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The synthesis, spectral and electrochemistry of (8-Quinolinolato)-Bis-{1-Alkyl-2-(Arylazo) imidazole} ruthenium (ii) Hexafluorophosphate

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Abstract

The reaction of $[Ru(OH_2)_2(RaaiR^{/})_2]^{2+}$ [$RaaiR^{/}$=1-alkyl-2-(arylazo)imidazole, *p*-R-C_6H_4-N=N-$C_3H_2NN(1)$-$R^{/}$, R=OMe (2), $R^{/}$=Me (a), Et (b), with 8-quinolinol (HQ) in acetone solution followed by the addition of NH_4PF_6 has afforded violet coloured mixed ligand complexes of the composition $[Ru(Q)(RaaiR^{/})_2](PF_6)$. The structure of $[Ru(Q)(OMeaaiMe)_2](PF_6)$ (2a) has been confirmed by x-ray diffraction studies. The solution electronic spectra exhibit a strong MLCT band at 560-580 nm in MeCN. Cyclic voltammograme 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 molecules due to their rich and well characterized photophysics and redox chemistry. Change in coordination environment around ruthenium plays a key role to monitor the redox properties of its complexes. So complexation of ruthenium by different type of ligands is of particular interest [1-7].

This attraction is due to its ability to form sulphur–bridged heteronuclear complexes of the type $[(LL)_2M(\mu\text{-}S)_2MoS_2]$, $[S_2Mo(\mu\text{-}S)_2 \ \text{–}M\text{--}MoS_2]$, $[(LL)M(\mu\text{-}S)_2Mo(\mu\text{-}S)_2M(LL)]$ (M = Fe, Ru or Os) [1-7, 20, 23] and, moreover, their relevance to the functional and structural models for the active sites of the nitrogenase enzyme [4-6, 22]. There has been continuous research activity in the area of transition metal complexes of the tetrathiomolybdate anion now-a-days. The present work originates from my interest in studing the interaction of ruthenium arylazopyrimidine complexes *ctc*-$[Ru(R\text{-}aapm)_2Cl_2]$ [8-14] (1) [R-aapm = 2-(arylazo)pyrimidine, *p*-R-C_6H_4-N=N-C_4H_3NN] with $(NH_4)_2MoS_4$ in 1:1 aqueous MeOH medium which has afforded red-violet mixed ligand complexes of the type $[(R\text{-}aapm)_2Ru(\mu\text{-}S)_2Mo(OH)_2]$ (2a-2e) where the terminal Mo=S bonds become hydroxylated with the concomitant two electron metal reduction [21, 23, 25, 26], Mo^{VI}-Mo^{IV}. The MoS_4^{2-} unit is known to be sufficiently stable, individually as well as on coordination, and consequently the identity of the MoS_4^{2-} unit has been retained in the earlier reported heteronuclear complexes [24, 26]. However involvement of the ruthenium azoimidazole moiety facilitates hydroxylation of the terminal Mo=S bonds in complexes. To the best of my knowledge this work demonstrates the first example of internal transformation of the MoS_4^{2-} unit on coordination [24-26]. Because of biological involvement of pyrimidine I am interested in synthesizing arylazopyrimidine [12-18]. Ruthenium chemistry of (arylazo) pyrimidine (R-aapm, *Scheme 1*) is known in some detail [9-15]. In recent years, ruthenium (II), osmium (II) and Rh (III) complexes of polypyridyl ligands have received much attention because of their rich electrochemical and photophysical properties, and their potential applications in various supramolecular structures as electronic and photomolecular devices 1–7. Multinuclear systems of this kind can be developed by covalent linking of building blocks with spacers which, therefore, is the key component because the size, shape and electronic nature of the bridge controls the electronic communication between the chromophores and thereby the molecule as a whole. The ligand 2, 4, 6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) is a potential spacer, which functions as a bis-bidentate or simultaneously as a tridentate and a bidentate bridging unit. The ligand tptz is believed to be stable towards nucleophilic attack and has been used as an analytical reagent for various metal ions 8–11. A few mono and dinuclear complexes of ruthenium (II) of tptz has also been reported 12–14. However, our studies reveal