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Synthesis, spectroscopy and electrochemistry of 2-(mercapto/hydroxyl)pyridine-bis-{1-(alkyl)-2-(aryloxy)imidazole}ruthenium(II)

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Ruthenium-pyridine complexes incorporating azoimidazole ligands, L, of the type $[Ru^{II}(RaaiR')_2(X\text{-pyridine})]$ 1-6 [$RaaiR' = p\text{-R-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{-NN-1-R}'$, (1-6), abbreviated as N,N' -chelator, where N(imidazole) and N(azo) represent N and N' , respectively; R=H (a), Me (b), Cl (c) and $R' = \text{Me}$ (1,4), CH_2CH_3 (2,5), Bz(3,6), X=S, 2-mercaptopyridine(1-3), X=O, 2-hydroxy-pyridine(4-6)] have been synthesized and their spectroelectrochemical aspects investigated. The complexes show intense charge-transfer bands in the UV-visible region which have been found to be reasonably blue shifted. The complexes systematically exhibit two oxidation processes and two successive one-electron reductions.

Key words: Ruthenium (II), aryloxyimidazole, Infrared spectroscopy (IR), Nuclear magnetic resonance (NMR), Electrospray Ionization Mass Spectrometry (ESIMS), Cyclic Voltammetry (CV).

INTRODUCTION

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, $[(\text{NH}_3)_5\text{Ru-O-Ru}(\text{NH}_3)_4\text{-O-Ru}(\text{NH}_3)_5]^{6+}$ is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy and electron microscopy (Wang et al 2005). 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 nitrogenous molecules and related ligands have been reported to date (Maiti et al., 2001; Pal et al 1996; Chakraborty et al 2005). 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. Since the discovery of important redox, photophysical and photochemical properties of ruthenium complexes having 2,2-bipyridine (bipy) as ligand, there has been continuous research activity in the direction of developing newer ruthenium–bipyridine systems with the perspective of interesting physicochemical properties (Ghosh et al 2013; Shivakumar et al 2000; Pramanik et al 2000; Das et al 2002; Shivakumar et al 1998). In this context, different kinds of mixed ligand ruthenium–bipyridine complexes have been synthesized and studied over the last fifteen years (Rasmussen et al 1996; Krause and Kirsten 1984). The basic strategies behind all these activities are either to incorporate different groups within the bipyridine moiety itself or use other types of donor sites like azoimine function along with the Ru(bipy)₂ core to form mixed-ligand tris-chelates to modulate the photo-redox activities of this class of complexes (Santra et al., 2002). The present work originates in preparing new mixed-ligand ruthenium–arylaazoimidazole complexes of type [Ru(RaaiR)₂L], where L is a ligand which can form a four membered chelate ring on co-ordination and in studying the redox and

spectroscopic properties of the Ru(RaaiR)₂ core (Bag et al., 1988). The author has chosen pyridine-2-thiol and pyridin-2-ol as ligand L. This work demonstrates example of [Ru(RaaiR)₂(X-Pyridine)] [RaaiR' = *p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', (1-6), abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R=H (a), Me (b), Cl (c) and R'=Me (1,4), CH₂CH₃ (2,5), Bz(3,6), X=S, 2-mercaptopyridine(1-3), X=O, 2-hydroxypyridine(4-6)] systems. Herein, the author reports the synthesis of two complexes having RuN₅S and RuN₅O chromophores, their spectroscopic characterisation, electron-transfer properties, preliminary photophysical aspects.

EXPERIMENTAL

Materials and physical measurements

Published methods were used to prepare ctc-RuCl₂(RaaiR)₂, ctc-[Ru(OH)₂(RaaiR)₂](ClO₄)₂, (Bag et al., 1988). Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 spectrophotometer. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm⁻¹). The H nmr spectra in CDCl₃ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using SiMe₄ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration 10 M in acetonitrile. Electrochemical work was carried out using an EG and G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N₂ atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs⁻¹. All results were referenced to a saturated calomel electrode (SCE).

