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HETEROLEPTIC TRIS CHELATES OF RUTHENIUM(II): RU-1,10-PHENANTHROLINE-OXINE-RAAIR: THE SYNTHESIS, SPECTRAL STUDY AND ELECTROCHEMISTRY OF (8-QUINOLINOLATO)-(1,10-PHENANTHROLINE)-{1-ALKYL-2-(ARYLAZO)IMIDAZOLE} RUTHENIUM(II) HEXAFLUOROPHOSPHATE

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ABSTRACT

The reaction of $[Ru(OH_2)_2(RaaiR^{/})(1,10\text{-phenanthroline})]^{2+}$ [RaaiR$^{/}$ = 1-alkyl-2-(arylazo)imidazole, *p*-R-C_6H_4-N=N-C_3H_2NN(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 has afforded violet coloured mixed ligand complexes of the composition $[Ru(Q)(RaaiR^{/})(1,10\text{-phenanthroline})](PF_6)$. The structure of [Ru(OXINE)(MeaaiMe)(1,10-phenanthroline](PF_6) (**2a**) has been confirmed. 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; 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] Ruthenium is a component of mixed-metal oxide (MMO) anodes used for cathodic protection of underground and submerged structures, and for electrolytic cells for chemical processes such as generating chlorine from salt water. The fluorescence of some ruthenium complexes is quenched by oxygen, which has led to their use as optode sensors for oxygen. Ruthenium red, $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$, is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy and electron microscopy. The beta-decaying isotope 106 of ruthenium is used in radiotherapy of eye tumors, mainly malignant melanomas of the uvea. Ruthenium-centered complexes are being researched for possible anticancer properties. Compared with platinum complexes, those of ruthenium show greater resistance to hydrolysis and more selective action on tumors. NAMI-A and KP1019 are two drugs undergoing clinical evaluation against metastatic tumors and colon cancers. Because of its ability to harden platinum and palladium, ruthenium is used in platinum and palladium alloys to make wear-resistant electrical contacts. In this application, only thin plated films are used to achieve the necessary wear-resistance. Because of its lower cost and similar properties compared to rhodium, the use as plating material for electric contacts is one of the major applications. The thin coatings are either applied by electroplating or sputtering. Ruthenium dioxide and lead and bismuth ruthenates are used in thick-film chip resistors. These two electronic applications account for 50% of the ruthenium consumption. Only a few ruthenium alloys are used other than those with other platinum group metals. Ruthenium is often used in small quantities in those alloys to improve some of their properties. 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(OXINE)(MeaaiMe)(2,2-bipyridine)](PF_6) $[Ru(OH_2)_2(RaaiR^{/})(2,2\text{-bipyridine})]^{2+}$ [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.[15-36] It may be noted that the chemistry of ruthenium–Q appears to have received less attention.[5] 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. Silver assisted aquation of green *ranscis-t-cis*-$RuCl_2(RaaiR)_2$ (**1**) leads to the synthesis of solvento species, blue-violet *rans cis-cis*-$[Ru(OH_2)_2(RaaiR^{/})_2](ClO_4)_2$ [RaaiR = *p*-R-C_6H_4-N=N-C_3H_2-NN, (**2**), abbreviated as N,N/-chelator, where N(imidazole) and N(azo) represent N and N/, respectively; R = H (**a**), p-Me (**b**), p-Cl (**c**) that have been reacted with NCS^- in warm EtOH resulting in red-violet dithiocyanato complexes of the type, $[Ru(NCS)_2(RaaR)_2]$ (**3-5**). The solution structure and stereoretentive transformation in each step have been established from ^1H n.m.r. results. All the complexes exhibit strong MLCT transitions in the visible region. They are redox active and display one metal-centred oxidation and successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.Ruthenium is a component of mixed-metal oxide (MMO) anodes used for cathodic protection of underground and submerged structures, and for electrolytic cells for chemical processes such as generating chlorine from salt water. The fluorescence of some ruthenium complexes is quenched by oxygen, which has led to their use as optode sensors for oxygen. Ruthenium