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The synthesis, spectral studies and electrochemistry of 1,10-(phenanthroline)-bis-{1-alkyl-2-(arylazo)imidazole}ruthenium(II) perchlorate. Single crystal X-ray structure of $[Ru(phen)(HaaiMe)_2](ClO_4)_2$ [phen = 1,10-phenanthroline, HaaiMe = 1-methyl-2-(phenylazo)imidazole]

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Abstract

The hetero-tris-chelates of the formulae $[Ru(phen)(RaaiR')_2](ClO_4)_2$ [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 (**2**), Et (**3**), CH_2Ph (**4**)] 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 the dark followed by the addition of $NaClO_4$(aq). The structure of $[Ru(phen)(HaaiMe)_2](ClO_4)_2$ has been confirmed by X-ray diffraction study and suggested stereoretentive nucleophilic substitution. The structure and stereochemistry of the complexes have been supported by ^1H NMR data. Electronic spectra exhibit a strong metal-to-ligand charge transfer (MLCT) band at 515–530 nm along with a weak transition at 700–710 nm. Cyclic voltammograms show a Ru(III)/Ru(II) couple at 1.3–1.4 V versus saturated calomel electrode (SCE) along with three successive ligand reductions. The plot of the difference in potential of the first oxidation and reduction versus energy of the main MLCT band ($\bar{\nu}_{CT}$) is linear.

Keywords: Arylazoimidazoles; 1,10-Phenanthroline; Ruthenium(II) complexes; Electrochemistry; X-ray structures; EHMO

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1. Introduction

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, photophysical properties, directional electron and energy transfer, potential anticancer property [1–12]. 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 [13]. We have been engaged for the last several years in designing unsymmetric N,N′-donor ligands incorporating an azoaryl group in a N-heterocyclic backbone belong to pyridine [14], pyrimidine [15] and imidazole [16–22]. The ligands bear an azoimine, –N=N–C=N–, functional group. They have excellent ability to stabilize low valent metal oxidation states, interesting redox chemistry, stabilization of the azoanion radical and metal assisted organic transformations [15–29]. As a sequel of our endeavor to explore ruthenium chemistry of arylazoheterocycles the present work is concerned with the heteroleptic tris-chelates of ruthenium(II)-{1-alkyl-2-(arylazo)-imidazole}(RaaiR′) and 1,10-phenanthroline (phen). The structure of the complex is established in one case by a single crystal X-ray diffraction study; their spectral and electrochemical properties are reported in this work.

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2. Experimental

2.1. Materials

Published methods were used to prepare RaaiR′, *ctc*-[RuCl$_2$(RaaiR′)$_2$] [17] *ctc*-[Ru(H$_2$O)$_2$(RaaiR′)$_2$](ClO$_4$)$_2$ [20,21]. All other chemicals and organic solvents used for preparative work were of reagent grade available from SRL, India. The purification of MeCN and preparation of tetrabutylammonium perchlorate [*n*-Bu$_4$N][ClO$_4$], respectively, used as solvent and supporting electrolyte were done following the literature method [20].

2.2. Physical measurements

The UV–Vis (in MeCN) and IR (KBr discs, 4000–300 cm^{-1}) spectra were run with JASCO UV–Vis-NIR model V-570 and JASCO FT IR model 420 spectrophotometers, respectively. Electrical conductivities (in MeCN, solute concentration $\sim 10^{-3}$ M) were recorded using a Systronics conductivity bridge. Magnetic susceptibilities were measured with a PAR 155 vibrating sample magnetometer. The ^{1}H NMR spectra in CDCl$_3$ were carried out on a Bruker 300 and 500 MHz FT NMR spectrometer using SiMe$_4$ as internal standard. Microanalyses (C, H and N) were done with a Perkin–Elmer 2400 CHNS/O elemental analyser. Electrochemical studies (in MeCN) were performed with a PARC electrochemistry system as described elsewhere. In cyclic voltammetry (CV) the following parameters and relation were used: scan rate, 50 mV s^{-1}; formal potential $E^\circ = 0.5(E_{pa}+E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. In constant potential coulometry experiments (oxidation done at potential $E^\circ + 200$ mV); $n = Q/Q'$ where Q' is the calculated Coulomb count for 1e transfer and Q is the Coulomb count found after exhaustive electrolysis of 0.01 mmol of solute. All experiments were done under a dry N$_2$ atmosphere at 295(2) K in a three electrode configuration by using a Pt-disk milli working electrode and a Pt-wire auxiliary electrode. The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for the junction contributions.

2.3. Preparation of (1,10-phenanthroline)-bis-{1-methyl-2-(phenylazo)imidazole}ruthenium(II) perchlorate [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ (2a)

Caution! Perchlorates of heavy metal ions with organic ligands are potentially explosive. The synthesis involves in some cases the use of perchlorate ions. Due care must be exercised to avoid explosion hazards, although we have not encountered any problem using a small quantity at a time.

(i) Method (a): 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 the mixture was refluxed for 15 min, AgCl so precipitated was filtered off over a G4 crucible. An acetone solution (10 cm^3) of 1,10-phenanthroline (phen) (0.04 g, 0.24 mmol) was then added and the resulting mixture was stirred at 40 °C in the 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$_4$ (ca. 1 g in 20 cm^3 water) was added. The brown precipitate then obtained was filtered and dried in vacuum over P$_4$O$_{10}$. The dry mass was then dissolved in a minimum volume of CH$_2$Cl$_2$ and subjected to chromatography on a silica gel column (60–120 mesh). A reddish brown band was eluted with C$_7$H$_8$–CH$_3$CN (1:1, v/v). This was collected and slowly evaporated in air. Crystals were collected in 70% yield (0.22 g). Other complexes were also prepared following the above general process and yields varied from 60 to 75%.