Preparation of the complexes

Preparation of 2-mercaptopyridine-bis-{2-(*p*-tolylazopyrimidine)ruthenium(II), [Ru(RaaiR)₂(SHPy)]

Initially a solution of [Ru(RaaiR')₂(EtOH)₂]²⁺ was prepared by stirring under reflux condition, a mixture of Ru(RaaiR')₂Cl₂ (100 mg, 0.186 mmol) and AgNO₃ (79 mg, 0.465 mmol) in dry ethanol (20 cm³) for 1 h and removing the AgCl precipitate. To the filtrate were added 2 mercaptopyridine (65 mg, 0.471 mmol) and NaOMe (38 mg, 0.95 mmol) and the solution was heated to reflux for 12 h under a dinitrogen atmosphere, during which time changed from purple to blue-violet. The solvent was then removed under reduced pressure and the solid mass thus obtained purified by using a alumina (neutral) column. A red-violet band corresponding was eluted with acetonitrile. On evaporation, the solid complex was obtained in 72% yield (81 mg). Finally, the product was recrystallised from 1:4 v/v dichloromethane–light petroleum. Analysis for [Ru(S-Pyridine)(HaaiMe)₂](ClO₄), (**1a**), Found: C, 43.98, H, 3.6, N, 18.4, Calcd for [C₂₅H₂₄N₉SRu](ClO₄), C, 43.93, H, 3.5, N, 18.8, IR ν(N=N) 1379, ν(C=N) 1598, ν(S-Py) 1600,1450, ESIMS, 682.5[M⁺], 583[M-ClO₄]; ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10), 134(C6); Analysis for [Ru(S-Pyridine)(MeaaiMe)₂](ClO₄), (**1b**), Found: C, 45.98, H, 3.9, N, 17.74, Calcd for [C₂₇H₂₈N₉SRu](ClO₄), C, 45.93, H, 3.9, N, 17.8, IR ν(N=N) 1370, ν(C=N) 1590, ν(S-Py) 1600,1450, ESIMS, 710.5[M⁺], 611[M-ClO₄]; Analysis for [Ru(S-Pyridine)(ClaaiMe)₂](ClO₄), (**1c**), Found: C, 39.98, H, 2.96, N, 16.84, Calcd for [C₂₅H₂₂N₉SRuCl₂](ClO₄), C,

39.93, H, 2.5, N, 16.8, IR $\nu(\text{N}=\text{N})$ 1370, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{S-Py})$ 1600,1459, ESIMS, 751.5[M⁺], 652[M-CIO₄]; Analysis for [Ru(S-Pyridine)(HaaiEt)₂](ClO₄), (**2a**), Found: C, 45.98, H, 3.9, N, 17.74, Calcd for [C₂₇H₂₈N₉SRu](ClO₄), C, 45.93, H, 3.9, N, 17.8, IR $\nu(\text{N}=\text{N})$ 1370, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{S-Py})$ 1600,1450, ESIMS, 710.5[M⁺], 611[M-CIO₄]; Analysis for [Ru(S-Pyridine)(MeaaiMe)₂](ClO₄), (**2b**), Found: C, 47.18, H, 4.39, N, 17.14, Calcd for [C₂₉H₃₂N₉SRu](ClO₄), C, 47.93, H, 4.3, N, 17.18, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1599, $\nu(\text{S-Py})$ 1609, 1450, ESIMS, 738.5[M⁺], 639[M-CIO₄]; Analysis for [Ru(S-Pyridine)(ClaaiEt)₂](ClO₄), (**2c**), Found: C, 41.68, H, 3.39, N, 16.24, Calcd for [C₂₇H₂₆N₉SRuCl₂](ClO₄), C, 41.63, H, 3.3, N, 16.28, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1597, $\nu(\text{S-Py})$ 1607,1450, ESIMS, 779.5[M⁺], 680[M-CIO₄]; Analysis for [Ru(S-Pyridine)(HaaiBz)₂](ClO₄), (**3a**), Found: C, 53.28, H, 3.9, N, 15.14, Calcd for [C₃₇H₃₂N₉SRu](ClO₄), C, 53.23, H, 3.9, N, 15.18, IR $\nu(\text{N}=\text{N})$ 1371, $\nu(\text{C}=\text{N})$ 1599, $\nu(\text{S-Py})$ 1600,1450, ESIMS, 834.5[M⁺], 735[M-CIO₄]; Analysis for [Ru(S-Pyridine)(MeaaiBz)₂](ClO₄), (**3b**), Found: C, 54.38, H, 4.29, N, 14.74, Calcd for [C₃₉H₃₆N₉SRu](ClO₄), C, 54.39, H, 4.19, N, 14.8, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{S-Py})$ 1609,1450, ESIMS, 862.5[M⁺], 763[M-CIO₄]; Analysis for [Ru(S-Pyridine)(ClaaiBz)₂](ClO₄), (**3c**), Found: C, 49.18, H, 3.3, N, 13.74, Calcd for [C₃₇H₃₀N₉SRuCl₂](ClO₄), C, 49.13, H, 3.3, N, 13.8, IR $\nu(\text{N}=\text{N})$ 1373, $\nu(\text{C}=\text{N})$ 1593, $\nu(\text{S-Py})$ 1603,1450, ESIMS, 903.5[M⁺], 804[M-CIO₄].

