

Heteroleptic tris-chelates of ruthenium(II)-bipyridine-aryla- imidazoles: Synthesis, spectral characterisation and electrochemical properties. Single crystal X-ray structure of [(2,2'-bipyridine)-bis- {1-methyl-2-(*p*-tolylazo)imidazole}ruthenium(II)] perchlorate

Prithwiraj Byabartta,^a Joydev Dinda,^a Prasanta Kumar Santra,^a Chittaranjan Sinha,^{*a}
Kaliyamoorthy Panneerselvam,^b Fan-Ling Liao^c and Tian-Huey Lu^b

^a Department of Chemistry, The University of Burdwan, Burdwan, 713104, India.

E-mail: c_r_sinha@yahoo.com

^b Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

^c Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

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The reaction of *cis-trans-cis*-RuCl₂(RaaiR')₂ [RaaiR' = 1-alkyl-2-(aryla)imidazole, *p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', where R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**1**), Et (**2**) and CH₂Ph (**3**)] either with 2,2'-bipyridine (bpy) and AgNO₃ followed by NaClO₄ or [Ag(bpy)₂](ClO₄) in boiling acetone led to red-brown [Ru(bpy)(RaaiR')₂](ClO₄)₂. The complex may exist in three isomeric structures. The structure of [Ru(bpy)(MeaiMe)₂](ClO₄)₂ was confirmed by X-ray diffraction study and suggests that only one isomer is crystallised. Electronic spectra exhibit a strong MLCT band at 520 ± 5 nm along with two weak transitions at longer wavelength. The complexes emit at 77 K and quantum yields vary from 0.011–0.025. The ¹H NMR spectral measurements of the complexes suggest the existence of two isomers in 1 : 0.3 concentration ratio. The methylene, –CH₂–, in RaaiEt of [Ru(bpy)(RaaiEt)₂]²⁺ gives a complex AB type multiplet while the RaaiCH₂Ph moiety of [Ru(bpy)(RaaiCH₂Ph)₂]²⁺ shows AB type quartets. Cyclic voltammograms show a Ru(III)/Ru(II) redox couple along with three successive ligand reductions. The plot of difference in potential of first oxidation and reduction *versus* energy of main MLCT band ($\bar{\nu}_{CT}$) is linear. Electrochemical parametrization of the Ru(III)/Ru(II) redox couple determines ligand potential $E_L(L)$. Using $E_L(L)$ the potential of the present complexes has been predicted and is linearly related to the observed potential.

Introduction

Recent years have witnessed a great deal of interest^{1–20} in the synthesis of complexes of ruthenium with α -diimine type ligands because of their redox, photochemical, catalytic properties, energy conversion, DNA intercalation and ability to serve as building blocks in supramolecular arrays. Researchers have engaged in modifying the properties of Ru-bpy (bpy = 2,2'-bipyridine) complexes by replacing the ligands of other donor centres, altering the steric and electronic properties of the ligands, using differently substituted polypyridine mixed donor heterocycles, and to synthesise mixed-ligand tris-chelates, [Ru(bpy)_n(L)_{6–2n}]^{m+} (L = monodentate neutral/anionic ligand)/[Ru(bpy)_n(LL')_{3–n}]^{m+} (LL' = bidentate homo (L = L') or hetero donor ligand).

The present work is concerned with the heteroleptic tris-chelates of bis-chelated ruthenium(II)-1-alkyl-2-(aryla)imidazole (RaaiR') and bipyridine (bpy). The chelating group in RaaiR' is azoimine, –N=N–C=N–, and donor centres N(imidazole) and N(azo) are abbreviated N and N', respectively. The arylazoimidazole (RaaiR') chemistry of ruthenium(II) is known in some detail in our group.^{21–23} Dichloro-bis(aryla-azoimidazole)ruthenium(II), RuCl₂(RaaiR')₂, may exist in five geometrical isomeric forms of which two have been structurally characterised.²¹ With consideration of coordination pairs^{12,15} in the sequence Cl, N and N' the structurally characterised isomers are *trans-cis-cis* (*tcc*) and *cis-trans-cis* (*ctc*) RuCl₂(RaaiR')₂. The isomers *tcc* and *ctc* bear *trans*-RuCl₂ and *cis*-RuCl₂ motifs respectively. The Ru–Cl bond in the complexes of *cis*-RuCl₂ configuration (*ctc* isomer) is kinetically more labile

than that of the *trans*-RuCl₂ configuration (*tcc* isomer).^{4,5} The dechlorination is accelerated by Ag⁺ and thus solvento species [Ru(RaaiR')₂(solvo)₂]²⁺ are formed^{24–27} which may undergo different reactions *viz.*, nucleophilic substitution,²⁸ formation of oxo species,²⁹ and polynuclear complex formation.^{11,30}

In this paper, we wish to report on the synthesis, spectral characterisation and redox properties of [Ru(bpy)(RaaiR')₂]²⁺ derived from the solvento species, [Ru(RaaiR')₂(solvo)₂]²⁺. The structure of the complex is established by a single crystal X-ray diffraction study in one case. Electrochemical parametrization of Ru(III)/Ru(II) redox potentials of previously reported arylazoimidazole complexes of ruthenium(II) are also included in this work.