(ii) Method (b): General procedure for the synthesis of [Ru(phen)(RaaiR′)$_2$](ClO$_4$)$_2$: To a THF suspension of *ctc*-RuCl$_2$(HaaiMe)$_2$ (0.2 g, 0.24 mmol), [Ag(phen)$_2$]-(ClO$_4$) (0.12 g, 0.24 mmol) in acetone was added and stirred at 40 °C in the dark for 12 h under nitrogen. The solution was filtered through a G4 sintered glass funnel, insoluble AgCl was filtered, the solution evaporated to dryness and washed thoroughly with cold water (15 cm^3 × 6). The mass was dried over CaCl$_2$ and dissolved in minimum volume of methanol and an aqueous solution of NaClO$_4$ (ca. 1 g in 15 cm^3) was added to precipitate out the product. The reddish brown product was filtered and purified as before. The yield was 75% (0.24 g). All other complexes were prepared similarly. Yield 70–80%.

2.4. X-Ray structure determination of [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ (2a)

Crystals suitable for the X-ray diffraction study of (1,10-phenanthroline)-bis-[1-methyl-2-(phenylazo)imidazole]ruthenium(II)perchlorate, [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ (**2a**) were grown by slow diffusion of hexane into a dichloromethane solution of the complex at 295 K. X-Ray diffraction data were collected with the Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by the least-squares method. A summary of the crystallographic data and structure refinement parameters are given in Table 1. Data were corrected for Lorentzian polarization effects and for linear decay. Semi-empirical absorption corrections based on Ψ-scans were applied. The structure was solved by the direct method using SHELXS-86 and successive difference Fourier syntheses. All non-hydro-

Table 1
Crystallographic data of [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ (**2a**)

Chemical formula	$C_{32}H_{28}N_{10}Cl_2O_8Ru$
Crystal size (mm^3)	$0.13 \times 0.10 \times 0.10$
Crystal system	monoclinic
Formula weight	852.61
Space group	$P2_1/n$
a (Å)	14.2183(9)
b (Å)	14.4201(10)
c (Å)	17.8417(12)
β (°)	103.5650(10)
V (Å^3)	3556.0(4)
Z	4
T (K)	295
λ (Å)	0.71073
2θ Range (°)	$3 < 2\theta < 56$
Reflections collected	8444
Unique reflections	6531
hkl Range	$-14 \leq h \leq 18,\ -19 \leq k \leq 19,\ -23 \leq l \leq 14$
ρ_{calc} (g cm^{-3})	1.593
μ (Mo Kα) (mm^{-1})	0.657
R [a]	0.0480
ωR_2 [b]	0.1184
Goodness-of-fit [c]	1.0270

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$.

[b] $\omega R = [\Sigma\ \omega(F_o^2 F_c{}^2)/\Sigma\ \omega F_o{}^4]^{1/2}$ $\omega = 1/[\sigma^2(F_o{}^2) + (0.0652P)^2 + 3.0628P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

[c] Goodness-of-fit is defined as $[\omega(F_o - F_c)/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

gen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier map the residual maxima and minima were 0.016 and −1.848 e Å^{-3}. All calculations and refinement were carried out using SHELXL-93 [21].

3. Results and discussion

3.1. Synthesis and formulation

Dichloro-bis-{1-alkyl-2-(arylazo)imidazole}ruthenium(II) complexes of *cis–trans–cis* (*ctc*) configuration (**1**) have been used as the precursor complex. 1-Alkyl-2-(arylazo)imidazole (RaaiR′) is an unsymmetric N,N′-chelating ligand. (N(imidazole) refers to N and N(azo) refers to N′). The stereochemistry has been specified with reference to the coordination pairs of Cl,Cl; N,N; and N′,N′; respectively.

Addition of AgNO$_3$(aq) to an 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 at 40 °C in the dark for a period of 3 days isolated heteroleptic tris-chelates as the perchlorate salt [Ru(phen)(RaaiR′)$_2$](ClO$_4$)$_2$ in 30–40% yield (Eq. (1)). In another method (Eq. (2)) the same product has been isolated in higher yield (60–70%) using [Ag(phen)$_2$](ClO$_4$) as the reagent.

$$\begin{aligned}&ctc\text{-RuCl}_2(\text{RaaiR}')_2 \xrightarrow[40\ ^\circ\text{C/dark}]{\text{AgNO}_3(\text{aq}),\text{acetone},}\\ &\qquad ctc\text{-[Ru(acetone)}_2(\text{RaaiR}')_2](\text{NO}_3)_2 + 2\ \text{AgCl}\downarrow\\ &ctc\text{-[Ru(acetone)}_2(\text{RaaiR}')_2](\text{NO}_3)_2\\ &\qquad \xrightarrow{\text{phen,NaClO}_4(\text{aq})} [\text{Ru(phen)(RaaiR}')_2](\text{ClO}_4)_2 \qquad (1)\end{aligned}$$

$$\begin{aligned}&ctc\text{-RuCl}_2(\text{RaaiR}')_2 + 2\ [\text{Ag(phen)}_2](\text{ClO}_4)\\ &\qquad \xrightarrow[\text{NaClO}_4]{\text{acetone,}\ \ 40\ ^\circ\text{C}} [\text{Ru(phen)(RaaiR}')_2](\text{ClO}_4)_2\\ &\qquad +3\ \text{phen} + 2\ \text{AgCl}\downarrow \qquad (2)\end{aligned}$$

Under refluxing conditions a the mixture of isomers has been generated and has not been separated by chromatography due to small band separation on the TLC plate. For this reason, the reaction temperature is strictly maintained at 40 °C in the dark and the compound, *ctc*-[Ru(phen)(RaaiR′)$_2$](ClO$_4$)$_2$ is purified by column chromatography. Due to the higher yield of the product, reaction (2) has been used for the synthesis of heteroleptic tris-chelates. Due to the better lability of the Ru–Cl bond in the presence of Ag$^+$ reaction 2 has yielded a higher percentage of product than that of reaction (1). The composition of the compound was formulated by microanalytical data. The complexes are diamagnetic (t_{2g}^6, s = 0) and a 1:2 electrolyte in MeCN (Λ_M = 140–160 Ω^{-1} cm^{-1} mol^{-1}).