Preparation of 2-hydroxypyridine-bis-(2-(p-tolylazopyrimidine)ruthenium(II), [Ru(RaaiR')₂(OHPy)]

Initially, a solution of [Ru(RaaiR')₂(EtOH)₂]²⁺ was prepared by stirring under reflux condition, a mixture of Ru(RaaiR')₂Cl₂ (100 mg, 0.186 mmol) and AgNO₃ (79 mg, 0.465 mmol) in dry ethanol (20 cm³) for 1 h and removing the AgCl precipitate. To the filtrate were added 2 hydroxypyridine (65 mg, 0.471 mmol) and NaOMe (38 mg, 0.95 mmol) and the solution was heated to reflux for 12 h under a dinitrogen atmosphere, during which time changed from purple to blue-violet. The solvent was then removed under reduced pressure and the solid mass thus obtained purified by using a alumina (neutral) column. A red-violet band corresponding was eluted with acetonitrile. On evaporation, the solid complex was obtained in 72% yield (81 mg). Finally the product was recrystallised from 1: 4 v/v dichloromethane-light petroleum. Analysis for [Ru(O-Pyridine)(HaaiMe)₂](ClO₄), (**4a**), Found: C, 43.98, H, 3.6, N, 18.4, Calcd for [C₂₅H₂₄N₉ORu](ClO₄), C, 43.93, H, 3.5, N, 18.8, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1598, $\nu(\text{O-Py})$ 1600,1450, ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10), 134(C6); Analysis for [Ru(O-Pyridine)(MeaaiMe)₂](ClO₄), (**4b**), Found: C, 45.98, H, 3.9, N, 17.74, Calcd for [C₂₇H₂₈N₉ORu](ClO₄), C, 45.93, H, 3.9, N, 17.8, IR $\nu(\text{N}=\text{N})$ 1370, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{O-Py})$ 1600,1450, ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10), 134(C6); Analysis for [Ru(O-Pyridine)(ClaaiMe)₂](ClO₄), (**4c**), Found: C, 39.98, H, 2.96, N, 16.84, Calcd for [C₂₅H₂₂N₉ORuCl₂](ClO₄), C, 39.93, H, 2.5, N, 16.8, IR $\nu(\text{N}=\text{N})$ 1370, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{O-Py})$ 1600,1459, ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C7,11), 129(C8,10), 134(C6); Analysis for [Ru(O-Pyridine)(HaaiEt)₂](ClO₄), (**5a**), Found: C, 45.98, H, 3.9, N, 17.74, Calcd for [C₂₇H₂₈N₉ORu](ClO₄), C, 45.93, H, 3.9, N, 17.8, IR $\nu(\text{N}=\text{N})$ 1370, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{O-Py})$ 1600,1450, Analysis for [Ru(O-Pyridine)(MeaaiMe)₂](ClO₄), (**5b**), Found: C, 47.18, H, 4.39, N, 17.14, Calcd for [C₂₉H₃₂N₉ORu](ClO₄), C, 47.93, H, 4.3, N, 17.18, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1599, $\nu(\text{O-Py})$ 1609,1450, Analysis for [Ru(O-Pyridine)(ClaaiEt)₂](ClO₄), (**5c**), Found: C, 41.68, H, 3.39, N, 16.24, Calcd for [C₂₇H₂₆N₉ORuCl₂](ClO₄), C, 41.63, H, 3.3, N, 16.28, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1597, $\nu(\text{O-Py})$ 1607,1450, Analysis for [Ru(O-Pyridine)(HaaiBz)₂](ClO₄), (**6a**), Found: C, 53.28, H, 3.9, N, 15.14,

