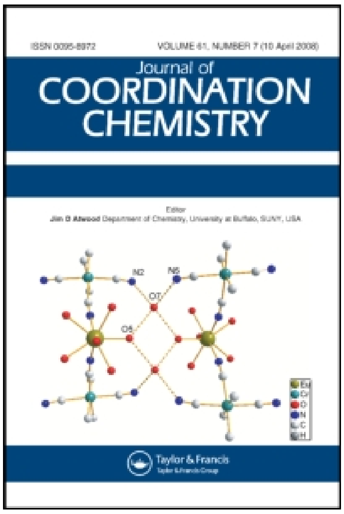

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The synthesis, spectroscopic properties and electrochemistry of (8-quinolinolato)-bis-{1-alkyl-2- (arylazoimidazole)}ruthenium(ii) hexafluorophosphate: single crystal X-ray structure of [ru(q)(meaaime)$_2$](PF$_6$)·CH$_2$Cl$_2$ [Q = 8-quinolinolate, meaaime = 1-methyl-2-(*p*-tolylazoimidazole)]

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To cite this Article Jasimuddin, S. K. , Byabartta, P. , Mostafa, G. , Liou, J. -C. , Lu, T. -H. and Sinha, C.(2004) 'The synthesis, spectroscopic properties and electrochemistry of (8-quinolinolato)-bis-{1-alkyl-2-(arylazoimidazole)}ruthenium(ii) hexafluorophosphate: single crystal X-ray structure of [ru(q)(meaaime)$_2$](PF$_6$)·CH$_2$Cl$_2$ [Q = 8-quinolinolate, meaaime = 1-methyl-2-(*p*-tolylazoimidazole)]', Journal of Coordination Chemistry, 57: 1, 75 — 85
To link to this Article: DOI: 10.1080/00958970410001662426
URL: http://dx.doi.org/10.1080/00958970410001662426

J. Coord. Chem., Vol. 57, No. 1, 10 January 2004, pp. 75–85

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THE SYNTHESIS, SPECTROSCOPIC PROPERTIES AND ELECTROCHEMISTRY OF (8-QUINOLINOLATO)-BIS-{1-ALKYL-2-(ARYLAZOIMIDAZOLE)}RUTHENIUM(II) HEXAFLUOROPHOSPHATE: SINGLE CRYSTAL X-RAY STRUCTURE OF $[Ru(Q)(MeaaiMe)_2](PF_6)\cdot CH_2Cl_2$ [Q = 8-QUINOLINOLATE, MeaaiMe = 1-METHYL-2-(*p*-TOLYLAZOIMIDAZOLE)]

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(Received in final form 2 October 2003)

The reaction of $[Ru(OH_2)_2(RaaiR')_2]^{2+}$ [RaaiR′ = 1-alkyl-2-(arylazo)imidazole, *p*-R–C_6H_4–N=N–C_3H_2–NN(1)–R′, R=H (**1**), Me (**2**), Cl (**3**); R′ = Me (**a**), Et (**b**), CH_2Ph (**c**)] with 8-quinolinol (HQ) in acetone solution followed by the addition of NH_4PF_6 afforded violet, mixed ligand complexes of composition $[Ru(Q)(RaaiR')_2](PF_6)$. The structure of $[Ru(Q)(MeaaiMe)_2](PF_6)$ (**2a**) has been confirmed by X-ray diffraction studies. Solution electronic spectra exhibit a strong MLCT band at 560–580 nm in MeCN. Cyclic voltammogrames show a Ru(III)/Ru(II) couple at 1.0–1.1 V *versus* SCE along with three successive ligand reductions. The electronic properties are correlated with EHMO results.

Keywords: Ruthenium(II); 1-Alkyl-2-(arylazo)imidazole; 8-Quinolinol; X-ray structure; Electrochemistry

INTRODUCTION

Ruthenium polypyridine complexes are among the most studied of molecules owing to their rich and well-characterized photophysics and redox chemistry. Change in coordination environment around ruthenium plays a key role in altering the redox properties of its complexes and thus complexation of ruthenium by different ligands is of particular interest [1–7].