red, $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$, is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy and electron microscopy. The beta-decaying isotope 106 of ruthenium is used in radiotherapy of eye tumors, mainly malignant melanomas of the uvea. Ruthenium-centered complexes are being researched for possible anticancer properties. Compared with platinum complexes, those of ruthenium show greater resistance to hydrolysis and more selective action on tumors. NAMI-A and KP1019 are two drugs undergoing clinical evaluation against metastatic tumors and colon cancers. Because of its ability to harden platinum and palladium, ruthenium is used in platinum and palladium alloys to make wear-resistant electrical contacts. In this application, only thin plated films are used to achieve the necessary wear-resistance. Because of its lower cost and similar properties compared to rhodium, the use as plating material for electric contacts is one of the major applications. The thin coatings are either applied by electroplating or sputtering. Ruthenium dioxide and lead and bismuth ruthenates are used in thick-film chip resistors. These two electronic applications account for 50% of the ruthenium consumption. Only a few ruthenium alloys are used other than those with other platinum group metals. Ruthenium is often used in small quantities in those alloys to improve some of their properties. The beneficial effect on the corrosion resistance of titanium alloys led to the development of a special alloy containing 0.1% ruthenium. Ruthenium is also used in some advanced high-temperature single-crystal superalloys, with applications including the turbine blades in jet engines. Several nickel based superalloy compositions are described in the literature. Among them are EPM-102 (with 3% Ru) and TMS-162 (with 6% Ru), as well as TMS-138 and TMS-174. both containing 6% rhenium. Fountain pen nibs are frequently tipped with alloys containing ruthenium. From 1944 onward, the famous Parker 51 fountain pen was fitted with the "RU" nib, a 14K gold nib tipped with 96.2% ruthenium and 3.8% iridium. A wide number of ruthenium complexes containing heterocyclic nitrogeneous molecules and related ligands have been reported to date. They are of considerable interest primarily due to variable oxidation states, building blocks for supramolecular assemblies, photo-physical properties, directional electron and energy transfer, potential anticancer property. Modification of heterocyclic ligands may be carried out by incorporating new donor centers, spectator groups, change of ring size and number of Heteroatoms. They can significantly influence the physical and chemical properties of the complex molecules. The elimination of functional groups from organic molecules has immense significance in chemistry, including the synthesis of natural products.[1,2] In this context, decarbonylation reactions have become an indispensable aspect in the advancement of chemical synthesis. The key challenge of the decarbonylation reaction lies in the high bond dissociation energy of the C−C bond. Complexes of platinum group metals have been used to address this issue, as the metal center destabilizes the C−C bond through single- or two-electrontransfer processes. Hence, the platinum-group metals have drawn considerable attention over the decades.[3−5] Among the platinum-group metals, ruthenium exhibits the largest range of stable oxidation states (from −II to + VIII).[6] Hence, there is interest in the exploration of new ruthenium-based catalysts capable of decarbonylation reactions, especially after an initial report by Dolphin and co-workers on the stoichiometric decarbonylation using a ruthenium−porphyrin-based complex.[7] An iridium-catalyzed decarbonylation method has also been reported by Tsuji and co-workers, wherein a variety of functional groups were tolerated under mild reaction conditions.[8] In this way, effective synthetic decarbonylation processes can be beneficial for the generation of fuel-grade alkanes and should be attractive alternatives to existing expensive hydrogenation methodologies.[9] Bhattacharya and co-workers,[10] Jayanthi et al.,[11] and Dinger et al.[12] have