3.2. Single crystal X-ray structure of [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ (2a)

The molecular structure of the complex [Ru(phen)-(HaaiMe)$_2$](ClO$_4$)$_2$ is shown in Fig. 1 and the bond parameters are given in Table 2. The ruthenium center is coordinated with six N centers (RuN$_6$ type); four N centers are of 1-methyl-2-(phenylazo)imidazole and two N donor centers of the phen unit. The stereochemistry about the Ru center is compared with the structure of the precursor compound, *ctc*-RuCl$_2$(MeaaiMe)$_2$, and stereochemistry about Ru is retained [30,31]. The atomic groups Ru, N(5), N(7), N(3), N(9) (plane 1) constitute a good plane and are deviated from the mean plane by < 0.06 Å. The atomic groups Ru, N(1), N(3), N(7), N(10) (plane 2) exhibit maximum deviation of N(7) and N(10) by −0.149 and 0.156 Å, respectively, in opposite directions. Maximum distortion in the atomic arrangement has been observed in the case of Ru, N(1), N(5), N(9), N(10) (plane 3). The N(9) and N(10) deviate in opposite directions by ~0.12 Å while N(1) and N(5) deviate similarly by 0.10 Å from the least-squares plane. Planes 1 and 2 are mutually orthogonal (dihedral angle 91.8°) while the third plane (plane 3) deviates exceptionally from orthogonality and makes dihedral angles of 79 and 98° with planes 1 and 2, respectively. This supports distortion of the geometry from a regular octahedral symmetry. Three atomic groups Ru, N(1), N(2), C(7), N(3); Ru, N(5), N(6), C(17), N(7) and Ru, N(9), C(32),

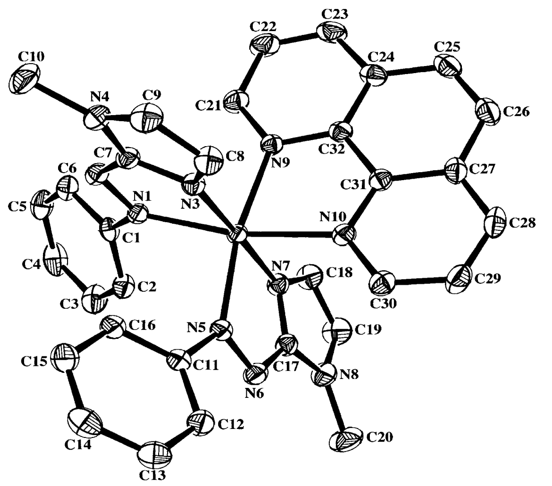


Fig. 1. Single crystal X-ray structure of $[Ru(phen)(HaaiMe)_2](ClO_4)_2$ (**2a**).

C(31), N(10) separately constitute three chelate planes (mean deviation ∼0.08 Å). The planes are mutually orthogonal (dihedral angle av. 83°). The chelate angles N(1)–Ru–N(3), N(5)–Ru–N(7) and N(9)–Ru–N(10) are 76.9(4)°, 76.6(4)° and 79.0(1)°, respectively. The trans angles N(1)–Ru–N(10), N(3)–Ru–N(7) and N(5)–Ru–N(9) are 168.0(2)°, 177.3(8)° and 169.4(1)°, respectively. The deviation of these angles from 180° undoubtedly originates from the acute chelate bite angles. The chelate angles, $(\overline{\text{Ru–N=N–C=N}})$–, constituted from the azoimine group suffers severe perturbation compared with the chelate angle constituted by the diimine (–N=C–C=N–) group and are responsible for the deviation from octahedral geometry. The pendant phenyl ring to each chelated azoimine group is no longer planar and makes a dihedral angle of 32°. The hydrogen bonded molecular packing shows the existence of C–H···X (X = N, O) hydrogen bonding interaction. The C(5)–H and C(19)–H phenyl ring carbons of the arylazo system and C(22)–H of the phen ring system are hydrogen bonded with perchlorate oxygen atoms. The methyl substituted carbon, C(20) is linked with an azo nitrogen (N(6)) through hydrogen bonding (C(20)–H···N(6)).

3.3. Spectral characterization

IR spectra of the complexes have been compared with the spectra of *ctc*-$RuCl_2(RaaiR')_2$ [17] and $[Ru(bpy)(R\text{-}aaiR')_2](ClO_4)_2$ [21]. The absence of ν(Ru–Cl) at 340 and 310 cm^{-1} (corresponding to a *cis*-$RuCl_2$ moiety as is observed in *ctc*-$RuCl_2(RaaiR')_2$) supports the substitution of Ru–Cl bonds. The spectra are almost superimposable with the spectra of $[Ru(bpy)(R\text{-}aaiR')_2](ClO_4)_2$ and the following conclusions have been drawn. The ν(N=N) and ν(C=N) appear at 1375–1390 and 1590–1600 cm^{-1}, respectively. The $\nu(ClO_4)$ appears as split bands at 1140–1150, 1110–1120 and 1080–1090 cm^{-1} along with a weak band at 620–630 cm^{-1}.