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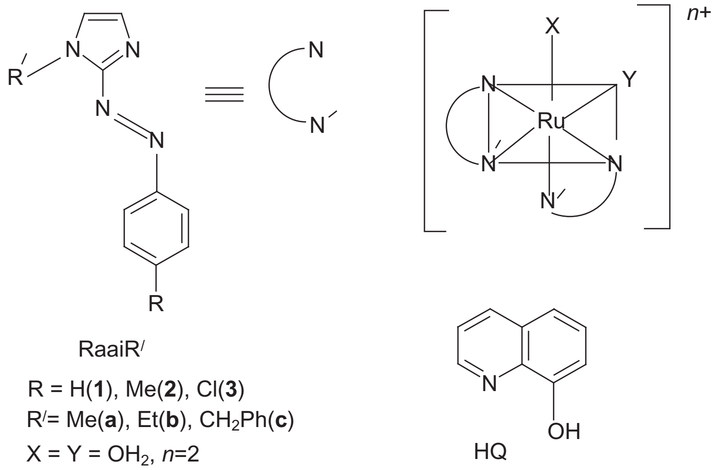
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001662426

Recently, we developed the arylazoimidazole chemistry of ruthenium(II) [8–11] and synthesized dichloro-bis-(arylazoimidazole)ruthenium(II) compounds and their diaquo species,



$[Ru(OH_2)_2(RaaiR')_2]^{2+}$ [RaaiR' = *p*-R–C_6H_4–N=N–C_3H_2–NN(1)–R'][**1**–**3**] R = H, Me, Cl; R' = Me, Et, CH_2Ph. The ligand is an *N*,*N'*-chelator where N(imidazole) and N(azo) represent *N* and *N'* respectively. *Pseudo*-octahedral $RuCl_2(N,N')_2$ species may exist in five geometrical isomers. Of these, three have *cis*-$RuCl_2$ and two *trans*-$RuCl_2$ configurations. According to the sequence of coordination of pairs of Cl, *N* and *N'* one of the isomers belongs to *cis–trans–cis* (*ctc*) geometry. The abbreviation suggests *cis*-$RuCl_2$, *trans*-$Ru(N)_2$ and *cis*-$Ru(N')_2$-configuration. The Ru–Cl bonds are labile in *ctc*-$RuCl_2(N,N')_2$ and this has been used to synthesize tris chelates by Ag^+-assisted Cl substitution followed by solvent species formation [9–11]. 8-Hydroxyquinoline (HQ) complexes of transition and nontransition metals are the topic of current interest [12,13] with respect to OLED materials. This molecule has been used for analytical determination of Al^{3+}, Ga^{3+}, Pd^{2+}, etc. [14]. Because of its optoelectronic efficiency, research in the field of synthesis of different complexes of HQ is of renewed interest [15–18]. It may be noted that the chemistry of ruthenium–Q appears to have received little attention [5]. In this article, we report some mixed ligand of ruthenium–arylazo-imidazole–quinolinato complexes, $[Ru(RaaiR')_2(Q)]^+$. The structure of one complex was established by an X-ray diffraction study.

EXPERIMENTAL

Materials

$RuCl_3 \cdot nH_2O$ was obtained from Arrora Matthey, Calcutta and was digested three times with concentrated HCl before use. 1-Alkyl-2-(arylazo)imidazole were synthesized by the reported procedure [7]. 8-Hydroxyquinoline, Et_3N and NH_4PF_6 was purchased from SRL, Merck and Fluka respectively. Commercially available silica gel (60–120 mesh) from SRL was used for chromatographic separations. The purification of solvents for electrochemical and spectroscopic measurements and preparation of [*n*-Bu_4N][ClO_4] (TBAP) were as described earlier [10]. All other solvents and chemicals were of reagent grade and were used without further purification.

Physical Measurements

Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a Jasco V-570 spectrophotometer. IR spectra were obtained using a Jasco 420 spectrophotometer (using KBr disks, 4000–200 cm^{-1}). ^1H NMR spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}$ M in acetonitrile. Electrochemical work was carried out using a PAR model 250 Versastat potentiostat/galvanostat with EG and G 270 electrochemistry software. All experiments were performed under an N_2 atmosphere at 298 K using a Pt-disk working electrode and Pt-wire auxiliary electrode. All results are referenced to SCE. Reported potentials are uncorrected for junction potentials. $K_4[Fe(CN)_6]$ was used as standard showing the Fe(III)/Fe(II) couple at 0.19 V *versus* SCE in MeCN–0.1(M) TBAP and 50 mV s^{-1} scan rate.

Preparation of (8-Quinolinolato)-bis-{1-alkyl-2-(arylazo)imidazole}ruthenium(II) Hexafluorophosphate, [Ru(Q)(MeaaiMe)$_2$](PF_6) (2a)

Aqueous $AgNO_3$ (0.06 g, 0.36 mmol) was added to a suspension of *ctc*-$RuCl_2$-$(MeaaiMe)_2$ (0.1 g, 0.18 mmol) in acetone (25 cm^3) and the mixture was refluxed for half an hour. After cooling, precipitated AgCl was filtered off. 8-Hydroxyquinoline (HQ) (0.02 g, 0.14 mmol) was dissolved in acetone (10 cm^3) and deprotonated with Et_3N (0.02 cm^3, 0.14 mmol). The resulting solution was mixed with the solvated compound $[Ru(acetone)_2(MeaaiMe)_2]^{2+}$ and stirred at 40°C in the dark for 8 h under nitrogen. After evaporating the solvent the resulting mass was dissolved in the minimum volume of methanol and precipitated with an aqueous solution of NH_4PF_6 (*ca.* 0.1 g in 20 cm^3 water). The violet precipitate was then filtered off, washed with a minimum volume of cold water and dried in vacuum over P_4O_{10}. The dry mass was then dissolved in the minimum volume of CH_2Cl_2 and chromatographed on a silica-gel column (60–120 mesh). A violet band was eluted with C_7H_8/CH_3CN (1 : 1, v/v). This was collected and slowly evaporated. Crystals were collected in 45% yield (0.06 g). Other complexes were prepared by the above procedure and yields varied from 40 to 50%.