Calcd for [C₃₇H₃₂N₉ORu](ClO₄), C, 53.23, H, 3.9, N, 15.18, IR $\nu(\text{N}=\text{N})$ 1371, $\nu(\text{C}=\text{N})$ 1599, $\nu(\text{O-Py})$ 1600,1450, ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10); Analysis for [Ru(O-Pyridine)(MeaaiBz)₂](ClO₄), (**6b**), Found: C, 54.38, H, 4.29, N, 14.74, Calcd for [C₃₉H₃₆N₉ORu](ClO₄), C, 54.39, H, 4.19, N, 14.8, IR $\nu(\text{N}=\text{N})$ 1379, $\nu(\text{C}=\text{N})$ 1590, $\nu(\text{O-Py})$ 1609,1450, Analysis for [Ru(O-Pyridine)(ClaaiBz)₂](ClO₄), (**6c**), Found: C, 49.18, H, 3.3, N, 13.74, Calcd for [C₃₇H₃₀N₉ORuCl₂](ClO₄), C, 49.13, H, 3.3, N, 13.8, IR $\nu(\text{N}=\text{N})$ 1373, $\nu(\text{C}=\text{N})$ 1593, $\nu(\text{O-Py})$ 1603,1450, ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10);

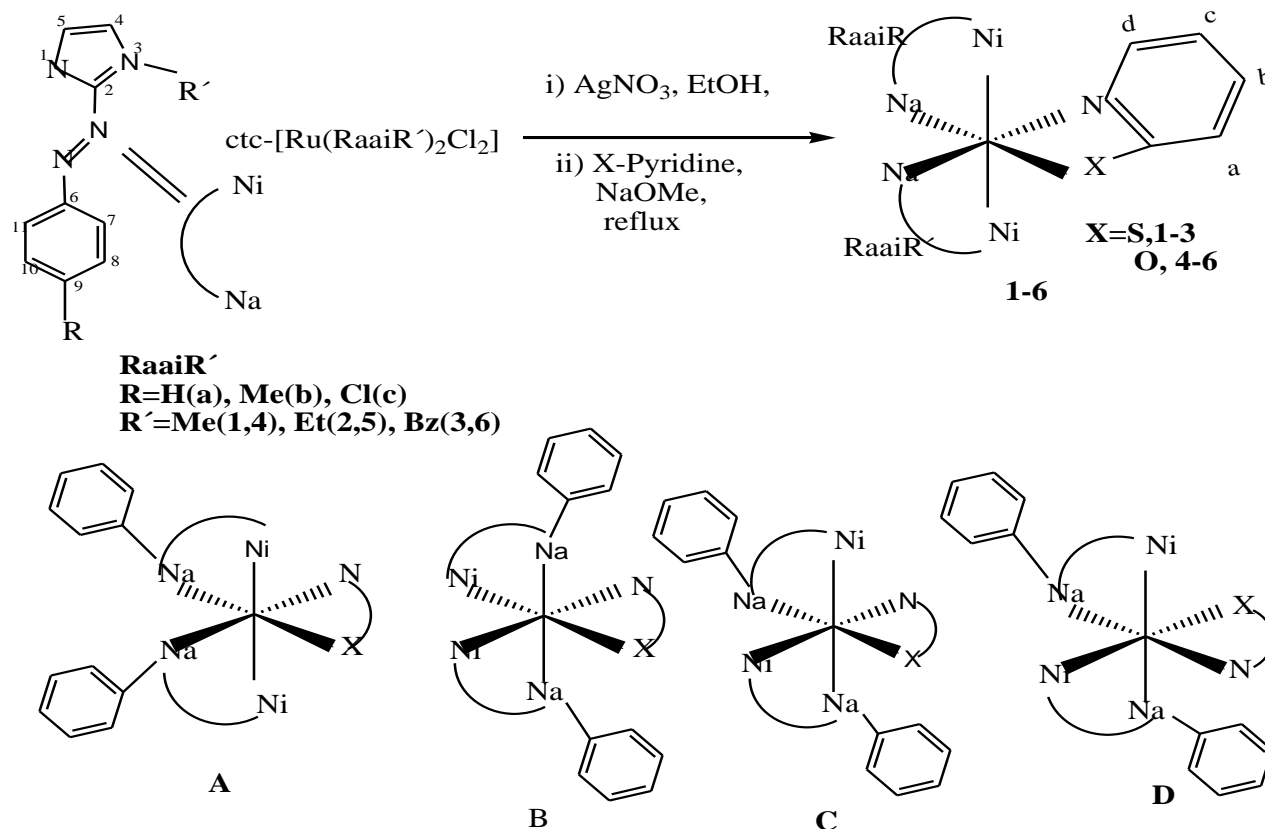
RESULTS AND DISCUSSION

Synthesis and formulation

The two ligands pyridine-2-thiol and pyridin-2-ol are good chelating and the anionic forms of the ligands (L) bind to the metal ion in a bidentate N,S and N,O manner respectively forming four-membered chelate rings. The complex [Ru(RaaiR')₂(X-Pyridine)], **1-6**, [RaaiR'=*p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', (**1-6**), abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H (*a*), Me (*b*), Cl (*c*) and R' = Me (**1,4**), CH₂CH₃ (**2,5**), Bz(**3,6**), X=S, 2-mercaptopyridine(**1-3**), X=O, 2-hydroxy-pyridine(**4-6**)] has been synthesized from [Ru(RaaiR')₂Cl₂] following the synthetic route shown in Scheme 1 (Bhattacharya et al., 1993). The complex cation was precipitated directly from the reaction mixture as its perchlorate salt. The yield of the complexes was approximately 80% in each case. The unsymmetric nature of X-Pyridine functions lead to the possibility of coexistence of four geometrical isomers (**A-D**). However, the reported complexes incorporating the Ru(RaaiR')₂ moiety, it may be assumed that the reactions in Scheme 1 also follow the stereoretentive pathway (structure **A**). The complexes are soluble in both polar and non-polar solvents and slightly in water. Their microanalytical data are in good agreement with the calculated values and thus confirm the composition of the mixed-ligand tris-chelates. The complexes act as 1: 1 electrolytes in acetonitrile solution. Solid-state magnetic moment measurements at room temperature show that the monocations **1** and **2** are diamagnetic (t_{2g}^6 , idealised, S=0) (Tokel-Takvoryan et al., 1973).

