ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 8, pp. 582–587. © Pleiades Publishing, Ltd., 2009.

1,10-(Phenanthroline)-bis{1-Alkyl-2-(Arylazo)Imidazole} Ruthenium(II) Perchlorate: Synthesis, Spectral Study, and Electrochemistry[1]

P. Byabartta

Department of Inorganic Chemistry-ICMA, University of Zaragaza-CSIC, Zaragaza 50009, Spain
GIST, ICARE, Complex Haldia Institute Technology, Haliberia, Haldia 721657, India
E-mail: prithwis33@yahoo.com; pribatta@rediffmail.com

Received June 30, 2008

Abstract—The hetero-tris-chelates of the formula $[Ru(Phen)(RAaiR')_2](ClO_4)_2$ (Phen = 1,10-phenanthroline, RAaiR' = 1-alkyl-2-(arylazo)imidazole, *p*-R-C_6H_4–N=N–C_3H_2–NN-1-R', where R = H (a), Me (b), Cl (c) and R' = Me (II), Et (III), CH_2Ph (IV)) have been isolated from the reaction of *ctc*-$[RuCl_2(RAaiR')_2]$ with $AgNO_3$ + Phen or $[Ag(Phen)_2](ClO_4)$ in acetone at 40°C in dark followed by the addition of $NaClO_4$ (aq). The stereo-chemistry of the complexes have been supported by ^1H NMR data. Considering the arylazoimidazole and phenanthroline moietie there are twenty different carbon atoms in the molecule which gives a total of twenty different peaks in the ^{13}C NMR spectrum of complex Ia. Cyclic voltammograms show Ru(III)/Ru(II) couple at 1.3–1.4 V *vs* SCE along with three successive ligand reductions.

DOI: 10.1134/S1070328409080053

INTRODUCTION

Complexes of Ru(II) with polypyridine ligands have been extensively studied because of their potential industrial applications [1–4]. Since the peculiar photochemical properties of $[Ru(Bipy)_3]^{2+}$ (Bipy = 2,2'-bipyridine) were discovered almost 30 years ago, much effort has been devoted to enhancing the properties of those systems via different functions of the polypyridine ligands or their derivatives with different molecules such as cyanide and dimethyl sulfoxide. The chemistry of 2,2',6',2''-terpyridine (**Terpy**) complexes has also significantly expanded in recent years, and particular attention has been focused on ruthenium(II) complexes because of their attractive photochemical and electrochemical properties. The present work is concerned with the heteroleptic tris-chelates of bis-chelated ruthenium(II)–1-alkyl-2-(arylazo)imidazole and bipyridine. Arylazoimidazole (**RAaiR'**) chemistry of ruthenium(II) are known in some detail from our group [3–9]. Dichloro-bis-(arylazoimidazole)ruthenium(II), $[RuCl_2(RAaiR')_2]$ may exist in five geometrical isomeric forms and two of them have been structurally characterised. RAaiR' bear unsymmetric azoimine (–N=N–C=N–) chelating group and the donor centres are abbreviated N(imidazole) as N and N(azo) as N'. With consideration of coordination pairs [2, 10–12] in sequence of Cl, Cl; N, N and N', N' the structurally characterised isomers are *trans-cis-cis* (***tcc***) and *cis-trans-cis* (***ctc***) $RuCl_2(RAaiR')_2$. The isomer *tcc* carries *trans*-$RuCl_2$ and *ctc* carries *cis*-$RuCl_2$ motif. The Ru–Cl bond in the complexes of *cis*-$RuCl_2$ configuration (*ctc* isomer) is kinetically labile than the complexes of *trans*-$RuCl_2$ configuration (*tcc* isomer) [5, 9]. Dechlorination is accelerated by Ag^+ and thus solvated species $[Ru(RAaiR')_2(S)_2]^{2+}$ is formed [4–7]. The solvated species may undergo different reactions viz., nucleophilic substitution, formation of oxo species, polynuclear complex formation [11]. In the present work, the hetero-tris-chelates $[Ru(Phen)(RAaiR')_2](ClO_4)_2$ (Phen = 1,10-phenanthroline, RAaiR' = 1-alkyl-2-(arylazo)imidazole, *p*-R–C_6H_4–N=N–C_3H_2–NN-1-R', where R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**II**), Et (**III**), CH_2Ph (**IV**)) were syntheized and charecterised by CHN analysis, IR, multinuclear NMR study and electrochemistry.