worked on ruthenium complexes wherein in situ solvent oxidation and decarbonylation had led to CO-coordinated Ru(II) complexes. These groups had proposed CO generation via either Ruassisted methyl oxidation or solvent oxidation in azo and hydrazone complexes. However, their findings lacked substantial experimental evidence to support the mechanism of Ru-assisted solvent oxidation. Thus, further experimental investigations into the precise mechanism of these Ru-assisted alcohol dehydrogenation reactions and CO coordination are needed.[11,12] These literature reports prompted us to synthesize some new ruthenium azo complexes and examine the possiblesolvent oxidation (by using 13C-labeled ethanol) and subsequent decarbonylation. We here focus on the synthesis of organometallic ruthenium complexes (1 & 2) derived from arylazo functionalized ligands, wherein an in situ solvent oxidation and subsequent decarbonylation to generate an alkane would be possible. To further see whether this decarbonylation is specific for ruthenium, we attempted to observe similar in situ decarbonylation in an organoiridium complex (3) using the same organic ligand. However, it is also known that arylazo complexes of the platinum-group metals have been the subject of substantial interest because of their rich redox and spectroscopic behavior, catalytic activities, and isomerization reactions.13−16 By comparison, the anticancer activity of platinum arylazo complexes has received rather limited attention.17a−c While conventional platinum anticancer drugs such as cisplatin, carboplatin, and oxaliplatin are potent against a range of tumors, their side effects like toxicity toward normal tissue and tumor resistance have motivated researchers to develop anticancer agents that diverge from the stereotypical complexes already in use.17d−f In this direction, ruthenium and iridium complexes have emerged as encouraging classes of metallodrug candidates and hold great promise for cancer chemotherapy.18 Moreover, recent reports have revealed ruthenium complexes as remarkable antiproliferative agents, for example, the Ru(III)- based anticancer drugs indazolium trans-[tetrachlorobis(1Hindazole)ruthenate(III)] (KP1019),19-80 its sodium salt analogue sodium trans-[tetrachlorobis(1H-indazole)ruthenate(III)] (NKP-1339),20 and the new antimetastasis inhibitor imidazolium trans-[tetrachlorobis(1H-imidazole)(S-dimethyl sulfoxide)-ruthenate(III)] (NAMI-A),21 which all have proceeded into the clinical stages of drug development. Furthermore, iridium complexes have been reported to generate reactive oxygen species and to induce apoptosis by acting on mitochondria as well as exerting anticancer effects through interaction with DNA.22−24 Phenylazo ligands have a crucial role in cytotoxicity against the A2780 ovarian and A549 lung-cancer cell lines as reported by Dougan et al. during investigation of η6 -areneruthenium(II) derivatives containing phenylazo ligands.17a The azo derivatives of ruthenium were found to be more cytotoxic as compared to the oxadiazole derivatives, on human glioblastoma cell lines, inspiring further study of azo-coordinated complexes.17c The redox reactions of the metal-coordinated azo ligands have been known to increase the cytotoxicity of half-sandwich organometallic (arene)-ruthenium(II) complexes.17a,c As compared to the free arylazo ligand, the transitionmetal chelated azo complexes target cancer cells better than normal cells due to increased lipophilicity on chelation; this prompts the design and exploration of more metal-coordinated azo compounds.25 Significant in vitro cytotoxic results of azovanadium complexes have also been reported in our earlier works, which further stimulates us to design and study azofunctionalized complexes.26 Another class of pharmacophoric interest are triphenylphosphine (PPh3)-coordinated metal complexes, as they exhibit excellent potential in chemotherapy by influencing mitochondrial metabolism. 27a−g Using hydrophobic PPh3-ligated complexes results in complexes with good cytotoxicity, presumably due to their increasing vehiculation property. 27h−j Some ruthenium phosphine complexes are known to inhibit the human topoisomerase IB enzyme (a potential biological target for complexes). 27h It has been demonstrated that the presence of a PPh3 ligand is important also to facilitate the binding of the Ru complex to DNA and then distort its secondary and tertiary structure.27j,k Also, wide investigations of platinum, ruthenium, copper, and gold complexes have led to conclusions that mixed-ligand complexes possessing PPh3 are highly cytotoxic in contrast to the phosphine-free ones, which inhibited cell proliferation only in relatively high concentrations. 27h,l−q Thus, the wide cytotoxic activity of azo- and PPh3-derived complexes stimulated us to investigate mixed azo- and PPh3-coordinated complexes. The nature of chemical reactions of organic substrates can vastly be affected by their coordination to metal ions. It is now known that organonitriles are activated by metal coordination toward addition reactions leading to a variety of synthetic transformations of RCN species. Thiocyanates, as ligand, have attracted considerable attention in recent years not only because of their versatile coordination abilities but also some of their transition metal complexes have been found to be useful. The ruthenium chemistry of diimine ligands is an area of significant current interest, particularly with regard to the photophysical and photo-chemical properties exhibited by such complexes. Di-imine ligands are strong π-acceptors and are recognized stabilizers of the +2 state of ruthenium (low-spin d^6, S=0). As a consequence, an interesting aspect of the ruthenium–diimine chemistry has been to study the remarkable π-interaction between the filled t_2 orbitals of ruthenium(II) and the low-lying vacant π*-orbital of the diimine chromophore. The extent of π-interaction in these complexes depends primarily on the nature of the diimine ligands, which again depends on the nature of the groups linked to the two carbons and the two imine-nitrogens. The presence of other π-acceptor ligands within the coordination sphere may also have significant influence on the π-interaction between the diimine ligands and ruthenium(II).[1-5] From the