X-ray Structure Determination

Crystals of $[Ru(Q)(MeaaiMe)_2](PF_6)$ suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution of the complex. X-ray diffraction data were collected at 294(2) K with a Siemens SMART CCD using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data are summarized in Table I. Unit cell parameters were determined by least-squares refinement of all reflections. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using the SAINT program.

TABLE I Crystallographic data for $[Ru(Q)(MeaaiMe)_2](PF_6) \cdot CH_2Cl_2$ (**2a**)

Formula	$C_{31.5}H_{32}Cl_2PF_6ON_9Ru$
Formula weight	869.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.7962(9)
b (Å)	13.1025(10)
c (Å)	13.3070(10)
α (°)	69.1550(10)
β (°)	84.4570(10)
γ (°)	85.9510(10)
V (Å)^3	1911.7(3)
λ (Å)	0.71073
Z	2
T (K)	294(2)
ρ_{cald} (gm cm^{-3})	1.511
Reflection collected	9117
Unique reflection	3942
2θ range (°	$3.28 < 2\theta < 56.84$
μ (Mo Kα) (mm^{-1})	0.66
hkl range	$-15 \leq h \leq 15,\ -17 \leq k \leq 17,\ -17 \leq l \leq 17$
R^a (%)	0.0653
wR^b (%)	0.1690
GOF^c	0.961

[a] $I > 2\sigma(\mathrm{I})$. [b] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^3)/3$. [c] Goodness-of-fit is defined as $[w(F_o - F_c)/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and variables, respectively.

The structure was solved by direct methods using SHELXS-97 followed by successive Fourier and difference Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all nonhydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the parent atom. The final difference Fourier map showed maximum and minimum peak heights of 0.749 and $-0.746\,\text{eÅ}^{-3}$, respectively; these have no chemical significance. Complex neutral atom scattering factors were used throughout. All calculations were carried out using SHELXS 97, SHELXL 97, PLATON 99 and ORTEP-3.

RESULTS AND DISCUSSION

Synthesis and Formulation

The Ag^+-assisted substitution of chloride ligands in *ctc*-$RuCl_2(RaaiR')_2$ has been used in acetone solution to prepare $[Ru(acetone)_2(RaaiR')_2]^{2+}$. The reaction of HQ (in the presence of Et_3N) with $[Ru(acetone)_2(RaaiR')_2]^{2+}$ at 40°C in the dark, after addition of saturated NH_4PF_6 solution, gave $[Ru(Q)(RaaiR')_2](PF_6)$ in 40–50% yield (Eq. (1)). Under refluxing conditions a mixture of isomers was generated. We were unable to separate the complexes from the mixture and this synthetic route has been avoided. For this reason the reaction temperature was strictly maintained at 40°C in the dark; the product was purified by chromatography. The composition of the complexes was confirmed by microanalytical data. Complexes are diamagnetic and 1 : 1 electrolytes in MeCN ($\Lambda_M = 70\text{–}90\,\Omega^{-1}\,\text{mol}^{-1}\,\text{cm}^{-2}$). The spectroscopic and electrochemical studies have determined the structural and electronic properties of the complexes. A structural confirmation has been provided in one case by a single-crystal X-ray diffraction study.

$$
\begin{aligned}
ctc\text{-RuCl}_2(\text{RaaiR}')_2 &\xrightarrow{\text{Ag}^+,\ \text{acetone}} ctc\text{-[Ru(acetone)}_2(\text{RaaiR}')_2]^{2+} \\
&\xrightarrow[\text{2. NH}_4\text{PF}_6]{\text{1. HQ, Et}_3\text{N}} ctc\text{-[Ru(Q)(RaaiR}')_2(\text{PF}_6)] \qquad (1)
\end{aligned}
$$