that under certain experimental conditions tptz undergoes various metal-assisted reactions 15–19. Here, we briefly account the reactivities of tptz in presence of rhodium (III), ruthenium (II) and osmium (II), stereochemistry of the products, mechanistic aspects of hydrolysis/hydroxylation and electrochemical properties. The ligands which bind the transition metal ion in a predictable way play important role in modern coordination chemistry since they may determine the reactive sites available at a metal centre and can modulate their reactivity. Fascinating chemistry of transition metal complexes incorporating ligands that are capable of binding the metal centre in facial manner, enhanced the interest on the synthesis of new tridentate ligands that are suitable for obtaining facially coordinated complexes. 1–7 Facially capped piano-stool type of platinum metal complexes have received attention due to their interesting catalytic and biological activity. Conversion of dimethyl oxalate to ethylene glycol and hydrogenation of esters to yield alcohols in homogeneous media using such metal complexes as catalyst are notable examples. 8–21 Although several tridentate facially coordinating ligands, such as 1,4,7 tri aza cyclononane, 1,4,7 trithia cyclononane, tris pyrazolyl borate, a few scorpionate and tripodal ligands, are known to form facially capped ∗For correspondence platinum metal complexes, 22–34 but only a few of the above mentioned ligands have been utilized for the preparation of Os(II) complexes. 35, 36 As a consequence, chemistry of Os(II) complexes with facially coordinating ligands have not been explored considerably. Coordination chemistry of osmium incorporating azo ligands has been studied with a few bidentate (N, N and N, O donors) and tridentate (C, N, O and N, N, N donors) ligands. 37–41 Whereas the coordination chemistry of osmium with tridentate N, N, O donor ligands has not been reported so far. These background information prompted us to study the coordination chemistry of osmium incorporating the N, N, O donor azo-imine ligand system, 1. Complexes with N-heterocycles exhibit rich electrochemistry and interesting optical properties. π-Deficient nitrogen donor ligands are excellent non-innocent molecules and their complexes comprise special interest in coordination chemistry. Transition metal complexes of 2, 2$^{/}$-bipyridine (bpy) and related ligands have attracted much attention in this regard [1-5]. This has led to the modification of M-bpy system by choice of substituents and metal. Ligands have been modified by substituting electron withdrawing/donating groups or bulky groups to the aromatic backbone, substituting other heterocycles, appending extra donor centers to aromatic and/or heterocyclic rings etc. [5-17]. Azo conjugated transition metal complexes can provide new opportunity towards redox, magnetic and optical properties originating from the d-orbitals [6-34]. A characteristic feature of these conjugated complexes that the transition metals can interact with each other through the π-conjugated backbone to permit electronic communi cation. Bis-/tris–hetero chelated complexes may exhibit inter-ligand charge transferences along with some structural distortion and/or backbone deformation [17, 18-27]. Modification has been done substituting six membered pyridine ring by less π-acidic, biologically important five membered imidazole ring e.g., 2-(arylazo)imidazole [12] and by increasing the number of N in pyridine ring *viz.* 2-(arylazo)pyrimidine [19]. Second modification has been carried out replacing pendent aryl group by sterically more crowded, electronically more susceptible naphthyl group from 2-(arylazo)imidazole to get 2-(naphthylazo) imidazoles [35]. Pseudooctahedral $OsCl_2$ $(RaaiR^{/})_2$ may exist, in principle, in five isomeric forms and we have isolated two isomers. One of the isomers has been structurally confirmed by X-ray diffraction measurements [12].