Experimental

Measurements

Microanalytical data (C,H,N) were collected on a Perkin-Elmer 2400 CHNS/O elemental analyser. Infrared spectra were obtained on KBr discs (4000–200 cm^{–1}) with a JASCO FTIR model 420 spectrophotometer. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V-570 spectrophotometer. The emission spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer at 298 K and 77 K in MeOH–EtOH (1 : 4 v/v) mixture. Quantum yields were calculated using the relation, $\phi_s = \phi_{std} (A_{std}/A_s) (I_s/I_{std}) (\eta_s^2/\eta_{std}^2)$ where the symbols have their usual meanings.²⁴ Solution electrical conductivity of the complexes were collected on a Systronics digital conductivity meter model 304 with a solute concentration of *ca.*

10^{-3} mol dm $^{-3}$. The ^1H NMR spectra in CDCl_3 were obtained on a Bruker 300 MHz FT NMR spectrometer using SiMe_4 as internal standard. The magnetic susceptibilities of the samples were measured on a PAR 155 vibrating sample magnetometer. Electrochemical work as carried out using a EG & G PARC Versastat computer controlled 270 electrochemical system. All experiments were performed under a N_2 atmosphere at 296(2) K in a three-electrode configuration by using a glassy carbon disc milli working electrode and a Pt-wire auxiliary electrode. All results are referenced to a saturated calomel electrode (SCE). The reported potentials are uncorrected for junction potential.

Materials

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ was obtained from Arrora Matthey, Calcutta and was digested three times with concentrated HCl before use.²¹ 1-Alkyl-2-(arylo)imidazoles (RaaiR') and $[\text{Ag}(\text{bpy})_2](\text{ClO}_4)$ were synthesised by a reported procedure.²¹ *ctc*- $\text{RuCl}_2(\text{RaaiR}')_2$ was prepared by a known method.²¹ The purification of solvents for electrochemical and spectral work and $[\text{Bu}_4\text{N}][\text{ClO}_4]$ were prepared as described earlier.²² All other chemicals and solvents used for the preparative work were of reagent grade and were used as received.

Preparation of complexes

CAUTION! Perchlorate salts of metal complexes are generally explosive. Care should be taken in handling the samples.

(2,2'-Bipyridine)-bis[1-methyl-2-(phenylazo)imidazole]-ruthenium(II) perchlorate monohydrate $[\text{Ru}(\text{bpy})(\text{HaaiMe})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Two independent methods have been employed to synthesise the complexes.

(i) *Method (a)*. To a suspension of *ctc*- $\text{RuCl}_2(\text{HaaiMe})_2$ (0.2 g, 0.24 mmol) in acetone (25 ml) was added an aqueous solution of AgNO_3 (0.08 g, 0.47 mmol) and refluxed for 15 min. AgCl so precipitated was filtered off over a G-4 crucible. Acetone solution (10 ml) of 2,2'-bipyridine (bpy) (0.04 g, 0.24 mmol) was then added and the resulting mixture was heated to reflux for 1 h under nitrogen. The solution was then evaporated to half its original volume by N_2 bubbling and an aqueous solution of NaClO_4 (ca. 1 g in 20 ml water) was added. The brown precipitate then obtained was filtered and dried *in vacuo* over P_4O_{10} . The dry mass was then dissolved in the 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 $\text{C}_6\text{H}_6\text{--CH}_3\text{CN}$ (3 : 4, v/v). This was collected and slowly evaporated in air. Crystals were collected in 70% yield.

Other complexes were also prepared following the same general process as discussed above and the yields varied from 60–75%.

(ii) *Method (b)*. General procedure for the synthesis of $[\text{Ru}(\text{bpy})(\text{RaaiR}')_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. To a THF suspension of *ctc*- $\text{RuCl}_2(\text{RaaiR}')_2$ (0.2 g, 0.24 mmol), $[\text{Ag}(\text{bpy})_2](\text{ClO}_4)$ (0.12 g, 0.24 mmol) in acetone was added and refluxed for 2 h under nitrogen. The solution was filtered through a G-4 sintered glass funnel, insoluble AgCl was filtered, the solution was evaporated to dryness and washed thoroughly with cold water ($15 \text{ cm}^3 \times 5$). The mass was dried over CaCl_2 and dissolved in 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 (Yield, 75%).

All other complexes were prepared similarly; yield, 70–85%. Calc. for $\text{C}_{30}\text{H}_{28}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Ru}$ (**1a**): C, 42.55; H, 3.78; N, 16.55. Found: C, 42.43; H, 3.72; N, 16.41%. Calc. for $\text{C}_{32}\text{H}_{32}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Ru}$ (**1b**): C, 43.94; H, 3.89; N, 16.02. Found: C, 43.89; H, 3.79; N, 16.10%. Calc. for $\text{C}_{30}\text{H}_{27}\text{N}_{10}\text{O}_8\text{Cl}_4\text{Ru}$ (**1c**): C, 39.34; H, 3.06; N, 15.30. Found: C, 39.30; H, 3.10; N, 15.28%. Calc. for $\text{C}_{32}\text{H}_{32}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Ru}$ (**2a**): C, 43.94; H, 3.89; N, 16.02. Found: C, 43.89; H, 3.93; N, 16.12%. Calc. for $\text{C}_{34}\text{H}_{26}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Ru}$ (**2b**):

Table 1 Crystallographic data of $[\text{Ru}(\text{bpy})(\text{MeaaiMe})_2](\text{ClO}_4)_2 \cdot \text{CH}_2\text{Cl}_2$