Single-crystal X-Ray Structure of [Ru(Q)(MeaaiMe)$_2$](PF$_6$)·CH$_2$Cl$_2$

The single-crystal X-ray structure of the molecule is shown in Fig. 1 and bond parameters are given in Table II. Ruthenium is chelated by two azoimidazole (*N*, *N*′) and one 8-quinolinato (*N*,*O*) unit, thus maintaining the RuN$_5$O octahedral arrangement. The disposition of the N(azo) [N(2) and N(6)] and N(imidazole) [N(1) and N(5)] atoms indicates the *tc*-configuration. Earlier, we designated different isomers in terms of the coordination of pairs of donors in the sequence N(imidazole),

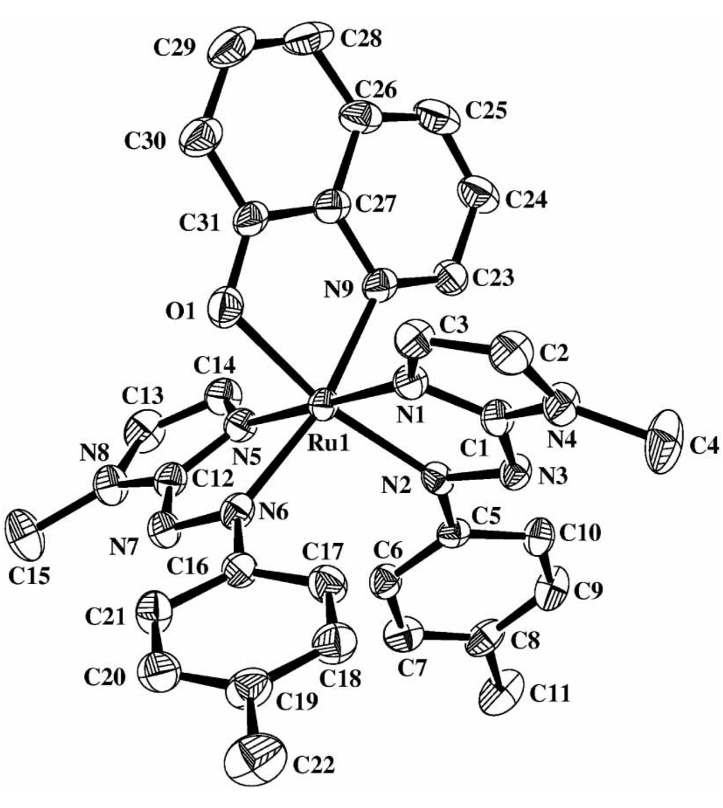
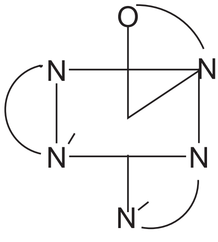


FIGURE 1 ORTEP plot and atom labeling scheme for [Ru(Q)(MeaaiMe)$_2$]$^+$ (**2a**).

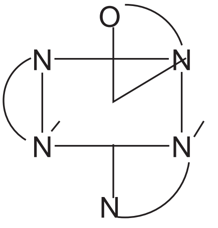
TABLE II Selected bond distances (Å) and angles (°) with standard deviations for $[Ru(Q)(MeaaiMe)_2](PF_6) \cdot CH_2Cl_2$ (**2a**)

Distances		*Angles*	
Ru(1)–N(2)	2.000(5)	N(2)–Ru(1)–N(5)	103.74(19)
Ru(1)–N(5)	2.025(5)	N(2)–Ru(1)–N(1)	77.3(2)
Ru(1)–N(1)	2.030(5)	N(5)–Ru(1)–N(1)	178.8(2)
Ru(1)–N(6)	2.033(5)	N(2)–Ru(1)–N(6)	99.50(19)
Ru(1)–O(1)	2.046(4)	N(5)–Ru(1)–N(6)	77.5(2)
Ru(1)–N(9)	2.068(6)	N(1)–Ru(1)–N(6)	101.7(2)
N(2)–N(3)	1.318(6)	N(2)–Ru(1)–N(9)	92.1(2)
N(6)–N(7)	1.298(7)	N(5)–Ru(1)–N(9)	93.5(2)
N(1)–C(1)	1.318(7)	N(1)–Ru(1)–N(9)	87.11(19)
N(1)–C(3)	1.369(8)	N(6)–Ru(1)–N(9)	166.70(19)
N(3)–C(1)	1.359(7)	O(1)–Ru(1)–N(9)	80.6(2)
N(4)–C(1)	1.361(7)	N(3)–N(2)–Ru(1)	119.2(4)
N(5)–C(12)	1.343(8)	N(7)–N(6)–Ru(1)	118.1(4)
N(5)–C(14)	1.353(8)		
N(7)–C(12)	1.354(8)		
N(6)–C(16)	1.445(8)		
N(8)–C(12)	1.358(8)		
O(1)–C(31)	1.329(8)		