According to the sequence of coordination pairs of Cl, N (imidazole) and N (azo) the isomer is *cis-trans-cis*-$OsCl_2$ $(RaaiR^{/})_2$; the abbreviation is *cis-trans-cis* (*ctc*). This molecule carries *cis*-$OsCl_2$ fragment which can undergo nucleophilic substitution to synthesise mixed ligand complexes. The complexes having *cis*-$OsBr_2$ bonds are more labile [34-80] than analogous complexes with *cis*-$OsCl_2$ group. Herein I report a detailed synthetic account of the formation of complex, and the spectroscopic and electrochemical properties of these complexes. I failed to bring the crystal of any one of these complex after trying different procedures of crystallization. Recently, we have 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 N, N$^{/}$-chelator where N (imidazole) and N (azo) represent N and N$^{/}$ respectively. Pseudooctahedral $RuCl_2$ $(N, N^{/})_2$ may exist in five geometrical isomers. Out of them three have *cis*-$RuCl_2$ and two *trans*-$RuCl_2$ configuration. 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 has been used to synthesise tris chelates by Ag^+ assisted Cl substitution followed by solvento species formation [9-11]. 8-Hydroxyquinoline (HQ) Complexes of transition and nontransition metals are topic of [12, 13] current interest of OLED materials. This molecule has been used for analytical determination of Al^{3+}, Ga^{3+}, Pd^{2+} etc [14]. Because of its optoelectronic efficiency the research in the field of synthesis of different complexes with HQ is of renewed interest [15-18]. It may be noted that the chemistry of ruthenium–Q appears to have received less attention [5].

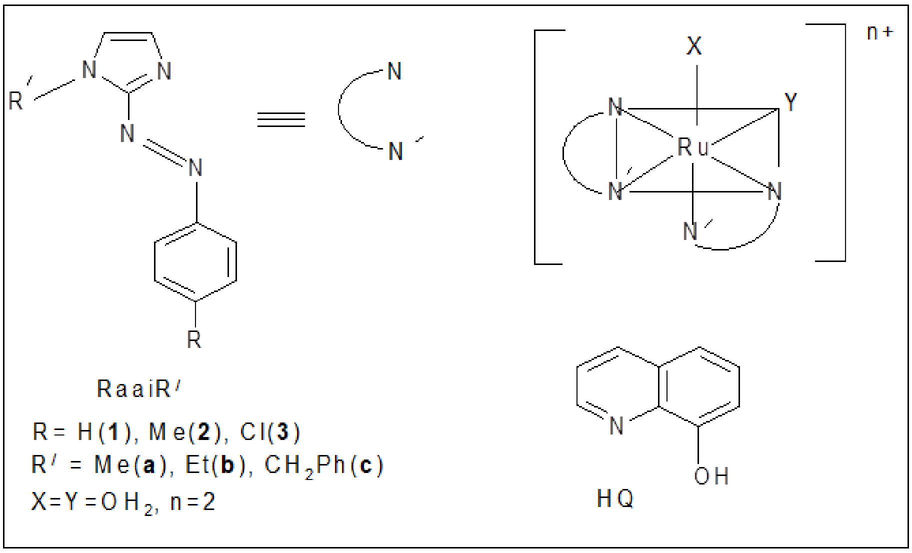

Fig 1

In this work, we have reported some mixed ligand complexes of ruthenium-arylazoimidazole-quinolinato, $[Ru(RaaiR^{/})_2(Q)]^+$.

The structure of one of the complex was established by an X-ray diffraction study.

Experimental

Materials

$RuCl_3.nH_2O$ 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 spectral work and [n-Bu_4N] [ClO_4] (TBAP) were prepared as describe 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 Elemental analyzer. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 sprctrophotometer. Infrared (IR) spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^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 Systronics 304 conductivity meter with solute concentration ~10^{-3} M in acetonitrile. Electrochemical work was carried out using PAR model 250 Versastat potentiostat/galvanostat with EG and G 270 software electrochemistry. All experiments were performed under a N_2 atmosphere at 298K using a Pt-disk milli working electrode and Pt-wire auxiliary electrode. All results were referenced to SCE Reported potentials are uncorrected for junction potential. $K_4[Fe(CN)_6]$ 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 scan rate.