Chemical formula	$\text{C}_{32}\text{H}_{32}\text{Cl}_2\text{N}_{10}\text{O}_8\text{Ru} \cdot \text{CH}_2\text{Cl}_2$
Crystal size/mm 3	$0.40 \times 0.30 \times 0.10$
Crystal system	Monoclinic
Formula weight	941.57
Space group	$P2_1/c$
$a/\text{\AA}$	17.649(2)
$b/\text{\AA}$	12.039(2)
$c/\text{\AA}$	19.374(2)
$\beta/^\circ$	102.834(3)
$V/\text{\AA}^3$	4013.5(9)
Z	4
T/K	293(2)
$\lambda/\text{\AA}$	0.71073
2θ range/ $^\circ$	$3 < 2\theta < 57$
Reflections collected	25269
Unique reflections ^a	9575
hkl range	$-20 \leq h \leq 23, -14 \leq k \leq 16, -25 \leq l \leq 25$
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.558
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.718
R^b	8.37
wR_2^c	19.61
Goodness of fit ^d	1.053

^a $I > 2\sigma(I)$. ^b $R = \Sigma|F_o - F_c|/\Sigma F_o$. ^c $wR = [\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 14.3394P]$, $P = (F_o^2 + 2F_c^2)/3$. ^d Goodness of fit is defined as $[\Sigma w(F_o - F_c)/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and variables, respectively.

C, 45.23; H, 4.21; N, 15.52. Found: C, 45.21; H, 4.29; N, 15.55%. Calc. for $\text{C}_{32}\text{H}_{30}\text{N}_{10}\text{O}_8\text{Cl}_4\text{Ru}$ (**2c**): C, 40.72; H, 3.39; N, 14.85. Found: C, 40.67; H, 3.46; N, 14.78%. Calc. for $\text{C}_{42}\text{H}_{36}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Ru}$ (**3a**): C, 50.50; H, 3.81; N, 14.03. Found: C, 50.41; H, 3.89; N, 13.89%. Calc. for $\text{C}_{44}\text{H}_{40}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Ru}$ (**3b**): C, 51.46; H, 4.09; N, 13.65. Found: C, 51.39; H, 3.98; N, 13.73%. Calc. for $\text{C}_{42}\text{H}_{34}\text{N}_{10}\text{O}_8\text{Cl}_4\text{Ru}$ (**3c**): C, 47.24; H, 3.37; N, 13.12. Found: C, 47.19; H, 3.28; N, 13.18%.

X-Ray structure determination

Crystals suitable for the X-ray diffraction study of 2,2'-bipyridine-bis{1-methyl-2-(*p*-tolylazo)imidazole}ruthenium(II) perchlorate, $[\text{Ru}(\text{bpy})(\text{MeaaiMe})_2](\text{ClO}_4)_2$ were grown by slow diffusion of hexane into a dichloromethane solution of the complex at 298 K. The crystal size was $0.40 \times 0.30 \times 0.10 \text{ mm}^3$. X-Ray diffraction data were collected at 293(2) K with the Siemens SMART CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell parameters were determined by the least-squares method. Data collection were performed in the 2θ range 3–57°. A summary of the crystallographic data and structure refinement parameters is given in Table 1. Of 25269 collected reflections 9575 unique reflections were recorded using the ω -scan technique. Data were corrected for Lorentzian polarisation effects and for linear-decay. Semi-empirical absorption corrections based on Ψ -scans were applied.³¹ The structure was solved by the heavy atom methods using SHELXS-97³² and successive difference Fourier syntheses. All non-hydrogen 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 1.247 and $-1.275 \text{ e \AA}^{-3}$. All calculations were carried out using SHELXL-97.³³

CCDC reference number 152560.

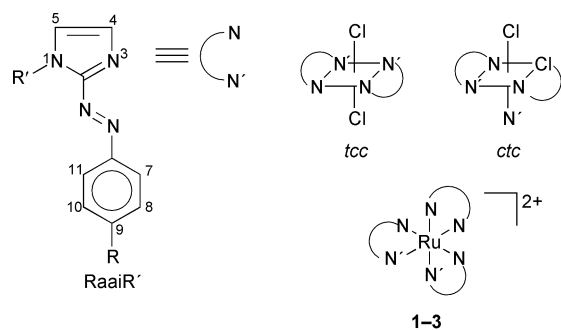
See <http://www.rsc.org/suppdata/dt/b1/b103782j/> for crystallographic data in CIF or other electronic format.

Results and discussion

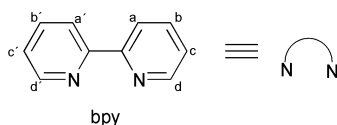
Synthesis and formulation

Dichloro-bis{1-alkyl-2-(arylo)imidazole}ruthenium(II) complexes were synthesised by a published procedure²¹ and isolated

as two isomers: *tcc*-RuCl₂(RaaiR')₂ and *ctc*-RuCl₂(RaaiR')₂ where RaaiR' = 1-alkyl-2-(arylo)imidazole, *p*-R-C₆H₄-N=N-C₃H₂NN-R'; R = H (a), Me (b), Cl (c) and R' = Me (1), Et (2), CH₂Ph (3), see Scheme 1. 1-Alkyl-2-(arylo)imidazole

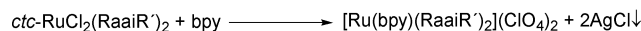


R = H (a), Me (b), Cl (c);
R = Me (1), CH₂-¹³CH₃ (2), ¹³CH₂Ph (14–18) (3)

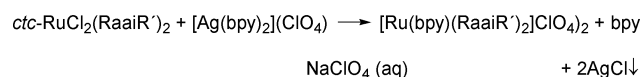


Scheme 1

(RaaiR') is an unsymmetric N,N'-chelating ligand; N(imidazole) refers to N and N(azo) refers to N'. The *ctc*-RuCl₂(RaaiR')₂ has *cis*-RuCl₂ configuration and the Ru–Cl bond is kinetically labile.^{24–27} On addition of AgNO₃ (aq) followed by 2,2'-bipyridine (bpy) to an acetone solution (eqn. (1)) of



ctc-RuCl₂(RaaiR')₂ and NaClO₄ the complexes [Ru(bpy)(RaaiR')₂](ClO₄)₂ (1–3) were obtained in 40–60% yield. This reaction has also been carried out by reacting [Ag(bpy)₂](ClO₄) with *ctc*-RuCl₂(RaaiR')₂ and the same product (eqn. (2)) isolated in high yield (70–80%).