EXPERIMENTAL

Materials and physical measurements. Published methods were used to prepare RAaiR', *ctc*-$[RuCl_2(RAaiR')_2]$, *ctc*-$[Ru(H_2O)_2(RAaiR')_2](ClO_4)_2$ [3–6]. All other chemicals and organic solvents used for preparative work were of reagent grade. The purification of MeCN and preparation of tetrabutylammonium perchlorate $[Bu_4N][ClO_4]$, respectively, used as solvent and supporting electrolyte were done by the following methods [7, 8]. Microanalyses (C, H, N) were performed using a PerkinElmer 2400 CHNO/S elemental analyzer. Spectroscopic measurements were carried out

[1] The article is published in the original.

using the following instruments: UV-VIS spectra, reflectance spectra, JASCO UV-VIS/NIR model V-570; IR spectra (KBr disk, 200–4000 cm^{-1}), JASCO FT-IR model 420. Room temperature magnetic moment was measured using vibrating sample 155 magnetometer at 298 K. Electrochemical measurements were carried out with the use of computer controlled EG & G PARC VersaStat model 250 electrochemical instrument using a Pt-disk working electrode. The reported results are referenced to Ag/AgCl,Cl^- in acetonitrile and are uncorrected for junction potential. Dichloro-bis-{1-alkyl-2-(arylazo)imidazole}ruthenium(II) complexes of *ctc* configuration (**I**) have been used as the precursor complex.

Preparation of (1,10-phenanthroline)-bis-{1-methyl-2-(phenylazo)imidazole}ruthenium(II) perchlorate [Ru(Phen)(HAaiMe)$_2$](ClO$_4$)$_2$ (IIa). To a suspension of *ctc*-$RuCl_2(HAaiMe)_2$ (0.2 g, 0.24 mmol) in acetone (25 ml) was added an aqueous solution of $AgNO_3$ (0.08 g, 0.48 mmol) and refluxed for 15 min, AgCl so precipitated was filtered off over a G4 crucible. Acetone solution (10 ml) of Phen (0.04 g, 0.24 mmol) was then added and the resulting mixture was stirred at 40°C in dark for 12 h under nitrogen. The solution was then evaporated to half its original volume by nitrogen bubbling and an aqueous solution of $NaClO_4$ (~1 g in 20 ml water) was added. The brown precipitate then obtained was filtered and dried in vacuum over P_4O_{10}. The dry mass was then dissolved in minimum volume of CH_2Cl_2 and subjected to chromatography on a silica gel column (60–120 mesh). A reddish brown band was eluted with C_7H_8–CH_3CN (1 : 1, v/v). This was collected and slowly evaporated in air. Crystals were collected in 70% yield (0.22 g). Other complexes (**IIb**, **IIc**, **IIIa**, **IIIb**, **IIIc**, **IVa**, **IVb**, **IVc**) were also prepared in accordance to the above general process and yields varied from 60–75%.

^{13}C NMR of $[Ru(Phen)(HAaiMe)_2]^{2+}$ (**IIa**) δ, ppm: 134.12 C(9), 131.76 C(8), 135.67 C(7), 137.68 C(11), 131.9 C(10), 156.7 C(2), 150.9 C(6), 131.9 C(4), 133.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 36 C(Me), IR spectra (cm^{-1}): 1375 ν(N=N), 1590 ν(C=N), 1080, 620 $\nu(ClO_4)$, 1600 ν(C=C), 3110 ν(C–H).

^{13}C NMR of $[Ru(Phen)(MeAaiMe)_2]^{2+}$ (**IIb**) δ, ppm: 132.12 C(9), 131.76 C(8), 133.67 C(7), 137.68 C(11), 131.9 C(10), 153.7 C(2), 150.9 C(6), 133.9 C(4), 133.6 C(5), 153.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 153 C(f), 150 C(g), 152 C(h), 33 C(Me), IR spectra (cm^{-1}): 1375 ν(N=N), 1590 ν(C=N), 1080, 620 $\nu(ClO_4)$, 1600 ν(C=C), 3110 ν(C–H).

^{13}C NMR of $[Ru(Phen)(ClAaiMe)_2]^{2+}$ (**IIc**) δ, ppm: 154.12 C(9), 131.76 C(8), 135.67 C(7), 137.68 C(11), 131.9 C(10), 156.7 C(2), 150.9 C(6), 131.9 C(4), 133.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 34 C(Me); IR spectra (cm^{-1}): 1375 ν(N=N), 1590 ν(C=N), 1089, 629 $\nu(ClO_4)$, 1609 ν(C=C), 3110 ν(C–H).