viewpoint of the principle of hard and soft acids and bases (R. Pearson, 1963), both the RuNCS and RuSCN isomers can occur in the ruthenium complexes. For the last few years, the search for a suitable precursor to synthesize NCS complexes is a challenging domain and the compounds are found to be useful in this context.[6-8] Recently, we have developed the arylazopyrimidine as well as arylazoimidazole chemistry of ruthenium(II) and have synthesised dichloro componds and diaquo species. Syntheses of hetero-tris-chelates, $[Ru(bpy)_n(RaaiR/)_{3-n}](ClO_4)_2$ [bpy = 2,2′-bipyridine; n = 1, n = 2) from the solvento complexes $[Ru(OH_2)_2(bpy)_2]^{2+}$/$[Ru(OH_2)_2(RaaiR/)_2]^{2+}$ containing labile reaction centres are reported from Prof. Sinha´s laboratory.[8-11] In this paper, We examine the reaction of NCS- towards $[Ru(OH_2)_2(RaaiR)_2]^{2+}$ and the reactions of the complexes derived there-from and also studied the dinuclear adduct formation pathway. The complexes were well charecterised by C.H.N, FT-I.R, U.V-Vis, and Cyclic Voltammetrically. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis. 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] 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.

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)(1,10-phenanthroline)(MeaaiMe)](PF_6) (2a)

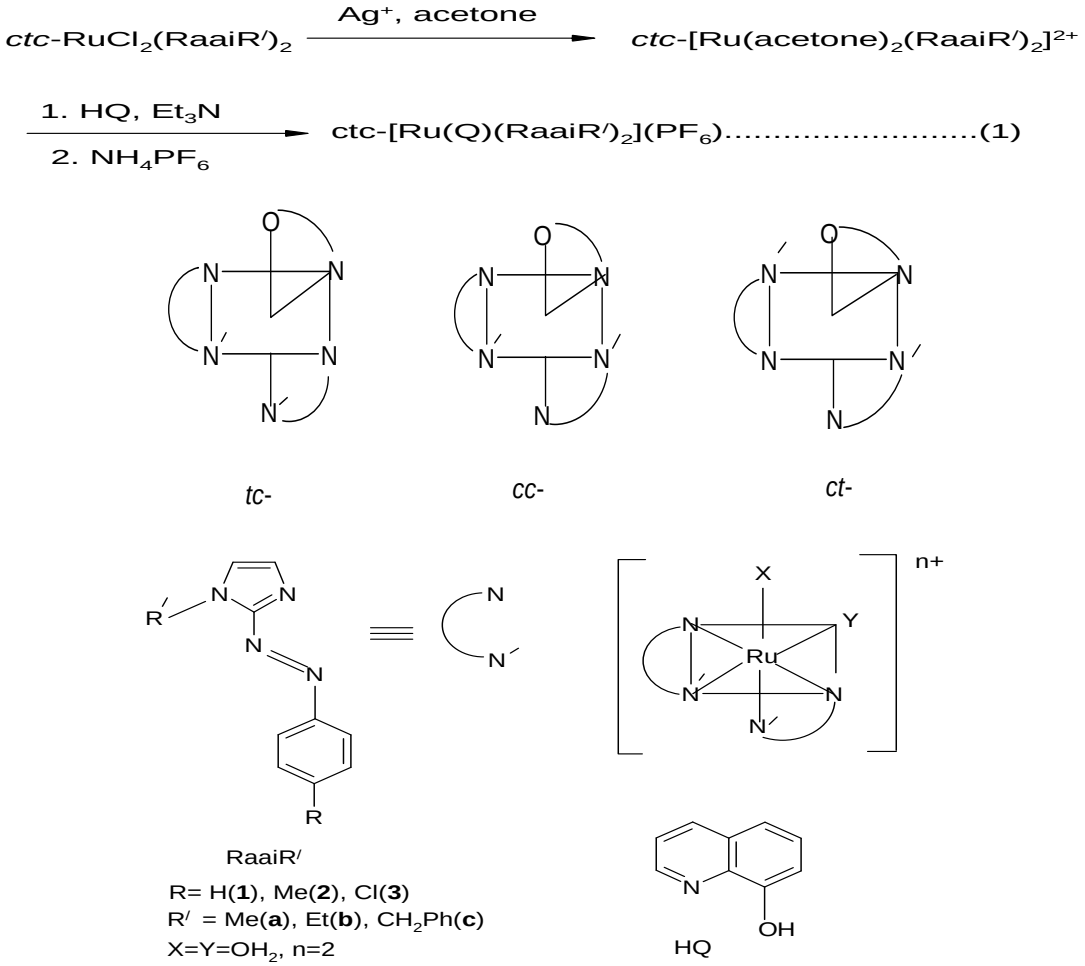
Aqueous $AgNO_3$ (0.06 g, 0.36 mmol) was added to a suspension of *ctc*-$RuCl_2$(MeaaiMe) (2,2-bioyridine) (0.1 g, 0.18 mmol) in acetone (25 ml) and the mixture was refluxed for half an hour. After cooling, precipitated AgCl was filtered off by a G4 crucible. 8-hydroxyquinoline (HQ) (0.02 g, 0.14 mmol) 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(OXINE)(MeaaiMe)(1,10-phenanthroline)]$(PF_6)^+$ 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 $[Ru(acetone)_2(RaaiR')(1,10\text{-phenanthroline})]^{2+}$. 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 $[Ru(Q)(RaaiR')(1,10\text{-phenanthroline})](PF_6)$ in 40-50% yield (Eqn.1). Under refluxing condition the mixture of isomers have been generated $[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$. 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$[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$ was formulated by microanalytical data $[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$. 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$[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$.