Preparation of (8-quinolinolato)-bis-{1-alkyl-2-(arylazo) imidazole} ruthenium (II) hexafluoro phosphate, [Ru (Q) (OMeaaiMe) 2] (PF6) (2a)

Aqueous $AgNO_3$ (0.06 g, 0.36 mmol) was added to a suspension of *ctc*-$RuCl_2$ $(OMeaaiMe)_2$ (0.1 g, 0.18 mmol) in acetone (25 ml) and the mixture was refluxed for half an hour. After cooling, precipitated AgCl was filtered off by a G4 crucible. 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 (Q) 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 minimum volume of methanol and precipitated with an aqueous solution of NH_4PF_6 (ca. 0.1g in 20 cm^3 water). The violet precipitate was then filtered, washed with minimum volume of cold water and dried in vacuum over P_4O_{10}. The dry mass then dissolved in a minimum volume of CH_2Cl_2 and was chromatograph 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 (0.06g). Other complexes were prepared by the above procedure and yields varied from 40-50%.

Results and Discussion

Synthesis and Formulation

The Ag^+-assisted substitution of chloride ligand from *ctc*-$RuCl_2\ (RaaiR^{/})_2$ has been used in acetone solution to prepare $[Ru(acetone)_2(RaaiR^{/})_2]^{2+}$.

The reaction of HQ (in presence of Et_3N) with $[Ru(acetone)_2(RaaiR^{/})_2]^{2+}$ on stirring at 40°C in the dark for a period of 8 hrs and upon addition of saturated NH_4PF_6 solution to it, have isolated hexafluorophosphate salt $[Ru(Q)(RaaiR^{/})_2](PF_6)$ in 40-50% yield (Eqn.1). Under refluxing condition the mixture of isomers have been generated.We are unable to separate the complexes from the mixture and has been avoided this synthetic route. For this reason the reaction temperature has strictly been maintained at 40°C in the dark and the compound is purified by chromatography. The composition of the compound was formulated by microanalytical data. The complexes are diamagnetic (t_{2g}^6, S=0) and a 1:1 electrolyte in MeCN (Λ_M= 70-90 $\Omega^{-1}mol^{-1}\ cm^{-2}$). The spectral and electrochemical studies determine structure and electronic properties of the complexes. The structural confirmation has been done in one case by single crystal X-ray diffraction study.

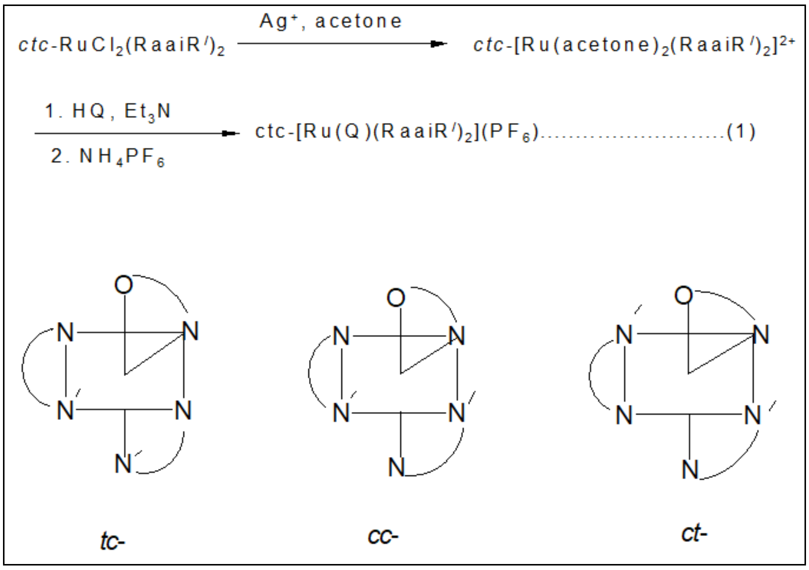

Fig 2

Spectral Characterization

The solution spectra of the complexes are also compared with the spectra of free ligands and *ctc*-$RuCl_2\ (RaaiR^{/})_2$ in MeCN solutions. Multiple transition <400 nm are assigned to intraligand ($n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$) transitions. The complexes display moderately intense (ε~$10^4\ M^{-1}cm^{-1}$) band at 560-580 nm. The transitions are of typical metal-to-ligand Charge transfer type (MLCT) (Fig. 3, Table 3). A weak band (ε~10^3) is observed at 685-705 nm which may be ascribed to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. The infrared spectral arrangement has been made on comparing with 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 *cis*-$RuCl_2$ motif) supports the substitution of Ru-Cl bonds. Besides a new bond appears at 480-500 cm^{-1} and is assigned to ν(Ru-O). The ν(N=N) and ν(C=N) appears at 1370-1380 and 1560-1580 cm^{-1} [16] respectively. The $\nu(PF_6)$ appears at 840 cm^{-1}.