^{13}C NMR of $[Ru(Phen)(HAaiEt)_2]^{2+}$ (**IIIa**) δ, ppm: 134.12 C(9), 133.76 C(8), 135.67 C(7), 137.68 C(11), 131.9 C(10), 156.7 C(2), 151.9 C(6), 131.9 C(4), 132.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 134 C(d,d'), 150 C(e), 151 C(f), 153 C(g), 152 C(h), 44.39 C(Et); IR spectra (cm^{-1}): 1375 ν(N=N), 1590 ν(C=N), 1088, 623 $\nu(ClO_4)$, 1603 ν(C=C), 3113 ν(C–H).

^{13}C NMR of $[Ru(Phen)(MeAaiEt)_2]^{2+}$ (**IIIb**) δ, ppm: 134.12 C(9), 131.76 C(8), 135.67 C(7), 137.68 C(11), 131.9 C(10), 156.7 C(2), 150.9 C(6), 131.9 C(4), 133.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 33.45 C(Et); IR spectra (cm^{-1}), 1371 ν(N=N), 1593 ν(C=N), 1081, 621 $\nu(ClO_4)$, 1601 ν(C=C), 3111 ν(C–H).

^{13}C NMR of $[Ru(Phen)(ClAaiEt)_2]^{2+}$ (**IIIc**) δ, ppm: 134.12 C(9), 131.76 C(8), 135.67 C(7), 137.68 C(11), 131.9 C(10), 156.7 C(2), 150.9 C(6), 131.9 C(4), 133.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 37.46 C(Et); IR spectra (cm^{-1}): 1371 1591 ν(N=N), ν(C=N), 1081, 621 $\nu(ClO_4)$, 1601 ν(C=C), 3110 ν(C–H).

^{13}C NMR of $[Ru(Phen)(HAaiBz)_2]^{2+}$ (**IVa**) δ, ppm: 131 C(9), 131 C(8), 135.6 C(7), 137.6 C(11), 131.9 C(10), 156.7 C(2), 150.9 C(6), 131.9 C(4), 133.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 45, 130–132 C(Bz); IR spectra (cm^{-1}): 1375 ν(N=N), 1591 ν(C=N), 1080, 621 $\nu(ClO_4)$, 1601 ν(C=C), 3111 ν(C–H).

^{13}C NMR of $[Ru(Phen)(MeAaiBz)_2]^{2+}$ (**IVb**) δ, ppm: 134 C(9), 131 C(8), 135.6 C(7), 137.6 C(11), 131.9 C(10), 156.7 C(2), 150.9 C(6), 131.9 C(4), 133 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,dí), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 44.130 133 C(Bz); IR spectra (cm^{-1}): 1375 ν(N=N), 1590 ν(C=N), 1080, 620 $\nu(ClO_4)$, 1600 ν(C=C), 3110 ν(C–H).

^{13}C NMR of $[Ru(Phen)(ClAaiBz)_2]^{2+}$ (**IVc**) δ, ppm: 144 C(9), 131 C(8), 135. C(7), 137.68 C(11), 131.9 C(10), 156.7 C(2), 150 C(6), 131.9 C(4), 133.6 C(5), 151.6 C(a,a'), 141 C(b,b'), 139 C(c,c'), 133 C(d,d'), 150 C(e), 151 C(f), 150 C(g), 152 C(h), 43, 130–133 C(Bz); IR spectra (cm^{-1}): 1375 ν(N=N), 1590 ν(C=N), 1080, 620 $\nu(ClO_4)$, 1600 ν(C=C), 3110 ν(C–H).