Spectral Characterization

The infrared spectral arrangement has been made on comparing with the spectra of free ligands and *ctc*-$RuCl_2(RaaiR')(1,10\text{-phenanthroline})$ and $[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$.[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 ν(PF_6) appears at 840 cm^{-1}.

The solution spectra of the complexes$[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$ are also compared with the spectra of free ligands and *ctc*-$RuCl_2(RaaiR')(1,10\text{-}$

phenanthroline) in MeCN solutions. Multiple transition <400 nm are assigned to intraligand ($n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$) transitions. The complexes display moderately intense ($\varepsilon\sim10^4M^{-1}cm^{-1}$) band at 560-580 nm. The transitions are of typical metal-to-ligand charge transfer type (MLCT) [Ru(OXINE)(MeaaiMe)(1,10-phenanthroline)](PF_6) (Fig. 1, Table 1). A weak band ($\varepsilon\sim10^3$) is observed at 685-705 nm which may be ascribed to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition.

Electrochemistry and correlation with solution spectra

In the potential range +2.0 to –2.0 V at scan rate 50 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, [Ru(OXINE)(MeaaiMe)(1,10-phenanthroline)](PF_6). The potential data negative to SCE are due to ligand reductions[Ru(OXINE)(MeaaiMe)(1,10-phenanthroline)](PF_6). 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 (Fig. 1, Table 1).. 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(Fig. 1, Table 1) of its complexes [Ru(OXINE)(MeaaiMe)(1,10-phenanthroline)](PF_6). 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[23-31], 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 $[d(Ru^{II}) \rightarrow \pi^*(L)]$ 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) (2,2-bipyridine)]$^{n+}$ (X,X = Cl, Cl[8], N, N(bpy)[10], N, N(phen)[11]; N, N$^{/}$ (MeaaiMe).[24-31] 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+}.

Table 1: FT-IR spectroscopic[b] data.

Complexes	ν(N=N)ν(C=N)ν(C=C)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**1a**)	1365 1570 1600 1300
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**2a**)	1367 1580 1602 1320
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**3a**)	1370 1590 1610 1325
Ru (8-HYDROXY-QUINOLINE)(H-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**1b**)	1375 1585 1613 1320
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**2b**)	1380 1590 1609 1310
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**3b**)	1370 1570 1609 1300
Ru (8-HYDROXY-QUINOLINE)(H-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**1c**)	1365 1575 1606 1310
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**2c**)	1380 1570 1609 1320
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**3c**)	1370 1575 1609 1310

On KBr disk

Table II: Elemental analysis data of Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (1A-3C).

Compounds	Elemental analyses % Found (% Calcd)		
	C	H	N
Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**1a**)	45.68 (45.67)	3.69 (3.41)	16.51 (16.54)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**2a**)	47.63 (47.09)	3.64 (3.80)	15.90 (15.95)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**3a**)	41.68 (41.83)	2.84 (2.88)	15.09 (15.14)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**1b**)	47.62 (47.09)	3.77 (3.80)	15.89 (15.95)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**2b**)	48.67 (48.41)	4.11 (4.16)	15.36 (15.40)

Ru (8-HYDROXY-QUINOLINE)(CL-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**3b**)	43.61 (43.26)	3.22 (3.26)	14.58 (14.65)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**1c**)	53.66 (53.83)	3.69 (3.72)	13.74 (13.79)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**2c**)	54.63 (54.78)	4.01 (4.03)	13.32 (13.38)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**3c**)	49.65 (49.80)	3.21 (3.24)	12.72 (12.75)

Oxin = QH,.