Reaction 2 has been particularly useful for the synthesis of heteroleptic tris-chelate. Although the tris-chelate may exist as three geometric isomers²⁵ they have not been separated by any chromatographic process. The mixed chelate cation [Ru(bpy)(RaaiR')₂]²⁺ (1–3) may exist in one chiral structure. The composition of the compound was formulated by elemental analyses. The complexes are diamagnetic (t_{2g}⁶) and 1 : 2 electrolytes in MeCN.

Molecular structure

A molecular view of the complex [Ru(bpy)(MeaiMe)₂](ClO₄)₂ is shown in Fig. 1 and the bond parameters are given in Table 2. The basal planes of the distorted RuN₆ octahedron are due to the coordination from four N-donor centres of 1-methyl-2-(*p*-tolylazo)imidazole and two N-donor centres of the bpy unit. The crystal structure shows distorted CH₂Cl₂ and ClO₄ units (Fig. 1). Two atomic groups Ru, N(5), N(7), N(10), N(3) (plane 1) and Ru, N(1), N(3), N(7), N(9) (plane 2) separately constitute two good planes and are deviated from the mean plane by <0.06 Å. The atomic groups Ru, N(1), N(5), N(9), N(10) do not constitute

Table 2 Selected bond distances (Å) and angles (°) for [Ru(bpy)(MeaiMe)₂](ClO₄)₂·CH₂Cl₂

Ru–N(1)	2.069(5)	C(28)–N(10)	1.353(8)
Ru–N(3)	2.040(5)	C(27)–N(9)	1.341(8)
Ru–N(5)	2.057(5)	Cl(1)–O(1)	1.409(6)
Ru–N(7)	2.066(6)	Cl(1)–O(2)	1.340(7)
Ru–N(9)	2.094(5)	Cl(1)–O(3)	1.376(8)
Ru–N(10)	2.072(5)	Cl(1)–O(4)	1.391(9)
N(1)–N(2)	1.309(7)	C(33)–Cl(41)	1.551(17)
N(5)–N(6)	1.282(7)	C(33)–Cl(3)	1.722(16)
C(8)–N(3)	1.339(8)	C(33)–Cl(42)	1.82(2)
C(19)–N(7)	1.319(8)		
N(1)–Ru–N(3)	76.8(2)	N(5)–Ru–N(9)	93.3(2)
N(5)–Ru–N(7)	75.9(2)	N(5)–Ru–N(10)	165.2(2)
N(9)–Ru–N(10)	78.4(2)	N(7)–Ru–N(9)	87.5(2)
N(3)–Ru–N(7)	178.9(2)	N(7)–Ru–N(10)	91.4(2)
N(3)–Ru–N(5)	103.9(2)	O(1)–Cl(1)–O(3)	113.5(5)
N(3)–Ru–N(10)	88.6(2)	O(1)–Cl(1)–O(2)	113.6(5)
N(3)–Ru–N(9)	91.4(2)	O(1)–Cl(1)–O(4)	106.2(5)
N(1)–Ru–N(5)	95.3(2)	O(2)–Cl(1)–O(3)	110.8(6)
N(1)–Ru–N(7)	104.3(2)	O(2)–Cl(1)–O(4)	105.4(8)
N(1)–Ru–N(9)	166.8(2)	O(3)–Cl(1)–O(4)	106.5(7)
N(1)–Ru–N(10)	95.1(2)		

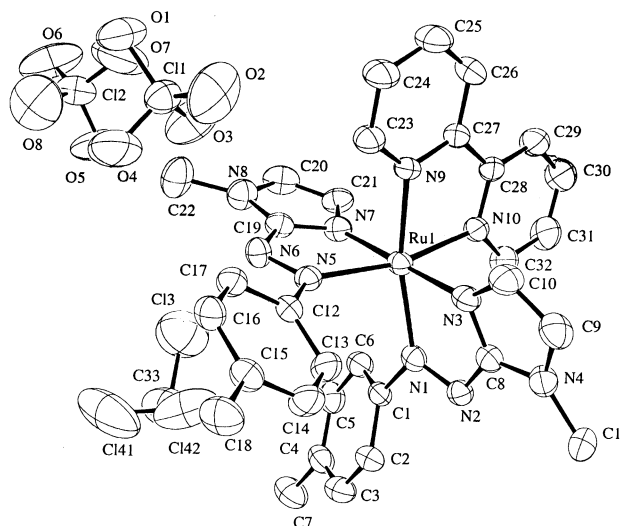


Fig. 1 Single crystal X-ray structure of [Ru(bpy)(MeaiMe)₂](ClO₄)₂ (1b).