Spectral and redox study

The Fourier-transform IR spectra for the complexes were recorded as KBr discs in the range 4000–400 cm⁻¹ and display several sharp bands of different intensities. A very strong and broad band near 1100 cm⁻¹ and a strong and sharp vibration band near 630 cm⁻¹ are observed for both complexes due to the presence of ionic perchlorate (Goswami et al., 1983). The other expected vibrations due to arylazoimidazole and X-Pyridine are systematically



Scheme 1. Synthetic route.

present in the spectra and are therefore not specifically reported here (Ghosh et al., 2013). Solution electronic spectra of the complexes were studied in acetonitrile solvent in the UV/VIS region (200 to 700 nm). Multiple absorptions may arise due to the presence of different acceptor levels in the complexes. Complex 1-3 exhibits one band at 510 nm associated with a shoulder at 456 nm and another band near 350 nm (Tables 1 and 2) (Rao et al., 1996). In the visible region the spectrum of complexes, 4-6 is virtually identical to that of 1-3, except the lowest-energy band does not have an associated shoulder and the bands are slightly blue shifted. The bands in the UV region are of intra-ligand ($p-p^*$) type or charge-transfer transitions involving levels which are higher in energy than those of the ligand lowest unoccupied molecular orbital (LUMO). The ^1H NMR spectra of the complexes 1-6 were recorded in CDCl_3 solvent (Tables 3 and 4). The presence of the unsymmetric X-Pyridine group in **1-6** makes all the five aromatic rings non-equivalent. The ^{13}C NMR spectra (measured in CDCl_3) of (**1-6**) complexes were done to assign molecular skeleton. The electron-transfer properties of both complexes have been studied by cyclic voltammetry in acetonitrile solvent. All the

potentials are referenced to the saturated calomel electrode (SCE) (Byabartta et al., 2002; Byabartta et al., 2001; Byabartta et al., 2003; Santra et al., 2002; Jasimuddin et al., 2004). Both complexes are electroactive with respect to the metal as well as the ligand centres and display the same four redox processes in the potential range ± 2 V at 298 K. The assignments of the responses to specific couples are based on the following considerations. Complexes exhibit one quasi-reversible oxidative response with E_{298} values of 0.54 and 0.64 V, respectively. The anodic and cathodic peak heights are approximately equal and vary with the square root of the scan rate. The peak potentials E_{pa} and E_{pc} are virtually independent of the scan rate. This quasi-reversible oxidative process is assigned to the ruthenium(III)-ruthenium(II) couple:

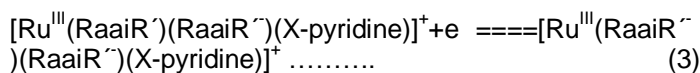
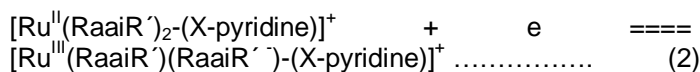
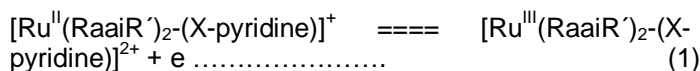


Table 1. Cyclic Voltammetric^b and UV-Vis^a spectral data of , [Ru^{II}(RaaiR')₂-(S-pyridine)],1.

Compd	Ru ^{II} -Ru ^{III} Couple-I	Ru ^{IV} -Ru ^{III} Couple-II	RaaiR' Couple-III	RaaiR' Couple-IV	UV-Vis [λ_{\max} (nm) (10 ⁻³ ϵ /dm mol ⁻¹ cm ⁻¹)]
(1a)	0.50(90)	1.37(140)	-1.61(80)	-1.91(90)	510(10200), 456(3908) ^d , 346(11566), 294(46709), 245(30222), 215(21333)
(1b)	0.51(90)	1.31(130)	-1.63(80)	-1.94(90)	512(10200), 452(3922) ^d , 342(11226), 292(46229), 242(30222), 212(21333)
(1c)	0.50(90)	1.37(140)	-1.61(80)	-1.91(90)	510(10200), 456(3908) ^d , 346(11566), 294(46709), 245(30222), 215(21333)

Table 2. Cyclic Voltammetric^b and UV-Vis^a spectral data of , [Ru^{II}(RaaiR')₂-(O-pyridine)],4.