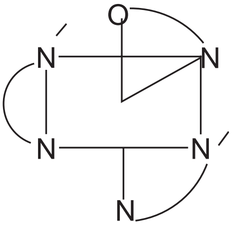
N(imidazole), (*N*,*N*), N(azo), N(azo) (*N′*,*N′*) as *tc*-, *cc*- and *ct*-. The present isomer belongs to the *tc*-configuration.



tc-



cc-



ct-

The Ru(*N*,*N′*)$_2$-motif is comparable with the structure of *ctc*-$RuCl_2(MeaaiMe)_2$ [8]. Bond distances (Table II) show a distorted octahedral geometry which is mainly due to the unsymmetrical anionic *N*,*O*-donor. The atoms Ru(1), N(1), N(9), N(5), N(6) (plane 1) and Ru(1), N(1), N(2), O(1), N(5) (plane 2) constitute good planes that deviate from ideality by <0.07 and 0.06 Å, respectively. The atoms Ru(1), N(9), O(1), N(2), N(6) (plane 3) exhibit considerable distortion and deviations are N(9), −0.16; O(1), 0.17; N(2), 0.15 and N(6), −0.14 Å. Planes 1 and 2 are mutually orthogonal (dihedral angle 88°) while plane 3, makes an angle of 81.6° with planes 1 and 2. The three separate chelate rings Ru(1), O(1), C(31), C(27), N(9); Ru(1), N(1), C(1), N(3), N(2); Ru(1), N(5), C(12), N(7), N(6) are planar (mean deviation <0.05 Å). Planes are mutually orthogonal (dihedral angle av. 85.9°). The chelate angles N(1)–Ru(1)–N(2); N(5)–Ru(1)–N(6) and N(9)–Ru(1)–O(1) are 77.3(2), 77.3(2) and 80.6(2)°, respectively. The *trans* angles N(1)–Ru(1)–N(5); N(2)–Ru(1)–O(1); N(6)–Ru(1)–N(9) are 178.8(2), 167.0(2) and 166.7(2)°, respectively. Deviation from 180° originates from the bite angles subtended by the azoimine ligand. The pendent *p*-tolyl ring is almost co-planar with the chelated azoimine ligand (dihedral 4°).

The Ru–N(azo) [Ru(1)–N(2) and Ru(1)–N(6)] distances are unequal. Ru(1)–N(2) is significantly shorter (~0.03 Å) than Ru(1)–N(6). The elongation of Ru–N(6) may be due to the *trans* influence provided by Ru–N(Q) (Q = 8-quinolinolate). This suggests that ruthenium has a higher affinity for pyridine–N in Q. Of two different heterocyclic-N donor centers in the complex, pyridine-N donor (from Q) and imidazole-N (from MeaaiMe), Ru–N(imidazole) [Ru(1)–N(1), 2.030(5) and Ru(1)–N(5), 2.025(5) Å] is shorter than Ru–N(pyridine) [Ru(1)–N(9), 2.068(6) Å]. Ru–O(Q) is in the range of literature values [15–18]. Usually, in series of Ru-azoimine complexes, Ru–N(azo) distances are shorter than Ru–N(heterocycle) [8–11], although exceptions are found because of strain in the structures. In this case Ru(1)–N(2) [N(2) is N(azo)] is shorter than Ru(1)–N(1) [N(1) is N(imidazole)] by ~0.03 Å while Ru(1)–N(5) [N(5) is N(azo)] and Ru(1)–N(6) [N(6) is N(imidazole)] are nearly equal, 2.025(5) and 2.033(5) Å, respectively. This may be due to the *trans* influence of Ru(1)–N(9) (8-quinolinol). On the other hand, the azo bond length (–N=N–) is longer by 0.05–0.07 Å than that (1.25 Å) in uncoordinated azo compounds [19]. Clearly strong d(Ru) → π*(azo) charge transfer is the reason for this elongation of the N=N bond in the complexes [20,21]. The excellent π-acceptor character of azoheterocycles originates from low-lying π* (azo) orbitals [8].

Intermolecular hydrogen bonding between two molecular units form a twelve member dimer (Fig. 2). Hydrogen-bonded metallo-*pseudo*-macrocycle arrangements are rarely observed in ruthenium–azoimine complexes. One of the *ortho* H atoms of