a good plane and deviate by 0.18 Å from the mean plane. The displacement of Ru from the least-squares plane is only –0.003 Å. The N(9) and N(10) deviate in opposite directions by 0.21 Å while N(1) and N(5) deviate similarly by 0.18 Å from the least-squares plane. Planes 1 and 2 are inclined at an angle around 85° while the third plane deviates exceptionally from orthogonality and makes an angle av. 78° with two other planes. Ru lies above plane 1 by 0.06 Å while it is below plane 2 by 0.04 Å. Three atomic groups Ru, N(5), N(6), C(19), N(7); Ru, N(1), N(2), C(8), N(3); Ru, N(9), C(27), C(28), N(10) separately constitute three chelate planes (mean deviation ≈ 0.06 Å). The planes are mutually orthogonal (dihedral angle av. 84°). The chelate angles N(1)–Ru–N(3), N(5)–Ru–N(7) and N(9)–Ru–N(10) are 76.8(2), 75.9(2) and 78.4(2)°, respectively. The *trans* angles N(1)–Ru–N(9), N(5)–Ru–N(10), N(3)–Ru–N(7) are 166.8(2), 165.2(2) and 178.9(2)°, respectively. The deviation from *trans* angular values undoubtedly originates from the acute chelate bite angles. The chelate rings constituted by the azoimine group (–N=N–C=N–) N(1)–Ru–N(3) and N(5)–Ru–N(7), experience severe perturbation and are responsible for the deviation from octahedral geometry^{21,24,34,35} compared to the chelate angle constituted by the diimine (–N=C–C=N–) group, N(9)–Ru–N(10). The dihedral angles between the chelate ring constituted by the azoimine group and the corresponding pendant *p*-tolyl

ring in the Ru(RaaiR')-unit are as follows: Ru,N(1),N(2),-N(8),N(3) and C(1) to C(6) make dihedral angle 35.67°, Ru,N(5),N(6),N(19),N(7) and C(12) to C(17) inclined at an angle of 33.80°. Two pendant *p*-tolyl rings also deviate from orthogonality (dihedral angle 76.91(0.18)°) possibly due to steric interaction between the groups.

The N–N distances are no longer equivalent in two azoimine chelates. The N(1)–N(2) bond (1.309(7) Å) is longer than N(5)–N(6) (1.282(7) Å). The N–N distance in general, is longer than the free ligand value (1.25 Å).³⁶ The increase in bond length is undoubtedly due to coordination of N(azo) (N(1)/N(5)) that can lead to a decrease in the bond order due to both the σ -donor and π -acceptor character of the ligands—the latter character having a more pronounced effect.²¹

The longer N(1)–N(2) bond compared to N(5)–N(6) remarkably affects the respective Ru–N distances. In Ru–N(azo): Ru–N(1), 2.069(5) is longer than Ru–N(5), 2.057(5) Å while in Ru–N(imidazole): Ru–N(3), 2.040(5) is shorter than Ru–N(7), 2.066(6) Å. In the complexes *cis-trans-cis*-dichloro-bis{1-methyl-2-(*p*-tolylazo)imidazole}ruthenium(II),²¹ *trans-cis-cis*-dichloro-bis{1-benzyl-2-(phenylazo)imidazole}ruthenium(II)²¹ and bis(2,2'-bipyridine){1-benzyl-2-(*p*-tolylazo)imidazole}ruthenium(II),²⁴ the Ru–N(azo) distances are shorter than Ru–N(imidazole). The results of isomeric dichloro-bis{2-(phenylazo)pyridine}ruthenium(II)³⁴ and dichloro-bis{2-(phenylazo)pyrimidine}ruthenium(II)³⁵ also show similar information, *viz.* that the Ru–N(azo) bond length is shorter than Ru–N(heterocycle) (pyridine/pyrimidine). Besides, the Ru–N(azo) (Ru–N(1)/Ru–N(5)) distances are shorter than the Ru–N(bpy) distances (Ru–N(9), 2.094(5) and Ru–N(10), 2.072(5) Å). The shortening of the Ru–N(azo) rather than the Ru–N(heterocycle) bond length has been considered as an indication of a metal–ligand π -interaction that is localized in the M–N(azo) fragment.^{21,24,34,35} However, in the present example, the Ru–N bond length in two chelated azoimine rings (Ru–N=N–C=N), behaves in opposite fashion (Ru–N(5) < Ru–N(7) while, Ru–N(1) > Ru–N(3)). In the chelate plane Ru,N(5),N(6),C(19),N(7) the Ru–N(azo) (Ru–N(5), 2.057(5) Å) is shorter (by *ca.* 0.01 Å) than Ru–N(imidazole) (Ru–N(7), 2.066(6) Å) while in the chelate ring Ru,N(1),N(2),C(8),N(3) the Ru–N(azo) (Ru–N(1), 2.069(5) Å) is unusually elongated by *ca.* 0.03 Å compared to Ru–N(imidazole) (Ru–N(3), 2.040(5) Å). To our knowledge, this is the first example where the Ru–N(azo) distance is longer than the Ru–N(heterocycle) distance in arylazoheterocycle complexes of ruthenium(II).^{21,24,34,37} The Ru–N(bpy) (Ru–N(9) and Ru–N(10)) distances are also not comparable within the esd limit; Ru–N(9) (2.094(5) Å) is elongated by *ca.* 0.02 Å compared to Ru–N(10) (2.072(5) Å). The average Ru–N(bpy) (2.08 Å) is longer than Ru–N(imidazole) (2.05 Å) and Ru–N(azo) (2.06 Å). This is in support of stronger π -interaction with azoimine (–N=N–C=N–) than with the diimine (–N=C–C=N–) function. Overall distortion of the RuN₆ co-ordination sphere from octahedral geometry is reflected in the Ru–N bond distance data.