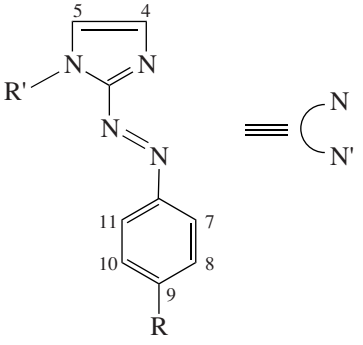
RESULTS AND DISCUSSION

RAaiR' is an unsymmetric N,N'-chelating ligand (N(imidazole) refers to N and N(azo) refers to N'). The Scheme of preparation of complexes is shown below:

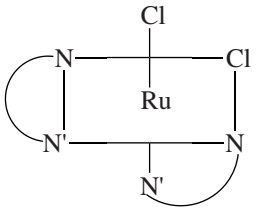
$$ctc\text{-}RuCl_2(RAaiR')_2 \xrightarrow{AgNO_3(aq.),\ acetone} \rightarrow ctc\text{-}[Ru(acetone)_2(RAaiR')_2](NO_3)_2 + 2AgCl\downarrow, \quad (1)$$

$$ctc\text{-}[Ru(acetone)_2(RAaiR')_2](NO_3)_2 \xrightarrow{40^\circ C/dark,\ Phen,\ NaClO_4(aq.)} [Ru(Phen)(RAaiR')_2](ClO_4)_2, \quad (2)$$

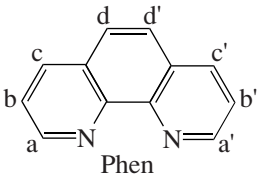
$$ctc\text{-}RuCl_2(RAaiR')_2 + [Ag(Phen)_2(ClO_4)] \xrightarrow{Acetone,\ 40^\circ C,\ NaClO_4} \longrightarrow [Ru(Phen)(RAaiR')_2](ClO_4)_2 + Phen + 2AgCl\downarrow, \quad (3)$$



RAaiR'



ctc-$Ru(RAaiR')_2Cl_2$ (**I**)



Phen

R = H (a), CH_3 (b), Cl (c); R' = $^{12}CH_3$ (**II**), $^{12}CH_2$–$^{13}CH_3$(**III**), $^{12}CH_2$–Ph (14H–18H) (**IV**).

The stereochemistry has been specified with reference to the coordination pairs of Cl, Cl; N, N; and N', N', respectively. Upon addition of $AgNO_3$ (aq.) to acetone solution of *ctc*-$RuCl_2(RAaiR')_2$ has eliminated Cl^- and gives $[Ru(acetone)_2(RAaiR')_2]^{2+}$. The reaction of Phen with $[Ru(acetone)_2(RAaiR')_2]^{2+}$ on stirring condition at 40°C in dark for a period of 3 days isolated heteroleptic tris-chelates as perchlorate salt $[Ru(Phen)(RAaiR')_2](ClO_4)_2$ in 30–40% yield (Eq. 2). In an another method (Eq. 3), the same product has been isolated in higher yield (60–70%) using $[Ag(Phen)_2](ClO_4)$ as reagent. Under refluxing condition the mixture of isomers has been generated and has not been separated by chromatography due to small band separation in TLC plate. For this reason, the reaction temperature is strictly maintained at 40°C in dark and the compound, *ctc*-$[Ru(Phen)(RAaiR')_2](ClO_4)_2$ is purified by column chromatography. Because of higher yield of product the reaction 3 has been used for the synthesis of heteroleptic tris-chelates. The complexes are diamagnetic (t_{2g}^6, $s = 0$) and 1 : 2 electrolyte in MeCN (Λ_M = 140–160 $Ohm^{-1}\,cm^2\,mol^{-1}$) and show reasonable CHN analysis (Table 1).

Spectral characterization IR spectra of the complexes have been compared with the spectra of *ctc*-$RuCl_2(RAaiR')_2$ [7–12] and $[Ru(Bipy)(RAaiR')_2](ClO_4)_2$. The absence of ν(Ru–Cl) at 340 and 310 cm^{-1} (corresponding to *cis*-$RuCl_2$ moiety as it is observed in *ctc*-$RuCl_2(RAaiR')_2$) supports the substitution of Ru–Cl bonds. The spectra are almost superimposable with the spectra of $[Ru(Bipy)(RAaiR')_2](ClO_4)_2$ and the following conclusion have been drawn. The ν(N=N) and ν(C=N) appear at 1375–1390 and 1590–1600 cm^{-1}, respectively. The ν(ClO_4) appears as split bands at 1140–1150, 1110–1120 and 1080–1090 cm^{-1} along with a weak band at 620–630 cm^{-1}.

The solution spectral studies of the complexes at 200–1000 nm reveal that the free ligand absorbs at < 400 nm and the bands are due to $n \longrightarrow \pi^*$and $\pi \longrightarrow \pi^*$ transitions. The visible region of the spectrum shows two high-intense absorptions ($\varepsilon \sim 10^4$ l $mol^{-1}\,cm^{-1}$) at 515–525 and 415–425 nm and a weak band ($\varepsilon \sim 10^3$ l $mol^{-1}\,cm^{-1}$) at 700–710 nm. The transitions are of typical metal-to-ligand charge transfer type (MLCT).