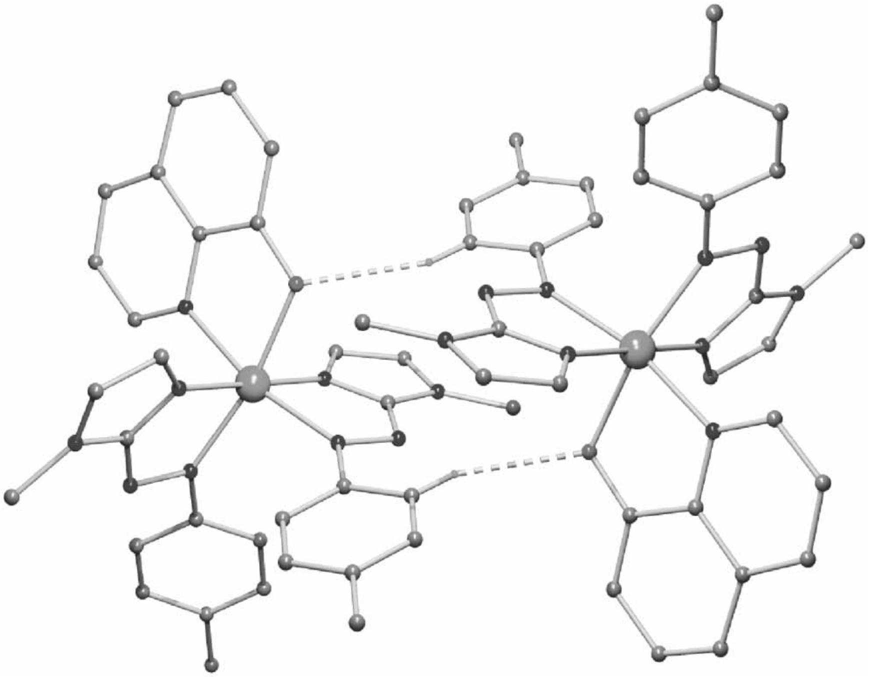


FIGURE 2 Hydrogen-bonded cyclic dimer showing the metallomacrocycle.

a pendent *p*-tolyl ring interacts with the coordinated 8-quinolato–O of a neighboring molecule. The (*p*-tolyl) *ortho* C–H(a)$\cdots$O(8-quinololato)(b) distance is 2.48(1) Å and ∠C–H$\cdots$O is 153.3(7)° [(a) and (b) refer to the respective units of two neighboring molecules]. Because of the electron-withdrawing ability of the –N=N– function, the *ortho*-C–H bond shows higher acidity and participates in a weak interaction. Charge-density calculations (using AM1, PM3) support this conjecture [22]. Less efficient H-bonding is observed between PF_6^- and imidazole-H and is not discussed further.

Spectroscopic Characterization

Infrared assignment has been made by comparing the spectra of free ligands and *ctc*-$RuCl_2(RaaiR')_2$ [8]. The absence of ν(Ru–Cl) at 340–310 cm^{-1} (corresponding to the *cis*-$RuCl_2$ motif) supports the substitution of Ru–Cl bonds. A new bond appears at 480–500 cm^{-1} and is assigned to ν(Ru–O). Both ν(N=N) and ν(C=N) appear at 1370–1380 and 1560–1580 cm^{-1} [16], respectively; $\nu(PF_6)$ appears at 840 cm^{-1}.

Solution spectra of the complexes can also be compared with those of free ligands and *ctc*-$RuCl_2(RaaiR')_2$ in MeCN solutions. Multiple transitions < 400 nm are assigned to intraligand ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) transitions. The complexes display a moderately intense ($\varepsilon \sim 10^4\ M^{-1}cm^{-1}$) band at 560–580 nm. The transitions are of typical metal-to-ligand charge-transfer type (Table III). A weak band ($\varepsilon \sim 10^3$) is observed at 685–705 nm and may be ascribed to the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition.

Electrochemistry and Correlation with Solution Spectra

In the potential range +2.0 to −2.0 V at scan rate 50 $mV\,s^{-1}$ *versus* SCE four redox couples are observed. A *quasi*-reversible couple at 1.0–1.1 V (*versus* SCE) may be assigned to the Ru(III)/Ru(II) couple since the ligands are insensitive in this potential range. *Quasi*-reversibility is assigned from peak-to-peak difference ($\Delta E_p \geq 100$ mV). Cyclic voltammetric data are summarized in Table III. Potential data negative to SCE are due to ligand reductions. Both RaaiR′ and Q are reducible ligands. The azo group (–N=N–) may be reduced easily due to the presence of low lying, vacant molecular orbitals dominated by azo group, as compared to the imine group (–C=N–) in 8-quinolionate. Thus, the first two reductions may be assigned to azo reduction. They are sensitive to the substituent (R) in the aryl ring and are linearly correlated with Hammett σ values. The third response refers to reduction of coordinated Q.