Table III: U.v.-vis spectroscopic[a] data of Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (1a-3C) [Ru(Q)(RaaiR/)(BPY)](PF_6).

Compounds	
Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**1a**)	690 (1.56), 567 (5.49), 380 (16.92), 236 (12.46)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**2a**)	688 (1.69), 572 (6.61), 378 (17.54), 246 (19.35)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**3a**)	689 (2.87), 566 (11.11), 376 (31.04), 237 (22.66)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**1b**)	688(1.85), 568 (6.91),378 (16.62), 240 (15.49)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**2b**)	704 (1.67), 573 (6.82), 380 (19.37), 242 (19.49)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**3b**)	693 (2.62), 566 (10.22), 377 (24.13), 232 (19.35)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**1c**)	692 (1.92), 569 (7.52), 386 (19.53), 243 (19.65)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**2c**)	706(1.71), 571 (6.950, 388 (19.61), 244 (19.84)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**3c**)	686 (1.81), 566 (6.45), 376 (16.32), 240 (15.43)

Oxin = QH, [a] u.v.-vis spectra are recorded in MeCN.

Table IV: Cyclic Voltammetric[b] data of Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (1a-3C).

Compounds				
Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**1a**)	1.046 (120)	-0.396 (139)	-1.016 (109)	-1.476 (80)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**2a**)	1.116 (112)	-0.515 (195)	-1.092 (143)	-1.418 (76)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-Me)(1,10-PHENANTHROLINE) (PF_6) (**3a**)	1.046 (135)	-0.406 (126)	-0.887 (124)	-1.532 (78)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**1b**)	0.995 (103)	-0.469 (127)	-1.139 (110)	-1.411 (119)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**2b**)	1.028 (124)	-0.542 (120)	-1.185 (122)	-1.481 (98)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-ET)(1,10-PHENANTHROLINE) (PF_6) (**3b**)	1.077 (149)	-0.408 (119)	-1.049 (120)	-1.443 (73)
Ru (8-HYDROXY-QUINOLINE)(H-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**1c**)	1.101 (143)	-0.441 (131)	-1.110 (122)	-1.416 (70)
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**2c**)	1.107 (135)	-0.459 (128)	-1.141 (119)	-1.451 (82)
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-BZ)(1,10-PHENANTHROLINE) (PF_6) (**3c**)	1.051 (115)	-0.442 (121)	1.021 (132)	-1.402 (87)

Oxin = QH, [a] u.v.-vis spectra are recorded in MeCN. [b] Solvent: MeCN, supporting electrolyte, [nBu_4N][ClO_4] (0.1 mol), working electrode: Pt-disk 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.

Table V: ^{1}H NMR data[a].