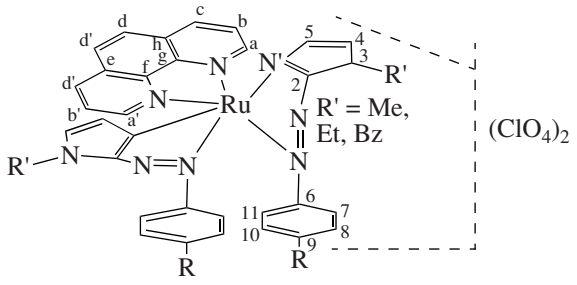
The ^1H NMR spectra have been recorded in $CDCl_3$ solution. The proton numbering pattern is shown in schemes. The assignment has been carried out based on the spin-spin interaction, effect of substituents and on comparing with the spectra of free ligands [3–12], $RuCl_2(RAaiR')$ [7] and $[Ru(Bipy)(RAaiR')_2](ClO_4)_2$. The spectral data are given in Table 2. The 1-R' (R' = Me, CH_2CH_3 and CH_2Ph) and Ar–Me are particularly useful to account the presence of isomer in the solution of the complex. The $[Ru(Phen)(RAaiR')_2](ClO_4)_2$ may exist as three different stereoisomeric forms: *tc* (*trans-cis*), *ct* (*cis-trans*) and *cc* (*cis-cis*) with reference to coordination pairs of N(imidazole), N and N(azo), N'. The chemical shift data are ~4.8 and 4.9 ppm for CH_2 protons along with two overlapping triplet signals for CH_3 group at 1.68, 1.73 for (**IIIa**); 1.67, 1.70 for (**IIIb**) and 1.73, 1.70 ppm for (**IIIc**). Similarly the methylene protons of 1-CH_2–(Ph) of $[Ru(Phen)(RAaiCH_2Ph)_2](ClO_4)_2$ show two pair of AB type quartets at frequency range of 5.5 to 5.9 ppm. The signal splitting may be due to combined effect of restricted rotation on the ligand coordination to the metal center and the geometrical perturbation from octahedron symmetry.

Table 1. Cyclic voltammetric* and elemental analysis data

Compound	Cyclic voltammetric data E, V (ΔE_p, mV)			Contents (found/calcd), %		
	E_M	$-E_{L1}$	$-E_{L2}$	C	H	N
$[Ru(Phen)(HAaiMe)_2](ClO_4)_2$ (**IIa**)	1.35 (100)	0.36 (70)	0.70 (100)	45.1/45.2	3.3/3.2	16.4/16.3
$[Ru(Phen)(MeAaiMe)_2](ClO_4)_2$ (**IIb**)	1.31 (110)	0.41 (80)	0.72 (110)	44.7/44.2	3.5/3.6	15.4/15.3
$[Ru(Phen)(ClAaiMe)_2](ClO_4)_2$ (**IIc**)	1.42 (100)	0.32 (80)	0.69 (90)	41.1/41.2	2.7/2.8	18.0/18.3
$[Ru(Phen)(HAaiCH_2CH_3)_2](ClO_4)_2$ (**IIIa**)	1.40 (105)	0.34 (90)	0.68 (90)	44.7/44.2	3.5/3.6	15.4/15.3
$[Ru(Phen)(MeAaiCH_2CH_3)_2](ClO_4)_2$ (**IIIb**)	1.33 (120)	0.40 (100)	0.70 (110)	45.9/46.0	3.8/3.8	14.9/15.0
$[Ru(Phen)(ClAaiCH_2CH_3)_2](ClO_4)_2$ (**IIIc**)	1.45 (110)	0.30 (90)	0.62 (100)	42.5/42.4	3.1/3.2	17.4/17.5
$[Ru(Phen)(HAaiCH_2Ph)_2](ClO_4)_2$ (**IVa**)	1.43 (100)	0.30 (75)	0.64 (110)	52.7/52.6	3.5/3.6	13.9/13.9
$[Ru(Phen)(MeAaiCH_2Ph)_2](ClO_4)_2$ (**IVb**)	1.40 (100)	0.35 (95)	0.69 (120)	51.7/51.8	3.8/3.8	13.2/13.3
$[Ru(Phen)(ClAaiCH_2Ph)_2](ClO_4)_2$ (**IVc**)	1.48 (115)	0.29 (100)	0.61 (100)			

* Solvent MeCN, supporting electrolyte [n-Bu_4N][ClO_4] (0.1 M), working electrode Pt-disk, auxiliary electrode Pt-wire, reference electrode SCE, solute concentration ~10^{-3} mol/l, scan rate 50 mV s^{-1}, E_M: eq. (3), E_{L1} and E_{L2} are the first and second ligand reductions, respectively.