Electrochemistry and correlation with solution spectra

In the potential range +2.0 to –2.0 V at scan rate 50 mVs^{-1} *versus* SCE four redox couples are observed. A quasireversible couple at 1.0 –1.1 V (*versus* SCE) may be assigned to Ru (III)/Ru (II) couple since the ligands are insensitive in this potential range. Quasireversibility is assigned from peak-to-peak difference ($\Delta E_p \geq 100$ mV). The cyclic voltammetric data are summarized in Table 3 and a representative voltammogram is shown in Fig. 4. The 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 than that of imine group (-C=N-) in 8-quinolionate group. Thus, first two reductions may be assigned to azo reductions. They are sensitive to the substituent (R) in the aryl ring and are linearly correlated with Hammett σ values. The third response is referred to reduction of coordinated Q. Variation of the coordination environment around ruthenium plays key role in monitoring 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 bpy and ophen [23], 2-(*p*-tolylazo)pyridine (tap) [15, 16]) systems are easier to oxidize than $[Ru(L^{/})(L)_2]^{3+}$,where L/ = bpy [10], phen [11]. This is also supported by red shifting of MLCT transition [d (Ru^{II}) → π^* (L)] in the complexes $[Ru(Q)(L)_2]^{+}$ relative to the $[Ru(L^{/})(L)_2]^{3+}$ systems. Because of lower ligand field strength provided by anionic oxygen donor center compared to the N(sp^2) donating center the LFSE is expected to be smaller in the RuL_2Q^+ than the $[Ru(L^{/})(L)_2]^{3+}$ complexes. A comparison of the spectral and redox data establish this proposition in the series of ruthenium(II)-{1-methyl-(*p*-tolylazo)imidazoles $[Ru(X,X)(MeaaiMe)_2]^{n+}$ (X,X = Cl, Cl [8], N, N(bpy) [10], N, N(phen) [11]; N, N/ (MeaaiMe) [24]. In a pseudo-octahedral geometry the lower LFSE in RuL_2Q^+ results in higher energy filled metal-centered t_{2g}-type orbitals and lower energy empty e_g-type orbitals. Therefore the transition for MLCT band is expected to be lower energy in RuL_2Q^+ compared to the homoleptic RuL_3^{2+}. This is indeed observed.

Table 1: Elemental analysis, u.v.-vis spectroscopic[a] and cyclic voltammetric[b] data of $[Ru(Q)(RaaiR^{/})_2](PF_6)$

Compounds	Elemental analyses % Found (% Calcd)			U.v.-vis. Spectral data	Cyclic voltammetry data			
	% C	%H	%N	λ_{max}, nm (10^{-3} ε $M^{-1}cm^{-1}$)	$E_{1/2}{}^1$,V (ΔE, mV)	$E_{1/2}{}^2$, V (ΔE, mV)	$E_{1/2}{}^3$, V (ΔE, mV)	$E_{1/2}{}^4$, V (ΔE, mV)
Ru (Q)(OMeaaiMe)$_2$ (PF$_6$) (2a)	47.03 (47.09)	3.74 (3.80)	15.90 (15.95)	690 (1.56), 567 (5.49), 380 (16.92), 236 (12.46)	1.116 (112)	-0.515 (195)	-1.092 (143)	-1.418 (76)
Ru (Q)(OMeaaiEt)$_2$ (PF$_6$) (1b)	47.02 (47.09)	3.77 (3.80)	15.89 (15.95)	689 (2.87), 566 (11.11), 376 (31.04), 237 (22.66)	0.995 (103)	-0.469 (127)	-1.139 (110)	-1.411 (119)

Oxin = QH, a u.v.-vis spectra are recorded in MeCN. b Solvent: MeCN, supporting electrolyte, [nBu4N][ClO4] (0.1 mol), working electrode: Pt-disk micro-electrode, auxiliary: Pt-wire, reference electrode: SCE, potential E1/2 = 0.5(Epa + Epc) in V, peak-to-peak separation □E (= □Epa - Epc□) in mV, Epa = anodic peak potential, Epc = cathodic peak potential.