Variation of the coordination environment around ruthenium plays a key role in moderating the redox properties of its complexes. In particular, the introduction of oxygen to the coordination sphere of the metal has been shown to facilitate Ru(II)/Ru(III) oxidation. $[Ru(L)_2(Q)]^{2+}$ (L = *N*,*N*-donor ligands such as 2,2′-bipyridyl (bpy) and 1,10-phenanthroline (phen) [23], 2-(*p*-tolylazo)pyridine (tap) [15,16]) systems are easier to oxidize than $[Ru(L_2)(L')]^{3+}$, where L′ = bpy [10], phen [11]. This is also supported by a red shift of the MLCT transition $[d(Ru^{II}) \rightarrow \pi^*(L)]$ in the complexes $[Ru(L)_2(Q)]^+$ relative to $[Ru(L)_2](L')]^{3+}$ systems. Because of lower ligand field strength provided by an anionic oxygen donor center compared to the $N(sp^2)$ center the LFSE is expected to be smaller in RuL_2Q^+ than in $[Ru(L)_2(L')]^{3+}$ complexes. A comparison of the spectroscopic and redox data establishes this proposition in the series of

TABLE III Elemental analyses, electronic spectroscopic[a] and cyclic voltammetric[b] data for $[Ru(RaaiR')(Q)_2](PF_6)$

Compounds	*Elemental analyses % Found (% Calcd)*			*Electronic spectra*	*Cyclic voltammetry*			
	C	*H*	*N*	λ_{max}, nm (10^{-1} ε $M^{-1}cm^{-1}$)	$E^1_{1/2}$, V (ΔE, mV)	$E^2_{1/2}$, V (ΔE, mV)	$E^3_{1/2}$, V (ΔE, mV)	$E^4_{1/2}$, V (ΔE, mV)
Ru (Q)$(HaaiMe)_2$ (PF_6) (**1a**)	45.58	3.39	16.51	685 (1.81), 565 (6.45), 376 (16.32), 240 (15.43)	1.042	−0.393	−1.016	−1.473
	(45.67)	(3.41)	(16.54)		(120)	(139)	(109)	(80)
Ru (Q)$(MeaaiMe)_2$ (PF_6) (**2a**)	47.03	3.74	15.90	690 (1.56), 567 (5.49), 380 (16.92), 236 (12.46)	1.116	−0.515	−1.092	−1.418
	(47.09)	(3.80)	(15.95)		(112)	(195)	(143)	(76)
Ru (Q)$(ClaaiMe)_2$ (PF_6) (**3a**)	41.78	2.84	15.09	688 (1.69), 572 (6.61), 378 (17.54), 244 (19.35)	1.048	−0.409	−0.887	−1.532
	(41.83)	(2.88)	(15.14)		(135)	(126)	(124)	(78)
Ru (Q)$(HaaiEt)_2$ (PF_6) (**1b**)	47.02	3.77	15.89	689 (2.87), 566 (11.11), 376 (31.04), 237 (22.66)	0.995	−0.469	−1.139	−1.411
	(47.09)	(3.80)	(15.95)		(103)	(127)	(110)	(119)
Ru (Q)$(MeaaiEt)_2$ (PF_6) (**2b**)	48.37	4.11	15.36	688(1.85), 568 (6.91), 378 (16.62), 240 (15.49)	1.028	−0.542	−1.185	−1.481
	(48.41)	(4.16)	(15.40)		(124)	(120)	(122)	(98)
Ru (Q)$(ClaaiEt)_2$ (PF_6) (**3b**)	43.21	3.22	14.58	704 (1.67), 573 (6.82), 380 (19.37), 242 (19.49)	1.077	−0.408	−1.049	−1.443
	(43.26)	(3.26)	(14.65)		(149)	(119)	(120)	(73)
Ru (Q)$(HaaiCH_2Ph)_2$ (PF_6) (**1c**)	53.76	3.69	13.74	693 (2.62), 566 (10.22), 377 (24.13), 232 (19.35)	1.101	−0.441	−1.11	−1.416
	(53.83)	(3.72)	(13.79)		(143)	(131)	(122)	(70)
Ru (Q)$(MeaaiCH_2Ph)_2$ (PF_6) (**2c**)	54.73	4.01	13.32	692 (1.92), 569 (7.52), 386 (19.53), 243 (19.65)	1.107	−0.459	−1.141	−1.451
	(54.78)	(4.03)	(13.38)		(135)	(128)	(119)	(82)
Ru (Q)$(ClaaiCH_2Ph)_2$ (PF_6) (**3c**)	49.75	3.21	12.72	706 (1.71), 571 (6.950, 388 (19.61), 244 (19.84)	1.051	−0.442	1.021	−1.402
	(49.80)	(3.24)	(12.75)		(115)	(121)	(132)	(87)

Oxin = QH, [a]Electronic spectra are recorded in MeCN; [b]Solvent: MeCN; supporting electrolyte, $[n\text{-}Bu_4N][ClO_4]$ (0.1 M); working electrode, Pt-disc micro-electrode; auxiliary, Pt-wire; reference electrode, SCE; potential $E_{1/2} = 0.5(E_{pa} + E_{pc})$ in V; peak-to-peak separation ΔE $(= |E_{pa} - E_{pc}|)$ in mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential.

ruthenium(II)-{1-methyl-(*p*-tolylazo)imidazoles [Ru(MeaaiMe)$_2$(X,X)]$^{n+}$ (X,X = Cl,Cl [8], N,N (bpy) [10], N,N (phen) [11]; N,N′ (MeaaiMe) [24]. In *pseudo*-octahedral geometry, the lower LFSE in RuL$_2$Q$^+$ results in higher energy, filled metal-centered t_{2g}-type orbitals and lower energy empty e_g-type orbitals. Therefore the transition for the MLCT band is expected to be at lower energy in RuL$_2$Q$^+$ than in the homoleptic RuL$_3^{2+}$, as is indeed observed.