The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the molecule as shown below. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum (δ = 170.12 and 168 ppm) effected by the magnetic interection of two bulky phenyl rings environment and the methyl, ethyl, benzyl substituted imidazole rings and the π electron delocalization on the =N–CC=N– and =N–CC=CC–. The methyl carbon atom of the



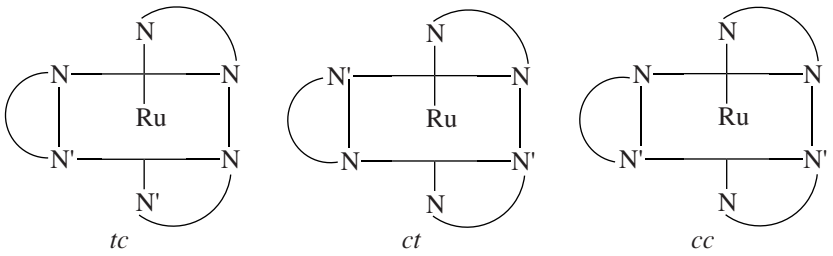


Table. 2. ^{1}H NMR spectral data (δ, ppm (*J*, Hz)) of $[Ru(Phen)(RAaiR')_2](ClO_4)_2$ in $CDCl_3$

Compound	4,4'-H[a]	5,5'-H[a]	7,7'-H[b]	8,8'-H	10,10'-H	11,11'-H[b]	a,a'-H[b]	b,b'-H[c]	c,c'-H[c]	d,d'-H[c]	1,1'-CH_2	1,1'-CH_3
IIa	6.70	6.44	7.40	7.28[c, d]	7.28[c]	7.77	8.51	8.32	8.01	7.86		
IIb	6.71	6.42	7.34	7.07[b, d]	7.07[b]	7.70	8.50	8.34	8.00	7.85		
IIc	6.75	6.46	7.47	7.39[b]	7.39[b]	7.81	8.53	8.36	7.98	7.88		
IIIa	6.67	6.42	7.44	7.34[c, d]	7.34[c]	7.79	8.49	8.39	7.99	7.89	4.91, 4.79[f]	1.70, 1.68[g]
IIIb	6.70	6.40	7.36	7.12[b, d]	7.12[b]	7.70	8.46	8.38	8.10	7.94	4.90, 4.75[f]	1.70, 1.67[g]
IIIc	6.72	6.41	7.47	7.35[b]	7.35[b]	7.84	8.49	8.40	8.14	8.08	4.80[f]	1.73, 1.70[g]
IVa	6.74	6.49	7.41	7.34[c, d]	7.34[c]	7.82	8.52	8.38	8.12	7.96	5.46, 5.52[e]	
IVb	6.68	6.47	7.37	7.15[b, d]	7.15[b]	7.80	8.55	8.45	8.08	7.99	5.46, 5.58[e]	
IVc	6.71	6.54	7.44	7.35[b]	7.35[b]	7.92	8.51	8.47	8.07	8.00	5.44, 5.55[e, h]	

[a] Weakly coupled doublet (*J* = 2.0–3.0 Hz); [b] doublet, *J* = 7.0–8.0 Hz; [c] multiplet; [d] δ(9.9'-H): 7.28[c] (**IIa**), 7.34[c] (**IIIa**), 7.34[c] (**IVa**), δ(9.9'-Me): 2.38 (**IIb**), 2.40 (**IIIb**), 2.34 (**IVb**); [e] δ(Ph–H): [f] sextet, geminal coupling constant (*J* = 10–12 Hz); [g] triplet; [h] doublet, geminal coupling constant (*J* = 8–10 Hz).

imidazole ring resonate at 40 ppm, resonably compare to the other carbon atoms resonance.