Table 2: Comparison between spectral[a], electrochemical[b] and theoretical data for $[Ru(bpy)(MeaaiMe)_2)](ClO_4)_2$, $[Ru(ophen)(HaaiMe)_2](ClO_4)_2$ and $Ru(Q)(MeaaiMe)_2](PF_6)$

Compound	ΔE^c, eV	λ, nm (10^{-3} ε, M^{-1} cm^{-1})	E, V	-E^1, V	-E^2, V
$[Ru(bpy)(MeaaiMe)_2](ClO_4)_2$	0.670	517(10.80)	1.66	0.39	0.68
$[Ru(ophen)(HaaiMe)_2](ClO_4)_2$	0.674	521 (11.95)	1.35	0.36	0.70
$[Ru(Q)(OMeaaiMe)_2](PF_6)$	0.647	567 (5.59)	1.09	0.40	0.68

[a] Solvent, MeCN. [b] Solvent, MeCN; Working Electrode GC for Ru (bpy) (MeaaiMe)$_2$)] (ClO$_4$)$_2$ and Pt-disk for other two compounds maintaining other conditions same, E^1 and E^2 refer to azo/azo$^-$ potential of metal bound two azoimine function from two arylazoimidazoles. [c] ΔE = E$_{LUMO}$ – E$_{HOMO}$.

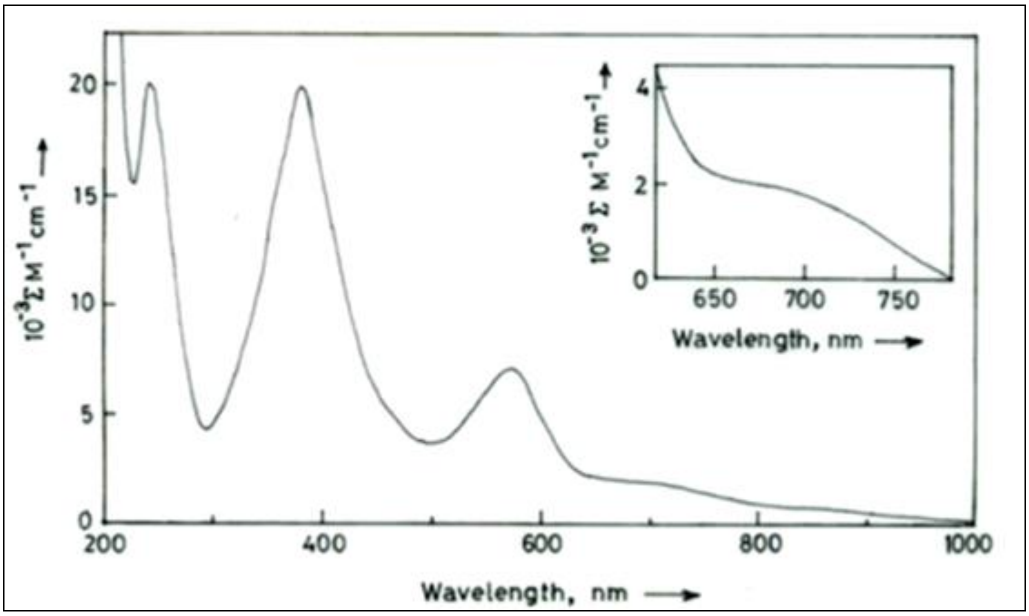

Fig 3: Electronic spectra of $[Ru(Q)(OMeaaiCH_2Ph)_2](PF_6)$ (2c) in MeCN at 298 K.