Compd	Ru ^{II} -Ru ^{III} Couple-I	Ru ^{IV} -Ru ^{III} Couple-II	RaaiR' Couple-III	RaaiR' Couple-IV	UV-Vis [λ_{\max} (nm) (10 ⁻³ ϵ /dm mol ⁻¹ cm ⁻¹)]
(4a)	0.64(100)	1.03(150)	-1.57(90)	-1.92(90)	500(6100), 338(10500), 292(49500), 245(26100), 218(21250)
(4b)	0.61(100)	1.01(140)	-1.51(90)	-1.91(90)	501(6100), 331(10500), 291(49110), 241(26101), 211(21150)
(4c)	0.64(100)	1.03(150)	-1.57(90)	-1.92(90)	500(6100), 338(10500), 292(49500), 245(26100), 218(21250)

^aSolvent dry MeCN; ^dshoulder; ^bSolvent dry MeCN, supporting electrolyte [nBu₄N][ClO₄] (0.1M), w.e. Pt-disk, a.e. Pt-wire, r.e. SCE, solute conc. $\sim 10^{-3}$ M, scan rate 50 mVs⁻¹, $\Delta E_p = |E_{pa} - E_{pc}|$ where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

Table 3. ¹H-n.m.r. spectral data, δ (J/Hz), ppm in CDCl₃ of the complexes, 1-3.

Compd	aH ^c	bH ^d	cH ^d	4-H ^c	5-H ^c	7,11-H ^c	8,10-H	N-CH ₃	N-CH ₂	dH ^e
(1a) ^a	8.52(5)	8.81(7)	8.63(4)	7.55(7.5)	7.46 (7.5)	8.03 (8.1)	7.75 (8.1) ^d	2.09 ^f		8.4(9)
(1b)	8.62(7)	8.81(7)	8.73(8)	7.58 (7.5)	6.96 (7.5)	8.07 (8.1)	7.84 (8.1) ^c	2.17 ^f		8.3(3)
(1c)	8.52(5)	8.81(7)	8.63(4)	7.3 (8.1)	7.42 (8.1)	8.05 (7.8)	7.85 (7.8) ^c	2.16 ^f		8.4(5)
(2a) ^a	8.22(5)	8.91(8)	8.63(9)	7.4 (7.5)	7.00 (7.5)	8.01 (7.8)	7.75 (8.1) ^d	1.52(8.1) ^d	4.65(10.0) ^e	8.1(9)
(2b)	8.52(5)	8.81(7)	8.63(4)	7.53 (8.1)	7.24 (8.1)	8.01 (7.5)	7.72 (7.5) ^c	1.58(8.1) ^d	4.56(10.0) ^e	8.4(3)
(2c)	8.52(5)	8.41(3)	8.13(5)	7.34 (8.1)	7.36 (8.1)	8.04 (7.5)	7.76 (7.5) ^c	1.55(8.1) ^d	4.53(11.0) ^e	8.1(9)
(3a) ^a	8.52(5)	8.81(7)	8.63(4)	7.53 (8.1)	7.24 (8.1)	8.01 (7.5)	7.72 (7.5) ^c	1.58(8.1) ^d	5.26(10.0) ^e	8.4(3)
(3b)	8.52(5)	8.81(7)	8.63(4)	7.53 (8.1)	7.24 (8.1)	8.01 (7.5)	7.72 (7.5) ^c	1.58(8.1) ^d	5.56(8.0) ^e	8.4(3)
(3c)	8.52(5)	8.81(7)	8.63(4)	7.53 (8.1)	7.24 (8.1)	8.01 (7.5)	7.72 (7.5) ^c	1.58(8.1) ^d	5.56(10.0) ^e	8.4(3)

^a δ (9-H) 7.45 ppm(m); ^b δ (9-Me); ^c doublet; ^d triplet; ^e AB type sextet, geminal coupling constant; ^f 1-Me, singlet.

Equation (1) is the one-electron nature of this process for both complexes was confirmed by

constant-potential coulometry. The complexes have an identical RuN₅ core but the sixth co-

ordination sites in nine cases are a thiolato group and in the other it is a phenolato group.

Table 4. ¹H-n.m.r. spectral data, δ (J/Hz), ppm in CDCl₃ of the complexes, 4-6.