EHMO Calculation and Correlation with Electronic Properties

Crystallographic parameters of **2a** have been used to carry out molecular orbital calculation in the framework of Hückel formalism. Although this process of calculation has a large number of approximations and excludes core–core repulsions, results may be used to correlate with spectroscopic and electrochemical properties. Results of calculation and experiment for [Ru(RaaiR′)$_2$(L′)]$^{2+}$ (L′ = bpy and ophen) may be compared to establish the electronic assignments of the present compounds.

In [Ru(MeaaiMe)$_2$(Q)](PF$_6$) the HOMO ($E_{\mathrm{HOMO}} = -11.220$ eV) is composed of 71% $d\pi$(Ru), 19% π(MeaaiMe) and 3% π(Q). The LUMO ($E_{\mathrm{LUMO}} = -10.573$ eV) consists of 67% π^* (MeaaiMe), 23% $d\pi$(Ru) and 3% π^*(Q). The results reveal that the HOMO is directed by metal functions. Although, MeaaiMe and Q serve as ligands, the LUMO is mainly composed of MeaaiMe functions. Thus the major transition in the visible region is assigned to $d\pi(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{MeaaiMe})$. In the cyclic voltammetry the couple positive to SCE has rightly been described as Ru(III)/Ru(II) and couples on the negative side to ligand reductions. Data in Table IV reveal that the nature of L has little influence on the LUMO of the complexes. It is observed that LUMOs are dominated by RaaiR′. The influence of L on HOMOs significantly affects both spectroscopic transitions and metal redox. However, the first two reductions observed are due to azo/azo$^-$ couples of two metal-bound azoimidazole ligands, and remain almost unperturbed by L′. The calculated energy differences between LUMO and HOMO ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) are comparable with the observed λ (MLCT; Table IV). Mono anionic oxine ligands (N, O$^-$) neutralize the overall charge of the complex which causes an increase in energy of MOs in [Ru(MeaaiMe)$_2$(Q)]$^+$ compared to [Ru(MeaaiMe)$_2$(bpy)]$^{2+}$ or [Ru(MeaaiMe)$_2$(ophen)]$^{2+}$. This reflects in ΔE values in Table IV and hence the transition wavelength. Observed differences in electronic properties of [Ru(MeaaiMe)$_2$)(bpy)]$^{2+}$ and [Ru(MeaaiMe)$_2$(ophen)]$^{2+}$ are not only associated with bpy/phen but are also due partly to substitutional effects in the azoimidazole ligands.

TABLE IV Comparison between spectroscopic[a], electrochemical[b] and theoretical data for [Ru(MeaaiMe)$_2$(bpy)](ClO$_4$)$_2$, [Ru(HaaiMe)$_2$(ophen)](ClO$_4$)$_2$ and Ru[(MeaaiMe)$_2$(Q)](PF$_6$)

Compound	ΔE^c, eV	λ, nm (10^{-3} ε, M^{-1} cm^{-1})	*E*, V	$-E^1$, V	$-E^2$, V
[Ru(MeaaiMe)$_2$(bpy)](ClO$_4$)$_2$	0.670	517 (10.80)	1.66	0.39	0.68
[Ru(HaaiMe)$_2$(ophen)](ClO$_4$)$_2$	0.674	521 (11.95)	1.35	0.36	0.70
[Ru(MeaaiMe)$_2$(Q)](PF$_6$)	0.647	567 (5.59)	1.09	0.40	0.68

[a]Solvent, MeCN. [b]Solvent, MeCN; working electrode is glassy carbon for [Ru(MeaaiMe)$_2$(bpy)](ClO$_4$)$_2$ and Pt-disc for the other two compounds, maintaining other conditions the same; E^1 and E^2 refer to azo/azo$^-$ potential of metal-bound bis-(azoimine) function. [c]$\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$.

Acknowledgments

Financial assistance from the Council of Scientific and Industrial Research (CSIR), and DSA phase-II, UGC, New Delhi, is gratefully acknowledged. One of us (SJ) is thankful to CSIR for a fellowship. THL and GM thank the National Science Council, ROC, for support.

Supplementary Data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ. UK [Fax: (internet) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk] on request. The deposition number is 221832. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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