In the potential range +2.0 to –2.0 at a scan rate 50 mV s^{-1} four redox couples are observed. The voltammograms display the Ru(III)/Ru(II) couple at positive potentials and the ligand reductions appear at negative potential compared to SCE. The potentials are summarized in Table 1. The oxidation couple at 1.3–1.5 V is quasireversible in nature as it is evident from the peak-to-peak separation, $\Delta E_p \geq 10$ mV and the redox reaction is assigned to Eq. (4)

$$[Ru(Phen)(RAaiR')_2]^{3+} + e \rightleftharpoons [Ru(Phen)(RAaiR')_2]^{2+}. \quad (4)$$

One electron nature of the redox process is supported by coulometric current count in one case only, $[Ru(Phen)(MeAaiMe)_2](ClO_4)_2$ (**IIb**). The controlled potential coulometric oxidation has been carried out in one case only at 1.52 V in dry MeCN for **IIb** corroborates with one electron stoichiometry of the couple ($n = Q/Q' = 1.02$ where Q' is the calculated coulomb count and Q is the observed coulomb count after exhaustive electrolysis. The potential data at negative to SCE are due to ligand reductions. Both RAaiR' and Phen are reducible ligands. The azo group (–N = N–) is more reducible than imine group (–C = N–). The first two responses (Eqs. 5 and 6) may be regarded azo reductions.

$$[Ru(Phen)(RAaiR')_2]^{2+} + e \rightleftharpoons [Ru(Phen)(RAaiR')(RAai\bar{R}')]^{2+}. \quad (5)$$

$$[Ru(Phen)(RAaiR')(RAai\bar{R}')]^{2+} + e \rightleftharpoons [Ru(Phen)(RAai\bar{R}')_2]^{2+}. \quad (6)$$

$$[Ru(Phen)(RAai\bar{R}')_2]^{2+} + e \rightleftharpoons [Ru(Phen^{-})(RAai\bar{R}')_2]^{2+}. \quad (7)$$

Hetero-tris-chelates $[Ru(Phen)(RAaiR')_2]^{2+}$ are described in this work. They have been synthesized by Ag^+-assited solvation route from *ctc*-$RuCl_2(RAaiR')_2$ followed by the addition of 1,10-phenanthroline. The stereochemistry of the complexes has been established by ^{1}H NMR spectral data. The complexes exhibit intense MLCT transition and the energy of transition is linearly related with difference in potential of Ru(III)/Ru(II) and the first bound ligand reduction.

ACKNOWLEDGMENTS

The Ministerio De Education Y Ciencia (Grant no. SB2004-0060), Madrid is thanked for financial support and Prof. C. Sinha, M. Laguna, B. Guchait, Pravas, Latika Byabartta for constant help and valuable comments on this work.

REFERENCES

1. Seddon, E.A. and Seddon, K., *The Chemistry Ruthenium,* Amsterdam: Elsevier, 1984.
2. Klyansundaram, K. and Gratzel, M., *Coord. Chem. Rev.*, 1998, vol. 177, p. 347.
3. Velders, A.H., Laguna A., Oro, L., and Falvello, L., *Inorg. Chem.,* 2000, vol. 39, p. 2966.
4. Ghosh, B.K., Goswami, S., Chakravorty, A., and Lahiri, G.K., *Coord.Chem. Rev.,* 1989, vol. 95, p. 239.
5. Constable, E.C., *Coord. Chem. Rev.*, 1989, vol. 93, p. 205
6. Santra, P.K., Sinha, C., Byabartta, P., and Dinda, J., *Polyhedron*, 1999, vol. 18, p. 2869.
7. Misra, T.K., Sinha, C., Byabartta, P., and Satra, P. K., *Inorg. Chem.*, 1998, vol. 37, p. 1672.
8. Dinda, J., Sinha, C., Byabartta, P., and Misra, T.K., *J. Organomet. Chem.*, 2001, vol. 629, p. 28.
9. Pal, S., Das D., Sinha C., and Kennard, C.H.L., *Inorg. Chim. Acta*, 2001, vol. 31, p. 321.
10. Misra, T.K., Das, D., and Sinha, C., *Polyhedron*, 1997, vol. 16, p. 4163.
11. Pal, C.K., Sinha, C., Misra, T.K., and Byabartta, P., *Polyhedron*, 1994, vol. 13, p. 999.
12. Santra, P.K., Byabartta, P., Chattopadhyay, S., et al., *Eur. J. Inorg. Chem.*, 2002, no. 5, p. 1124.