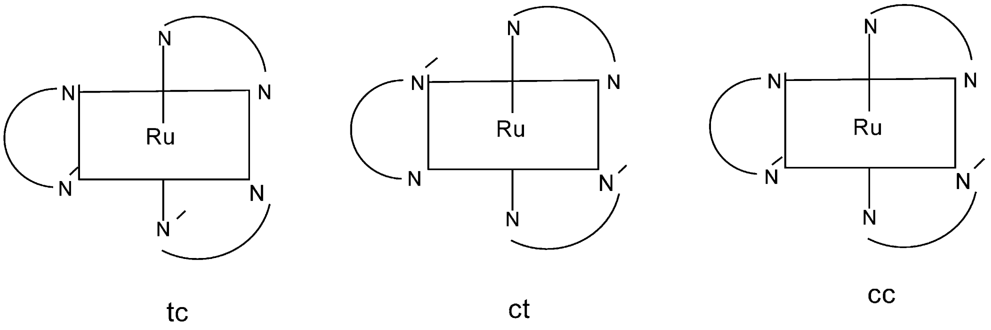
The solution spectral studies of the complexes in the range 200–1000 nm (Table 3, Fig. 2) reveal that the

Table 2
Selected bond distances (Å) and angles (°) for $[Ru(phen)(HaaiMe)_2](ClO_4)_2$ (**2a**)

Distances (Å)		Angles (°)	
Ru–N(1)	2.031(9)	N(1)–Ru–N(3)	76.9(4)
Ru–N(3)	2.029(9)	N(1)–Ru–N(9)	90.9(1)
Ru–N(5)	2.035(4)	N(3)–Ru–N(7)	177.4(1)
Ru–N(7)	2.058(8)	N(5)–Ru–N(7)	76.6(4)
Ru–N(9)	2.091(9)	N(7)–Ru–N(9)	95.9(1)
Ru–N(10)	2.095(6)	N(1)–Ru–N(7)	103.9(4)
N(3)–C(7)	1.334(7)	N(3)–Ru–N(5)	100.3(2)
N(2)–C(7)	1.355(4)	N(3)–Ru–N(10)	95.8(3)
N(2)–N(1)	1.304(1)	N(5)–Ru–N(10)	92.6(1)
N(7)–C(17)	1.326(5)	N(9)–Ru–N(10)	79.0(1)
N(6)–C(17)	1.363(6)	N(1)–Ru–N(5)	98.1(3)
N(6)–N(5)	1.296(0)	N(1)–Ru–N(10)	168.02
N(9)–C(32)	1.366(8)	N(3)–Ru–N(9)	86.5(4)
N(10)–C(31)	1.366(8)	N(5)–Ru–N(9)	169.4(1)
C(31)–C(32)	1.420(8)	N(7)–Ru-N(10)	83.7(1)
N(4)–C(10)	1.470(7)		
N(8)–C(20)	1.461(5)		

Donor (D)	H	Acceptor (A)	D–H (Å)	H–A (Å)	D–A (Å)	∠ DHA (°)
Hydrogen bonding parameters						
C(5)	H(5)	O(11)	0.9300	2.407(4)	3.296(2)	159.9(1)
C(19)	H(19)	O(42B)	0.9300	2.543(1)	3.312(8)	140.4(1)
C(20)	H(20A)	N(6)	0.9600	2.610(1)	3.006(1)	105.1(1)
C(22)	H(22)	O(42B)	0.9300	2.545(6)	3.210(1)	128.7(1)

absorptions <400 nm are due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The visible region of the spectrum shows two high-intense absorptions ($\varepsilon \sim 10^4$ dm^3 mol^{-1} cm^{-1}) at 515–525 and 415–425 nm and a weak band ($\varepsilon \sim 10^3$ dm^3 mol^{-1} cm^{-1}) at 700–710 nm. The transitions are of typical metal-to-ligand charge transfer type (MLCT). On comparison with the spectra of $[Ru(bpy)_2L]^{2+}$, $[Ru(bpy)L_2]^{2+}$ (L = RaaiR′, 1-alkyl-2-(arylazo)imidazole [21], bpy [32], aryl-(2-pyridylmethylene)amine [33], 2-(arylazo)pyridine [34], phen) it has been concluded that the transition at 415–425 nm corresponds to $t_2(Ru) \rightarrow \pi^*(phen)$ and 515–525 nm refers to $t_2(Ru) \rightarrow \pi^*(RaaiR')$. The weak band at longer wavelength, 700–710 nm, may be associated with a spin forbidden transition in spin-orbit coupled states of ruthenium 4d orbitals.



The ^{1}H NMR spectra have been recorded in $CDCl_3$ solution. The proton numbering pattern is shown in Scheme 1. The assignment has been carried out based on the spin–spin interaction, effect of substituent and on comparing with the spectra of free ligands [23], $RuCl_2(RaaiR')$ [17] and $[Ru(bpy)(RaaiR')_2](ClO_4)_2$ [21]. The spectral data are given in Table 4. The 1-R′ (R′ = Me, CH_2CH_3 and CH_2Ph) and Ar–Me are particularly useful to account for the presence of isomers in the solution of the complex. $[Ru(phen)(RaaiR')_2](ClO_4)_2$ 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 2,2′-bipyridine (bpy) analogue, $[Ru(bpy)(RaaiR')_2](ClO_4)_2$, exists as two isomers (*tc* and *cc*) which have been assigned from their ^{1}H NMR spectra. The *tc* isomer is confirmed by X-ray structure determination [21]. This experience has led us to synthesize the present series of complexes at controlled temperature (40 °C). The solution ^{1}H NMR spectra support the presence of only one isomer and it is obviously *tc*-configuration. $[Ru(phen)(RaaiMe)_2](ClO_4)_2$ exhibits two closely spaced equally intense 1-Me signals at approximately 4.4 and 4.5 ppm, $[Ru(phen)(MeaaiR')_2]^{2+}$ shows a single Ar–Me signal at approximately 2.4 ppm. The methylene signal of 1-CH_2–(CH_3) of $[Ru(phen)(RaaiCH_2CH_3)_2]^{2+}$ exhibits a complex splitting pattern. The chemical shift data are approximately 4.8 and 4.9 ppm for $-CH_2-$ protons along with two overlapping triplet signals for the $-CH_3$ group at 1.68, 1.73 for (**3a**); 1.67, 1.70 for (**3b**) and 1.73, 1.70 ppm for (**3c**). Similarly the methylene protons of 1-CH_2–(Ph) of $[Ru(phen)(RaaiCH_2Ph)_2](ClO_4)_2$ show two pairs of AB type quartets at the frequency range of 5.5–5.9 ppm. The signal splitting may be due to a combined effect of restricted rotation on the ligand coordination to the metal center and the geometrical perturbation from octahedral symmetry.