Compound	δ, ppm (J, Hz)													
	4-H 4′-H[b]	5-H 5′-H[b]	7-H 7′-H[b]	8,10-(8′-10′)- H		11-(11′)[b]- H	a,a′-H[b]	b,b′-H[c]	c,c′-H[c]	d,d′-H[b]		1-Me	13-Me	12-CH_2
Ru (8-HYDROXY-QUINOLINE)(H-AAI-Me)(PHEN) (PF_6) (**1a**)	7.14 (5.2)	6.96 (5.2)	7.27 (7.0)	7.87[e]		7.44 (7.0)	8.49 (8.0)	8.12 (8.0)	7.90 (8.0)	7.55 (8.0)		4.34, 4.40[e]		
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-Me)(PHEN l) (PF_6) (**2a**)	6.64 (6.0)	6.36 (7.0)	7.16 (7.0)	7.19[b] (8.0)		7.34 (7.5)	8.54 (8.0)	8.11 (8.0)	7.83 (8.0)	7.60 (8.0)		4.34, 4.36[e]		
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-Me)(PHEN) (PF_6) (**3a**)	7.14 (6.0)	6.96 (6.0)	7.16 (7.0)	7.95[b] (8.0)		7.45 (7.0)	8.54 (80)	8.14 (8.0)	7.90 (8.0)	7.60 (8.0)		4.35, 4.40[e]		
Ru (8-HYDROXY-QUINOLINE)(H-AAI-ET)(PHEN l) (PF_6) (**1b**)	7.14 (5.0)	6.86 (5.0)	7.26 (7.0)	7.82[e]	7.82[e]	7.44 (7.0)	8.44 (8.0)	8.11 (8.0)	7.85 (8.0)	7.59 (8.0)			1.34	3.52
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-ET)(PHEN) (PF_6) (**2b**)	6.64 (6.0)	6.44 (6.0)	7.30 (7.0)	7.20[b] (8.0)		7.34 (7.5)	8.54 (8.0)	8.14 (8.0)	7.91 (8.0)	7.62 (8.0)			1.42	3.92
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-ET)(PHEN) (PF_6) (**3b**)	7.12 (6.5)	6.90 (6.5)	7.12 (7.0)	7.95[b] (8.0)		7.47 (7.0)	8.50 (8.0)	8.10 (8.0)	7.86 (8.0)	7.50 (8.0)			1.44	4.30, 4.14
Ru (8-HYDROXY-QUINOLINE)(H-AAI-BZ)(PHEN) (PF_6) (**1c**)	7.09 (5.4)	6.94 (5.4)	7.30 (7.0)	7.90[e]	7.90[e]	7.46 (7.0)	8.50 (8.0)	8.12 (8.0)	7.88 (8.0)	7.60 (8.0)				5.53, 5.60[d]
Ru (8-HYDROXY-QUINOLINE)(ME-AAI-BZ)(PHEN) (PF_6) (**2c**)	7.02 (6.0)	6.81 (6.0)	7.11 (7.0)	7.17[b] (8.0)		7.31 (7.0)	8.54 (8.0)	8.11 (8.0)	7.88 (8.0)	7.58 (8.0)	2.40			5.56, 5.61[d]
Ru (8-HYDROXY-QUINOLINE)(CL-AAI-BZ)(PHEN) (PF_6) (**3c**)	7.11 (6.0)	6.94 (6.0)	7.18 (7.0)	7.92 (8.0)		7.49 (7.0)	8.52 (8.0)	8.14 (8.0)	7.85 (8.0)	7.54 (8.0)				5.55, 5.60[d]

[a]in CD_3CN, [b] Doublet; [c]Triplet; [d] Phenyl protons; [e] multiplet; δ 7.35-7.50, -CH_2- shows AB type quartets.

Table V: 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)(MeaaiMe)$_2$](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] $\Delta E = E_{LUMO} - E_{HOMO}$.

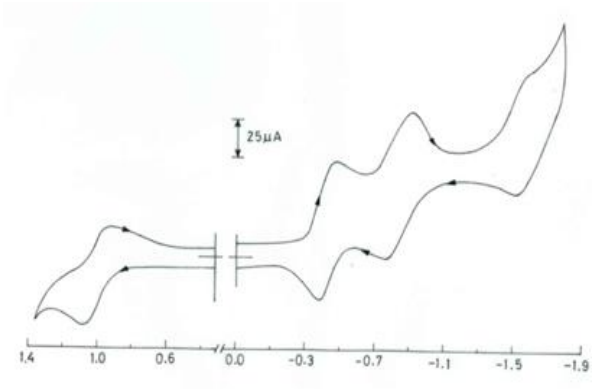


Figure 1: Cyclic voltammogram of $[Ru(Q)(ClaaiMe)_2](PF_6)$ (3a) in MeCN using Pt-disk working, SCE reference, Pt-wire auxiliary electrodes, $[nBu_4N][ClO_4]$ supporting electrolyte (0.1 M) at 50 mV S^{-1} scan rate at 298 K.

CONCLUSION

The mixed ligand complexes, $[Ru(Q)(RaaiR^{/})(1,10\text{-phenanthroline})]^{+}$ are described in this article. The complexes are synthesized by reacting $[Ru(acetone)_2(MeaaiMe)(1,10\text{-phenanthroline})]^{2+}$ 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 molecular confirmation$[Ru(OXINE)(MeaaiMe)(2,2\text{-bipyridine})](PF_6)$ has been done by single crystal X-ray diffraction study in one case, $[Ru(Q)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$. The cyclic voltammetry show Ru(III) / Ru(II) and ligand reductions$[Ru(OXINE)(MeaaiMe)(1,10\text{-phenanthroline})](PF_6)$.

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