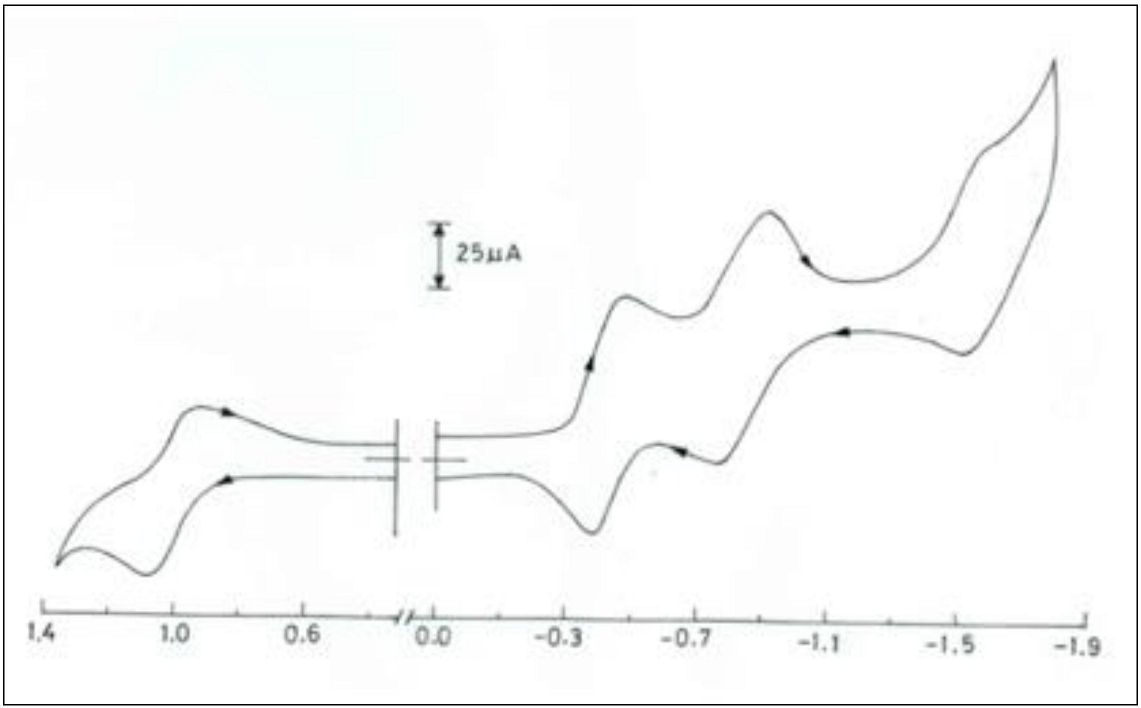

Fig 4: Cyclic voltammogram of $[Ru(Q)(ClaaiMe)_2](PF_6)$ (3a) in MeCN using Pt-disk working, SCE reference, Pt-wire auxiliary electrodes, $[nBu_4N][ClO_4]$ supporting electrolyte (0.1 M) at 50 mV S^{-1} scan rate at 298 K.

Conclusion

The mixed ligand complexes, $[Ru\ (Q)\ (RaaiR^{/})_2\ ]^+$ are described in this article. The complexes are synthesized by reacting $[Ru\ (acetone)\ _2\ (OMeaaiMe)_2]^{2+}$ with HQ in presence of Et_3N. The electronic spectra of the complexes show high intense MLCT transition along with intraligand charge transfer transition. The cyclic voltammetry show Ru (III) / Ru (II) and ligand reductions.