3.4. Electrochemistry, spectral correlation and electrochemical parametrization

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 potentials compared with SCE. The potentials are summarized in Table 3 and a representative voltammogram is shown in Fig. 3. The oxidation couple at 1.3–1.5 V is quasireversible in nature as is evident from the peak-to-peak separation, $\Delta E_p \geq 100$ mV and the redox reaction is assigned to Eq. (3)

$$[Ru(phen)RaaiR')_2]^{3+} \rightleftharpoons [Ru(phen)(RaaiR')_2]^{2+} \qquad (3)$$

The E_M values ($E_{1/2}$ of Ru(III)/Ru(II)) are expectedly higher than *ctc*-$RuCl_2(RaaiR')_2$ [17] but lower than that of $[Ru(bpy)(RaaiR')_2](ClO_4)_2$ [21]. This accounts the π-acidity order $Cl^- <$ phen < bpy. It is expected that phen is less π-acidic than bpy [13]. The one electron nature of the redox process is supported by the coulometric current count in one case only, [Ru(phen)(Meaai-

Table 3
Microanalytical, UV–Vis spectral and cyclic voltammetrical data

Compound	Elemental analysis: Calc. (Found) (%)			UV–Vis data (λ_{max} (nm) (10^{-3} ε s M^{-1} cm^{-1})) [a]	Cyclic voltammetric data E/V (ΔE_p (mV)) [b]					
	C	H	N		E^M	$-E^{L1}$	$-E^{L2}$	$-E^{L3}$	ΔE (V) [d]	$\bar{\nu}_{CT}$ (eV) [e]
$[Ru(phen)(HaaiMe)_2](ClO_4)_2$ (**2a**)	45.07 (45.15)	3.29 (3.21)	16.43 (16.38)	705 (0.570), 521 (11.951), 420 (13.061), 379 (29.682) [c]	1.35 (100)	0.36 (70)	0.70 (100)	1.41 (130)	1.71	2.382
$[Ru(phen)(MeaaiMe)_2](ClO_4)_2$ (**2b**)	46.36 (46.31)	3.64 (3.56)	15.91 (15.98)	700 (0.943), 522 (8.812), 419 (10.061), 396 (25.123) [c]	1.31 (110)	0.41 (80)	0.72 (110)	1.43 (160)	1.72	2.377
$[Ru(phen)(ClaaiMe)_2](ClO_4)_2$ (**2c**)	41.69 (41.61)	2.82 (2.85)	15.20 (15.26)	702 (0.481), 520 (9.051), 422 (11.362), 380 (23.061) [c]	1.42 (100)	0.32 (80)	0.69 (90)	1.38 (150)	1.74	2.387
$[Ru(phen)(HaaiCH_2CH_3)_2](ClO_4)_2$ (**3a**)	46.36 (46.31)	3.64 (3.62)	15.91 (15.89)	707 (0.541), 518 (9.342), 421 (10.142), 379 (21.612) [c]	1.40 (105)	0.34 (90)	0.68 (90)	1.40 (140)	1.74	2.396
$[Ru(phen)(MeaaiCH_2CH_3)_2](ClO_4)_2$ (**3b**)	47.57 (47.51)	3.96 (3.94)	15.42 (15.39)	705 (0.370), 517 (5.051), 421 (10.592), 393(15.141) [c]	1.33 (120)	0.40 (100)	0.70 (110)	1.42 (130)	1.73	2.400
$[Ru(phen)(ClaaiCH_2\ CH_3)_2](ClO_4)_2$ (**3c**)	42.99 (42.93)	3.16 (3.12)	14.75 (14.71)	709 (0.491), 522 (11.401), 421 (18.262), 397 (26.531) [c]	1.45 (110)	0.30 (90)	0.62 (100)	1.37 (170)	1.75	2.377
$[Ru(phen)(HaaiCH_2Ph)_2](ClO_4)_2$ (**4a**)	52.58 (52.55)	3.58 (3.53)	13.94 (13.91)	701 (0.431), 518 (8.402), 416 (16.382), 390 (20.901) [c]	1.43 (100)	0.30 (75)	0.64 (110)	1.39 (120)	1.73	2.396
$[Ru(phen)(MeaaiCH_2Ph)_2](ClO_4)_2$ (**4b**)	53.48 (53.44)	3.88 (3.85)	13.57 (13.54)	706 (0.580), 525 (8.861), 419 (18.861), 399 (24.551) [c]	1.40 (100)	0.35 (95)	0.69 (120)	1.43 (160)	1.75	2.364
$[Ru(phen)(ClaaiCH_2Ph)_2](ClO_4)_2$ (**4c**)	49.20 (49.16)	3.17 (3.15)	13.05 (13.01)	710 (0.691), 528 (10.482), 422 (20.591), 400 (22.352) [c]	1.48 (115)	0.29 (100)	0.61 (100)	1.37 (150)	1.77	2.350

[a] In MeCN.