Spectra and bonding

The infrared spectra of the complexes have been compared with the spectra of [Ru(bpy)₂(RaaiR')](ClO₄)₂·H₂O²⁴ and RuCl₂(RaaiR')₂²¹ and the following conclusions have been drawn. The ν (N=N), ν (C=N) and ν (H₂O) appear at 1365–1380, 1585–1600 and 3430–3445 cm⁻¹, respectively. The perchlorate (ClO₄) exhibits split bands at 1145–1155, 1110–1120 and 1080–1090 along with a weak band at 620–625 cm⁻¹. The splitting of ν (ClO₄) is in support of the reduced symmetry which may be due to some hydrogen bonding interaction with H₂O.³⁷

The solution spectral studies of the complexes at 200–1100 nm (Table 3) reveal that the free ligand absorbs at <400 nm and the bands are due to n→ π^* and π → π^* transitions.^{21,22} The transitions in the visible region are of typical metal-to-ligand

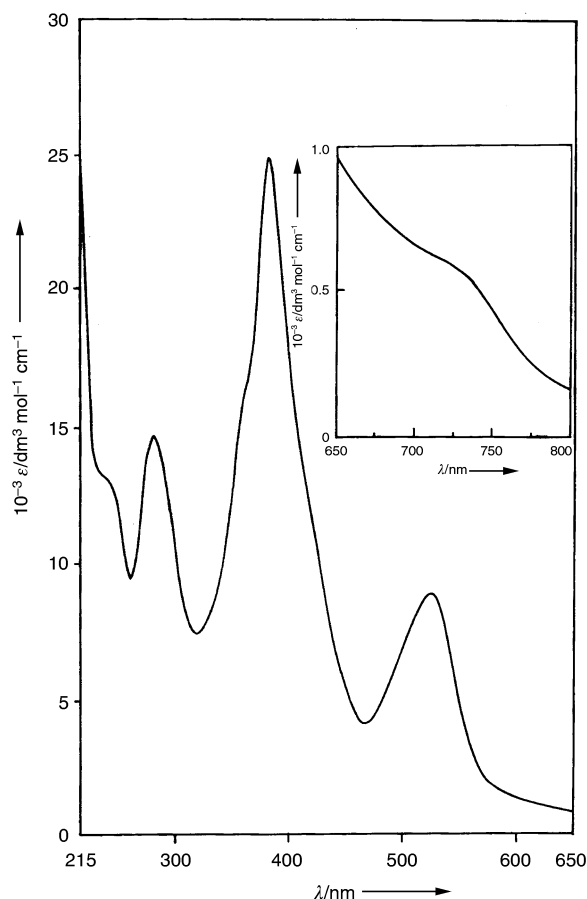


Fig. 2 Electronic spectra of [Ru(bpy)(HaaiMe)₂](ClO₄)₂ (**1a**) in CH₃CN.

charge transfer type (MLCT):^{21–27,38} two high-intense absorptions ($\epsilon \approx 10^4$ dm³ mol⁻¹ cm⁻¹) appear at 420–435 and 515–530 nm and two weak bands ($\epsilon \approx 10^3$ dm³ mol⁻¹ cm⁻¹) appear at 585–625 and 720–735 nm (Fig. 2). On comparison with the spectra of [Ru(bpy)₂(L)]²⁺ (L = RaaiR',²⁴ bpy,³⁹ 2-(arylo)pyridine,²⁵ and aryl-(2-pyridylmethylene)amine³⁸) it has been concluded that the transition at 420–435 nm corresponds to $t_2(\text{Ru}) \rightarrow \pi^*(\text{bpy})$ and that at 515–530 nm to $t_2(\text{Ru}) \rightarrow \pi^*(\text{RaaiR}')$. The low intense longer wavelength bands may be due to spin forbidden transitions and are made allowed by spin-orbit coupling with ruthenium 4d-orbitals.⁴⁰

The emission spectra of the complexes at 298 K are not recognisable because of very low quantum yields ($\phi \approx 10^{-4}$). The emission spectra in frozen glass (77 K) are sharper and considerably more intense than the room temperature spectra. The emission peaks and quantum yields at 77 K are given in Table 3. The complexes on excitation at 500–540 and 380–420 nm (where their two MLCT absorption maxima are observed) exhibit three/four luminescence bands at 450–600 nm. The peak at longer wavelength lies between 540–570 nm and remains unchanged with the energy of the excitation radiation. This emission may originate from the ³MLCT excited state which corresponds to a spin forbidden Ru→bpy transition^{4,24} and the quantum yields vary in the range 0.011–0.025. The emissions observed at 390 and 480 nm are unusual and may be either due to emission from the ¹MLCT state or from an impurity. The peak positions are affected by the excitation wavelength and may suggest that scattered light is the cause of this observation.

The ¹H NMR spectra have been recorded in CDCl₃ solution. The proton numbering pattern is shown in structures of RaaiR' and bpy (Scheme 1). The spectral data are given in Table 4. The 1-R' (R' = Me, CH₂CH₃ and CH₂Ph) and Ar–Me (9-Me) are particularly useful to determine the isomer composition of the mixture of complexes. [Ru(bpy)(RaaiR')₂]²⁺ may exist as three

