). Solution electrical conductivities were measured using a Philips PR9500 bridge with a solute concentration of about 10^{-3} mol dm^{-3}. Electrochemical measurements were made using the PAR model 273 electrochemistry system as before.[3b] All electrochemical experiments were performed under dinitrogen. Data were collected at 298 K and are uncorrected for junction potential.

Synthesis.—[Ru(bpy)(Q)$_2$]. [Ru(bpy)Cl$_3$] (200 mg, 0.55 mmol) and HQ (175 mg, 1.21 mmol) were taken together in ethanol (40 cm^3). To the solution was added NEt$_3$ (0.25 cm^3, 1.80 mmol) and the resulting solution was heated at reflux under a dinitrogen atmosphere. The initial light yellow solution turned deep brown within 10 min. Refluxing was continued for an additional 2 h, then the solvent was evaporated and the solid mass obtained was washed thoroughly with hexane. Recrystallization from dichloromethane-hexane (1:1 v/v) gave [Ru(bpy)(Q)$_2$] as a dark brown crystalline solid (235 mg, 78%) (Found: C, 61.5; H, 3.8; N, 10.3. C$_{28}$H$_{20}$N$_4$O$_2$Ru requires C, 61.6; H, 3.7; N, 10.27%).

[Ru(bpy)(Q)$_2$]ClO$_4$. To a stirred solution of [Ru(bpy)(Q)$_2$] (200 mg, 0.37 mmol) in acetonitrile (30 cm^3) was added an aqueous solution of cerium(IV) ammonium sulfate (240 mg, 0.38 mmol). The initial dark brown solution turned brownish-green within 15 min. Stirring was continued for an additional 30 min. The solution was then filtered to remove any insoluble material and to the filtrate was added saturated aqueous NaClO$_4$ (10 cm^3). After the solution had been allowed to stand for 2 h at room temperature, the [Ru(bpy)(Q)$_2$]ClO$_4$, which had separated out as a microcrystalline solid, was collected by filtration, washed with little cold water and dried *in vacuo* over P$_4$O$_{10}$ (yield 195 mg, 82%) (Found: C, 52.0; H, 3.3; N, 8.6. C$_{28}$H$_{20}$ClN$_4$O$_6$Ru requires C, 52.1; H, 3.1; N, 8.7%).

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