[b] Solvent MeCN, supporting electrolyte $[n\text{-}Bu_4N][ClO_4]$ (0.1M), working electrode Pt-disk, auxiliary electrode Pt-wire, reference electrode SCE, solute concentration $\sim 10^{-3}$ M, scan rate 50 mV s^{-1}, E^M: Eq. (3), E^L: ligand reductions, $\Delta E_P = |E_{pa} - E_{pc}|$ mV where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

[c] Shoulder.

[d] $\Delta E = E^M - E^{L1}$ (V).

[e] $\nu_{CT} = 1241/\lambda_{max}$ (main) (nm).

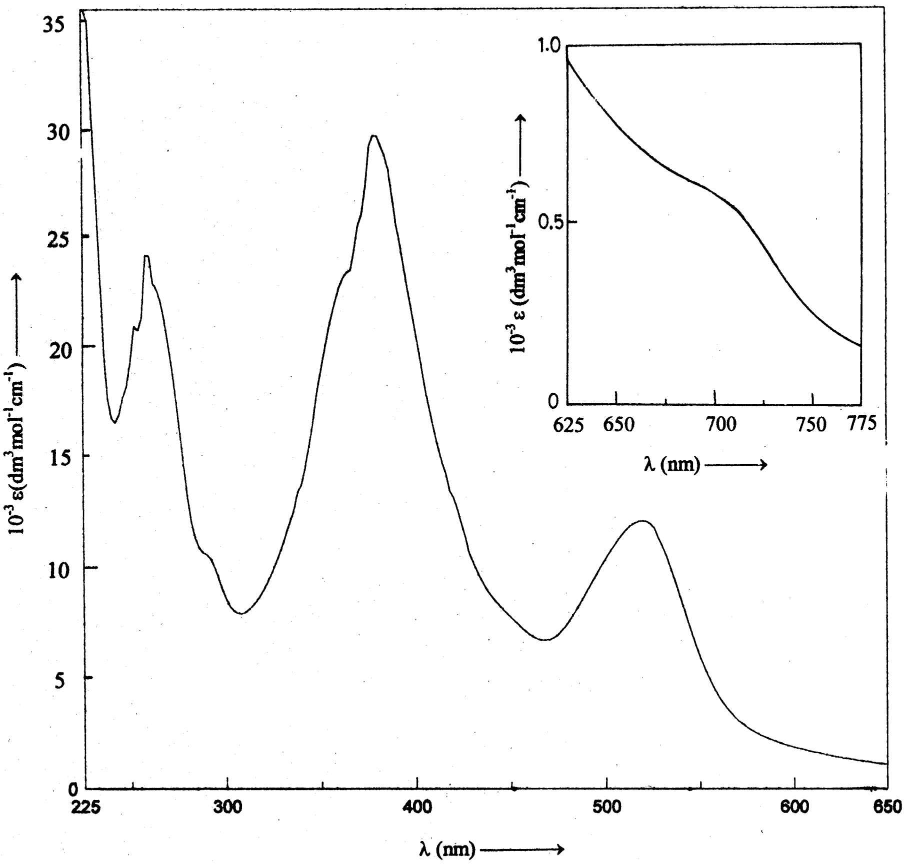
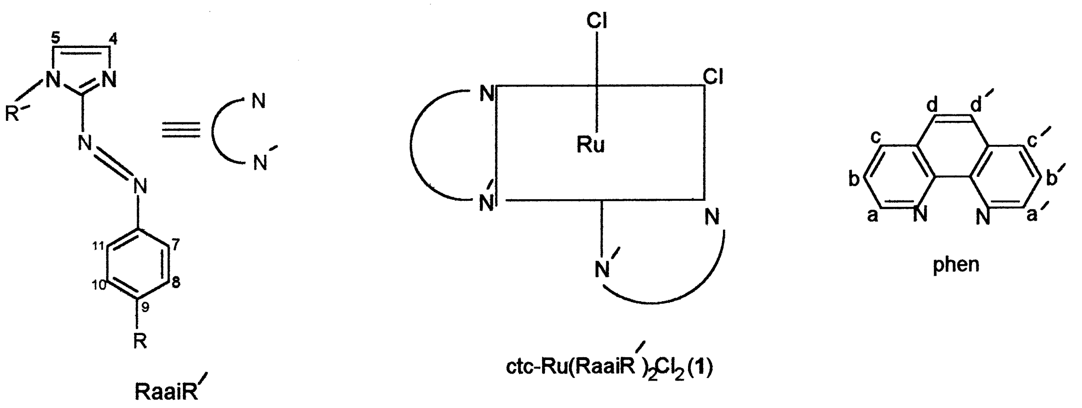


Fig. 2. Electronic spectra of $[Ru(phen)(HaaiMe)_2](ClO_4)_2$ (**2a**) (———) in dry acetonitrile.

$Me)_2](ClO_4)_2$ (**2b**). The controlled potential coulometric oxidation has been carried out in one case only at 1.52 V in dry MeCN for $[Ru(phen)(MeaaiMe)_2](ClO_4)_2$ (**2b**) and corroborates with the 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 ruthenium(III) congener so generated on electrolysis also exhibits an identical redox response but reductive in nature. The dark brown–red solution changes to orange–red after electrolysis.

The potential data negative to SCE are due to ligand reductions. Both RaaiR′ and phen are reducible ligands. The azo group (–N=N–) is more reducible than the



R = H(**a**), CH_3(**b**), Cl(**c**); R′ = $^{12}CH_3$(**2**), $^{12}CH_2$-$^{13}CH_3$(**3**), $^{12}CH_2$-Ph(14H-18H)(**4**).

Scheme 1.