Table 3 UV-Vis,^a emission^b spectral and cyclic voltammetric^c data

Compound	UV-Vis spectra λ_{\max}/nm (10^{-3} ϵ/dm^3 $\text{mol}^{-1} \text{cm}^{-1}$)	Emission spectra at 77 K		Cyclic voltammetric data E/V ($\Delta E_p/\text{mV}$)				$\Delta E^c/V$	$\tilde{\nu}_{\text{CT}}^f/\text{eV}$
		λ_{\max}/nm	ϕ ($\times 10^3$)	E^M	$-E^{L1}$	$-E^{L2}$	$-E^{L3}$		
[Ru(bpy)(HaaiMe) ₂](ClO ₄) ₂ (1a)	730(0.56), ^d 586(1.49), ^d 520(8.78), 434(9.95) ^d	560	18	1.68 (80)	0.33 (75)	0.69 (110)	1.35 (140)	2.01	2.387
[Ru(bpy)(MeaaiMe) ₂](ClO ₄) ₂ (1b)	728(0.24), ^d 585(1.15), ^d 517(10.80), 420(8.35) ^d	550	14	1.66 (90)	0.39 (90)	0.68 (120)	1.31 (110)	2.05	2.40
[Ru(bpy)(ClaaiMe) ₂](ClO ₄) ₂ (1c)	735(0.74), ^d 622(1.88), ^d 525(12.97), 430(10.98) ^d	565	11	1.72 (100)	0.30 (80)	0.67 (110)	1.33 (130)	2.02	2.364
[Ru(bpy)(HaaiEt) ₂](ClO ₄) ₂ (2a)	733(0.46), ^d 590(1.62), ^d 524(6.83), 422(8.99) ^d	555	23	1.69 (80)	0.30 (75)	0.65 (120)	1.36 (140)	1.99	2.368
[Ru(bpy)(MeaaiEt) ₂](ClO ₄) ₂ (2b)	727(0.61), ^d 589(1.36), ^d 520(11.43), 420(10.38) ^d	545	25	1.66 (90)	0.40 (80)	0.70 (110)	1.35 (120)	2.06	2.387
[Ru(bpy)(ClaaiEt) ₂](ClO ₄) ₂ (2c)	737(0.50), ^d 615(1.30), ^d 52 6(9.83), 425(7.84) ^d	560	18	1.73 (80)	0.29 (90)	0.61 (110)	1.40 (120)	2.02	2.359
[Ru(bpy)(HaaiCH ₂ Ph) ₂](ClO ₄) ₂ (3a)	729(0.40), ^d 590(1.20), ^d 524(8.74), 422(12.52) ^d	548	16	1.72 (90)	0.28 (70)	0.60 (120)	1.34 (120)	2.00	2.368
[Ru(bpy)(MaaiCH ₂ Ph) ₂](ClO ₄) ₂ (3b)	728(0.49), ^d 604(2.54), ^d 522(10.10), 430(11.32) ^d	540	19	1.68 (100)	0.36 (70)	0.70 (120)	1.31 (140)	2.04	2.377
[Ru(bpy)(ClaaiCH ₂ Ph) ₂](ClO ₄) ₂ (3c)	737(0.53), ^d 622(1.84) ^d 528(10.95), 427(11.85) ^d	552	15	1.75 (80)	0.28 (90)	0.62 (100)	1.34 (120)	2.03	2.350

^a Solvent, MeCN. ^b Solvent MeOH–EtOH (1 : 4, v/v) at 77 K. ^c Solvent, MeCN, supporting electrolyte: ⁿBu₄NClO₄ (0.1 M), working electrode: GC milli electrode, auxiliary electrode: Pt-wire, reference electrode: SCE, solute concentration: $\approx 10^{-3}$ M, scan rate: 50 mV s⁻¹, E^M : eqn. (3), $-E^{L1}$: eqn. (4), $-E^{L2}$: eqn. (5), $-E^{L3}$: eqn. (6), $\Delta E_p = |E_{pa} - E_{pc}|$ where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential. ^d Shoulder. ^e $\Delta E = E^M - E^{L1}$. ^f $\tilde{\nu}_{\text{CT}} = 1241/\lambda_{\max}$ (main).

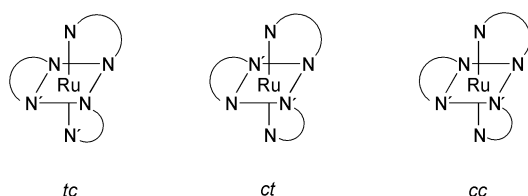
Table 4 ¹H-NMR spectral data of [Ru(bpy)(RaaiR')₂](ClO₄)₂ in CDCl₃

Compound	δ (J/Hz)												
	4,4'-H	5,5'-H	7,7'-H	8,8'-H	10,10'-H	11,11'-H	a,a'-H	b,b'-H	c,c'-H	d,d'-H	1-Me	1-CH ₂	9-R
1a	6.73 (7.0)	6.55 (8.0)	7.59 (8.0)	7.45 (m)	7.45 (m)	7.71 (8.0)	8.04 (8.0)	7.91 (8.0)	8.13 (8.0)	8.42 (8.0)	4.45, 4.40, 4.18		
1b	6.71 (7.0)	6.53 (7.0)	7.53 (7.0)	7.21 (8.0)	7.21 (8.0)	7.62 (7.0)	8.02 (8.0)	7.88 (7.0)	8.12 (8.0)	8.41 (8.0)	4.42, 4.40, 4.16		2.76 2.52 2.39
1c	6.74 (7.0)	6.58 (7.0)	7.63 (8.0)	7.66 (8.0)	7.66 (8.0)	7.80 (8.0)	8.08 (8.0)	8.00 (8.0)	8.17 (8.0)	8.48 (8.0)	4.46, 4.40, 4.20		
2a^a	6.71 (7.0)	6.56 (7.0)	7.61 (7.0)	7.47 (m)	7.47 (m)	7.73 (8.0)	8.05 (8.0)	7.94 (8.0)	8.15 (8.0)	8.45 (8.0)	4.78 4.56 4.40		
2b^b	6.73 (7.0)	6.55 (7.0)	7.54 (7.0)	7.23 (8.0)	7.23 (8.0)	7.68 (8.0)	8.03 (8.0)	7.90 (8.0)	8.15 (8.0)	8.52 (8.0)	4.78 4.57 4.42		2.74 2.50 2.40
2c^c	6.77 (7.0)	6.58 (7.0)	7.65 (8.0)	7.77 (8.0)	7.77 (8.0)	7.82 (8.0)	8.06 (8.0)	7.96 (8.0)	8.16 (8.0)	8.47 (8.0)	4.80 4.58 4.42		
3a^d	6.76 (7.0)	6.50 (7.0)	7.60 (8.0)	7.40 (m)	7.40 (m)	7.75 (8.0)	8.08 (8.0)	8.00 (8.0)	8.20 (8.0)	8.57 (8.0)	6.06, 5.8 0, 5.74, 5.47		
3b^d	6.74 (7.0)	6.49 (7.0)	7.58 (8.0)	7.26 (8.0)	7.26 (8.0)	7.73 (8.0)	8.06 (8.0)	7.99 (8.0)	8.18 (8.0)	8.55 (8.0)	6.04, 5.7 9, 5.72, 50.5, 2.40 46		2.78, 2.5
3c^d	6.77 (7.0)	6.52 (7.0)	7.68 (8.0)	7.80 (8.0)	7.80 (8.0)	7.86 (8.0)	8.10 (8.0)	8.01 (8.0)	8.23 (8.0)	8.60 (8.0)	6.08, 5.8 0, 5.75, 5.48		