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References

1. Reedijk J. in Comprehensive Coordination Chemistry, G. Wilkinson, RD Gillard and J. A. MeCleverty eds. Pergamon Press, oxford, 1987, l2.
2. Kalyansundaram K, Gratzel M. Coord. Chem. Rev,1998:177:347.
3. Ward MD. Chem. Soc. Rev,1995:24:121.
4. Wong WT. Coord. Chem. Rev,1994:131:45.
5. Balzani V, Credi A, Scandola F. in Transition Metals in Supramolecular Chemistry, L. Fabbrizzi and A. Poggi, Eds.,Kulwer, Dordrecht , The Nather lands, 1994, 1.
6. Anderson PA, Anderson RF, Furue M, Junk PC, Keene RF, Patterson BT. *et al*. Inorg. Chem,2000:39:2721.
7. Velders AH, Quiroga AG, Haasnoot JG, Reedijk J. Eur. J. Inorg. Chem., 713 and references therein, 2003.
8. Misra TK, Das D, Sinha C, Ghosh PK, Pal CK. Inorg. Chem,1998:37:1672.
9. Pal S, Misra TK, Sinha C, Slawin AMZ, Woollins JD. Polyhedron,2000:19:1925.
10. Byabarta P, Dinda J, Santra, Sinha C, Panneerselvam K, Liao F-L *et al*. J. Chem. Soc., Dalton Trans, 2001, 2825.
11. Byabartta P, Jasimuddin Sk, Mostafa G, Lu T-H. Sinha C. Polyhedron,2003:22:849.
12. MoulinJ–F, Brinkmann M. A. Thierry and J.-C. Wittmann. Advanced Mater,2002:14:436.
13. Sapochak LS, Benincasa FE, Schofield RS, Baker JL, Riccio KKC, Fogarty D *et al*. J. Am. Chem. Soc,2002:124:6119.
14. Svehila G. "Vogels Qualitative Inorganic Analysis" Longman, 1998.
15. Lahiri GK, Bhattacharya S, Ghosh BK, Chakravorty A. Inorg. Chem,1987:26:4324.
16. Bhattacharya S. Polyhedron,1993:12:235.
17. Menon M, Pramanik A, Bag N, Chakravorty A. J. Chem. Soc., Dalton Trans, 1995, 1417.
18. Pramanik NC, Bhattacharya S. J. Chem. Res. (s), 1997, 98.
19. Das D. Ph. D. Thesis, Burdwan University, Burdwan, India, 1998.
20. Goswami S, Chakravarty AR, Chakravorty A. Inorg. Chem., 20, 2246; (1982) Inorg. Chem., 21, 2737, (1983) Inorg. Chem,1981:22:602.
21. Santra PK, Misra TK, Das D, Sinha C, Slawin AMZ, Woolins JD. Polyhedron,1999:18:2869.
22. Dinda J, Bag K, Sinha C, Mostafa G, T –H Lu. Polyhedron,2003:22:1367.
23. Warren JT, Chen W, Johnston DH, Turro C. Inorg. Chem,1999:38:6187.
24. Jasimuddin Sk, Byabartta P, Mostafa G, T –H Lu, C Sinha. Unpublished results.
25. Chattopadhyay S, Ghosh K, Pattanayak S and Chakravorty A. J. Chem. Soc., Dalton Trans, 2001, 1259.
26. Ghosh P, Pramanik A, Bag N, Lahiri GK, Chakravorty A. J. Organomet. Chem,1993:454:237.
27. Shiva kumar M, Pramanik K, Ghosh P, Chakravorty A. Chem Chommun, 2103-1998.
28. Shivakumar M, Pramanik K, Ghosh P, Chakravorty A. Inorg. Chem. 375968, 1998.
29. Mondal B, Paul H, Puranik VG, Lahiri GK. J. Chem. Soc., Dalton Trans, 2001, 481

30. Deb AK, Goswami S. Polyhedron,1993:12:1419.
31. Deb AK, Paul PC, Goswami S. J. Chem. Soc., Dalton Trans. 2051, 1988.
32. Byabartta P, Jasimuddin Sk, Ghosh BK, Sinha C, Slawin AMZ, Woollins JD. New J. Chem,2002:26:1415.
33. Goswami S, Chakravorty AR, Chakravorty A. J. Chem. Soc., Chem. Commun, 1982.
34. Santra PK, Roy R, Sinha C. Proc. Indian Acad. Sci. (Chem. Sci.),2000:112:523.
35. Dinda J, Santra PK, Sinha C, Falvello LR. J. Organomet. Chem,2001:629:28.
36. Misra TK, Das D, sinha C, Ghosh PK, Pal CK. Inorg. Chem, 1992:37:1672.
37. Pal S, Misra TK, Sinha C, Slawin AMZ, Woollins JD. Polyhedron,2000:19:1925.