Table 4
^{1}H NMR spectral data in $CDCl_3$ at room temperature of $[Ru(phen)(RaaiR')_2](ClO_4)_2$

Compound	δ (ppm) (J (Hz))											
	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′-Me	13,13′-CH_3
2a	6.70	6.44	7.40 (7.2)	7.28 [c,d]	7.28 [c]	7.77 (7.4)	8.51 (8.0)	8.32	8.01	7.86		4.48, 4.40	
2b	6.71	6.42	7.34 (7.4)	7.07 (7.4) [b,d]	7.07 (7.4) [b]	7.70 (7.4)	8.50 (8.0)	8.34	8.00	7.85		4.45, 4.38	
2c	6.75	6.46	7.47 (7.4)	7.39 (7.6) [b]	7.39 (7.6) [b]	7.81 (7.4)	8.53 (8.0)	8.36	7.98	7.88		4.50, 4.42	
3a	6.67	6.42	7.44 (7.4)	7.34 [c,d]	7.34 [e]	7.79 (7.6)	8.49 (8.0)	8.39	7.99	7.89	4.91, 4.79 [f]		1.70, 1.68 [g]
3b	6.70	6.40	7.36 (7.2)	7.12 (7.4) [b,d]	7.12 (7.4)[b]	7.70 (7.6)	8.46 (8.0)	8.38	8.10	7.94	4.90, 4.75 [f]		1.70, 1.67 [g]
3c	6.72	6.41	7.47 (7.6)	7.35 (7.4) [b]	7.35 (7.4) [b]	7.84 (7.6)	8.49 (8.0)	8.40	8.14	8.08	4.95, 4.80 [f]		1.73, 1.70 [g]
4e	6.74	6.49	7.41 (7.4)	7.34 [c,d]	7.34 [c]	7.82	8.52 (8.0)	8.38	8.12	7.96	5.46, 5.52, 5.72, 5.82 [h]		
4e	6.68	6.47	7.37 (7.6)	7.15 (7.4) [b,d]	7.15 (7.4)[b]	7.80 (7.8)	8.55 (8.0)	8.45	8.08	7.99	5.46, 5.58, 5.75, 5.89 [h]		
4e	6.71	6.54	7.44 (7.4)	7.35 (7.4) [b]	7.35 (7.6) [b]	7.92 (7.6)	8.51 (8.0)	8.47	8.07	8.00	5.44, 5.55, 5.78, 5.90 [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] (**2a**), 7.34 [c] (**3a**), 7.34 [c] (**4a**), δ(9,9′-Me): 2.38 (**2b**), 2.40 (**3b**), 2.34 (**4b**).
[e] δ(Ph–H): 7.2–7.4 ppm.
[f] Sextet, geminal coupling constant ($J = 10$–12 Hz).
[g] Triplet ($J = 7.0$ –8.0).
[h] Doublet, geminal coupling constant ($J = 8$–10 Hz).

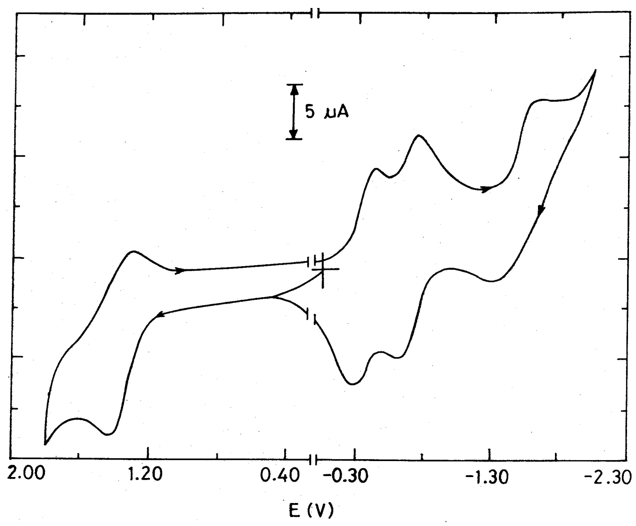


Fig. 3. Cyclic voltammogram of $[Ru(phen)(ClaaiMe)_2](ClO_4)_2$ (**2c**) (———) in MeCN using Pt-disk milli electrode at 298 K, SCE reference and TBAP (0.1 M) supporting electrolyte.

imine group (–C=N–). The first two responses (Eqs. (4) and (5)) may be regarded as azo reductions. They are highly sensitive to the substituent (R) in the aryl ring and are linearly correlated with Hammett σ values of the substituent. The third response is due to the $phen^-$/phen reaction and is quasireversible in nature.

$$[Ru(phen)(RaaiR')_2]^{2+} + e \rightleftharpoons [Ru(phen)(RaaiR')(Raai\bar{R}')]^{2+} \tag{4}$$

$$[Ru(phen)(RaaiR')(Raai\bar{R}')]^{2+} + e \rightleftharpoons [Ru(phen)(Raai\bar{R}')_2]^{2+} \tag{5}$$

$$[Ru(phen)(Raai\bar{R}')_2]^{2+} + e \rightleftharpoons [Ru(phe\bar{n})(Raai\bar{R}')_2]^{2+} \tag{6}$$

The E^L (E^{L1} and E^{L2}) values are systematically increased by 0.2 V from $RuCl_2(RaaiR')_2$ and decreased by 0.01–0.05 V from the analogous bpy complexes, $[Ru(bpy)(RaaiR')_2](ClO_4)_2$. The oxidation may be the electron extraction from the HOMO and the reduction is electron accommodation at the LUMO. In $[Ru(phen)(RaaiR')_2](ClO_4)_2$, the oxidation is taking place at metal center thus the HOMO is mostly characterized by metal t_2-orbitals. The reductions take place at ligand centers and the LUMOs are ligand dominated orbitals. The respective redox potentials refer to the thermodynamic energy of the levels. Thus the difference in potential between the first oxidation (E^M) and the first reduction (E^{L1}) ($\Delta E^\circ = E^M$(Eq. (3))$-E^{L1}$(Eq. (4))) may have some kind of correlation with MLCT absorption energies ($\bar{\nu}_{CT}$ for 517–528 nm). The MLCT transition is regarded as the internal redox transfer from the HOMO (metal t_2 level) to the LUMO (ligand π^* level) [7]. The plot of ΔE° versus $\bar{\nu}_{CT}$ follows a linear relationship as given in Eq. (7).