Compd	aH ^c	bH ^d	cH ^d	4-H ^c	5-H ^c	7,11-H ^c	8,10-H	N-CH ₃	N-CH ₂	dH ^c
(4a) ^a	8.42(5.8)	8.84(7)	8.64(4)	7.54(7.5)	7.44(7.5)	8.04(8.1)	7.75(8.1) ^d	2.09 ^f		8.4(9)
(4b)	8.62(7)	8.81(7)	8.73(8)	7.58(7.5)	6.96(7.5)	8.07(8.1)	7.84(8.1) ^c	2.17 ^f		8.3(6.6)
(4c)	8.54(5.7)	8.84(7)	8.64(4)	7.3 4(8.1)	7.42(8.1)	8.05(7.8)	7.85(7.8) ^c	2.14 ^f		8.4(5)
(5a) ^a	8.22(5)	8.91(8)	8.62(9)	7.42(7.5)	7.02(7.5)	8.04(7.8)	7.75(8.1) ^d	1.52(8.1) ^d	4.65 (10.0) ^e	8.1(9)
(5b)	8.52(5.5)	8.81(7.2)	8.63(4.9)	7.52(8.1)	7.24(8.1)	8.01(7.5)	7.72(7.5) ^c	1.58(8.1) ^d	4.56 (10.0) ^e	8.4(7.9)
(5c)	8.52(5)	8.41(6.2)	8.13(5.9)	7.34(8.1)	7.36(8.1)	8.04(7.5)	7.76(7.5) ^c	1.55(8.1) ^d	4.53 (11.0) ^e	8.1(9)
(6a) ^a	8.52(5.2)	8.81(7.7)	8.63(4.7)	7.53(8.1)	7.24(8.1)	8.01(7.5)	7.72(7.5) ^c	1.58(8.1) ^d	5.26 (10.0) ^e	8.4(3)
(6b)	8.52(5)	8.81(7)	8.63(4)	7.53(8.1)	7.24(8.1)	8.01(7.5)	7.72(7.5) ^c	1.58(8.1) ^d	5.26 (8.0) ^e	8.4(6.6)
(6c)	8.52(5.5)	8.81(7.6)	8.63(4.8)	7.53(8.1)	7.24(8.1)	8.01(7.5)	7.72(7.5) ^c	1.58(8.1) ^d	5.26 (10.0) ^e	8.4(7.7)

^a δ (9-H) 7.45 ppm(m); ^b δ (9-Me); ^c doublet; ^d triplet; ^e AB type sextet, geminal coupling constant; ^f 1-Me, singlet.

The monoanionic thiolate and phenolate ligands reduce the overall charge of the complex cation. The complexes display a second quasi-reversible oxidation above 1 V. For the thiolato complex 1, it appears near 1.41 V and for the phenolato complex near 1.03 V.

The one-electron nature of this oxidation process for both complexes is confirmed by direct comparison of the current height of these second processes with those of the previous one-electron Ru^{III}/Ru^{II} reduction process. Both complexes display two successive reversible one-electron reductions near -1.6 and -1.9 V (Tables 1 and 2). The ligand X-Pyridine does not exhibit any ligand reduction within the above-mentioned potential region.

Thus, the above reductions are assigned to the co-ordinated arylazoimidazole ligands. Complexes contain two ligands so that four successive reductions are expected from each.

In practice two, one-electron reductions have been observed for each complex, which are assigned to the azoimine groups of the co-ordinated RaaiR ligands as shown in Equations (2) and (3).

Conclusion

The present work demonstrates X-Pyridine function leading to the formation of a new class of coordinated complex. The complexes are well characterised by UV-Vis, i.r., ¹H n.m.r., C.V and ESI mass spectrometry. The complexes systematically exhibit two oxidation processes and two successive one-electron reductions. The stepwise electrochemical oxidations indicate that the initial one-electron oxidation process corresponds to stereoretentive oxidation of the ruthenium(II) centre to ruthenium(III).

Conflict of Interest

The authors have not declared any conflict of interest.

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