Table 5
Energy and metal/ligand population of MOs

	HOMO−1	HOMO	LUMO	LUMO+1
Energy (eV)	−11.632	−11.271	−10.597	−10.227
d(Ru) (%)	50	69	16	32
Ligand (HaaiMe)	37	20	73	62
Ligand (phen)	5	3	2	0

$$\bar{\nu}_{CT} = -0.56\Delta E + 3.35 \tag{7}$$

The results are comparable with other examples of ruthenium(II) with π-acidic ligands from our work [17–21] and others [33,34].

3.5. *EHMO calculation*

The frontier orbitals of $[Ru(phen)(HaaiMe)_2](ClO_4)_2$ (**2a**) (Table 5, Fig. 4) have been described by the extended Huckel calculation using crystallographic parameters of the complexes. The calculated MOs have been used in order to access the solution spectra and redox properties of the complexes belonging to this family. The approximate composition of the MOs (HOMO−1 to LUMO+1) are described in Table 5. The metal orbitals (d(Ru)) and azoimidazole (HaaiMe) ligands participate predominantly in the construction of MOs. 1,10-Phenanthroline contribution is unexpectedly much less ($\leq 5\%$) which may be due to higher energy of ligand group orbitals (LGOs) constructed from the diimine system compared with the azoimine function. Data in Table 5 show that the HOMOs are d(Ru) dominated and the LUMOs are dominated by HaaiMe orbitals. The HOMO is constituted by a 69% metal (d(Ru)) share and a 20% contribution from HaaiMe.

The LUMO is made up of 73% HaaiMe group and 16% d(Ru). The high-intense UV–Vis main transition and shoulders at approximately 515–530 and 700–710 nm may be demonstrated as d(Ru) → π* (HaaiMe). The cyclic voltammetric responses are similarly explained using the EHMO results. The oxidative couple positive to SCE may be assigned to electron extraction from the HOMO which is d(Ru) dominated. Thus the reversible to quasireversible couple at 1.3–1.4 V may be defined to the Ru(III)/Ru(II) redox process (vide supra) and the couples negative to SCE are reduction of the azoimine group of HaaiMe.

4. Conclusion

Hetero-tris-chelates $[Ru(phen)(RaaiR')_2]^{2+}$ are described in this work. They have been synthesized by a Ag^+-assisted solvation route from *ctc*-$RuCl_2(RaaiR')_2$ followed by the addition of 1,10-phenanthroline (phen). To avoid temperature dependent isomerisation a

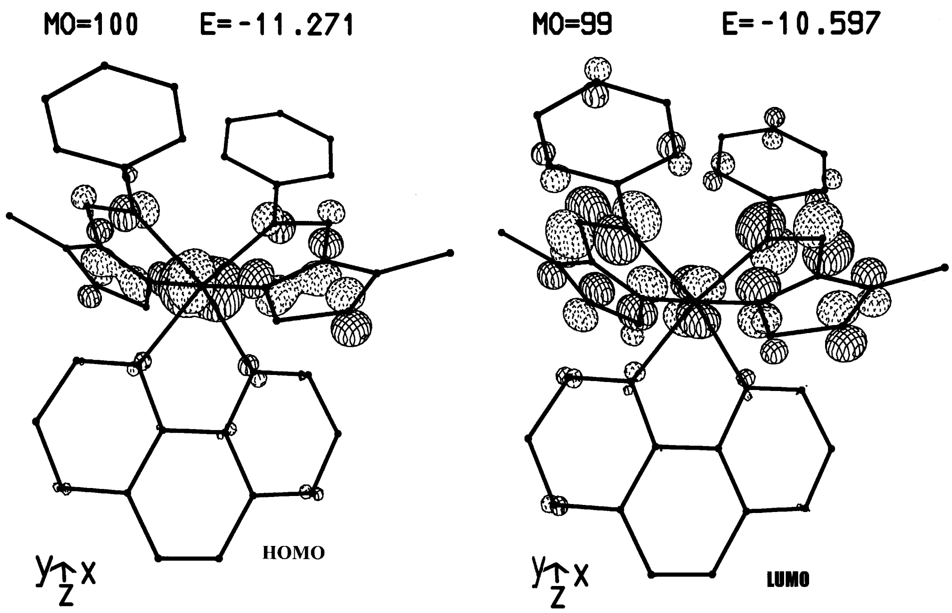


Fig. 4. Frontier orbitals, HOMO and LUMO of [Ru(phen)(HaaiMe)$_2$](ClO$_4$)$_2$ (**2a**).

thermo-regulated condition has been maintained at 40 °C. The stereochemistry of the complexes has been established by ^{1}H NMR spectral data. The X-ray structure determination suggests formation of a *trans*–*cis* isomer with reference to coordination pairs of N(imidazole) and N(azo). Thus a stereoretentive reaction is confirmed. The complexes exhibit an intense MLCT transition and the energy of the transition is linearly related to the difference in potential of Ru(III)/Ru(II) and the first bound ligand reduction. The Lever method of electrochemical parametrization of the Ru(III)/Ru(II) redox potential has been carried out to predict Ru(III)/Ru(II) redox potentials in the complexes.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 184645 for compound **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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