^a $\delta(^{13}\text{CH}_3)$: 1.71, 1.65 (cc); 1.40 (tc). ^b $\delta(^{13}\text{CH}_3)$: 1.70, 1.63 (cc); 1.38 (tc). ^c $\delta(^{13}\text{CH}_3)$: 1.72. ^d Phenyl protons (14 H–18 H): δ 7.35–7.50 m = multiplet.

different geometric isomers and with reference to co-ordination pairs of N(imidazole), N and N(azo), N' they are *trans-cis* (tc), *cis-trans* (ct) and *cis-cis* (cc).

The tc and ct geometric isomers belong to C₂-symmetry and cc has C₁-symmetry. The X-ray structure study suggests that the



compound belongs to *tc*-geometry (*vide supra*). The solution ¹H NMR spectra support the presence of two isomers in different proportions. [Ru(bpy)(RaaiR')₂]²⁺ exhibit three 1-Me signals and out of them two are of equal intensity at *ca.* 4.44 and 4.40 ppm, and the third signal, which is the major signal, appears at *ca.* 4.18 ppm. The intensity ratio of the third signal to first/second is 1 : 0.3. [Ru(bpy)(MeaaiR')₂]²⁺ also exhibit three Ar–Me signals and out of them two are of equal intensity at *ca.* 2.5 and 2.8 ppm, and the third signal (which is the major one) appears at *ca.* 2.4 ppm. The methylene (–CH₂–) signal of [Ru(bpy)(MeaaiCH₂CH₃)₂]²⁺ exhibits a complex splitting pattern (Fig. 3a). [Ru(bpy)(MeaaiCH₂Ph)₂]²⁺ shows –CH₂– signals of AB type quartets²¹ (Fig. 3b). There are three over-

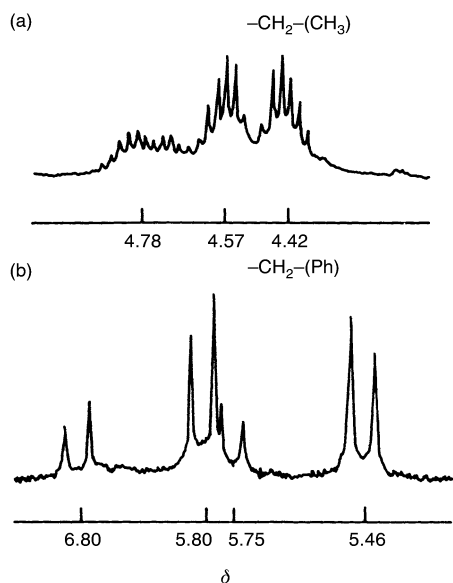


Fig. 3 $^1\text{H-NMR}$ spectra of (a) methylene ($-\text{CH}_2-$) protons of $[\text{Ru}(\text{bpy})(\text{MeaiiCH}_2\text{CH}_3)_2]^{2+}$; (b) methylene ($-\text{CH}_2-$) protons of $[\text{Ru}(\text{bpy})(\text{MeaiiCH}_2\text{Ph})_2]^{2+}$ in CDCl_3 at 298 K.

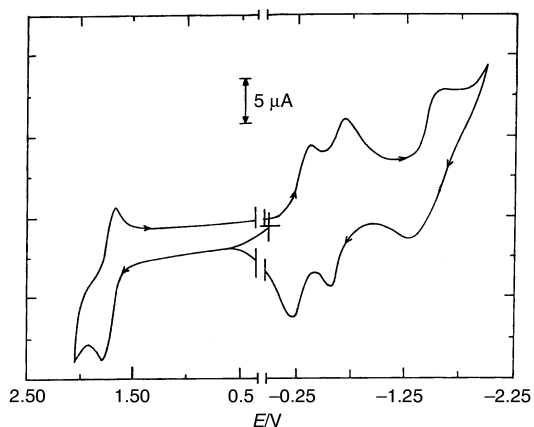


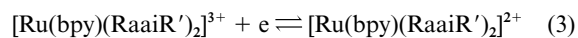
Fig. 4 Cyclic voltammogram of $[\text{Ru}(\text{bpy})(\text{ClaiiMe})_2](\text{ClO}_4)_2$ in MeCN using a Pt-disk milli electrode at 298 K, SCE reference and TBAP (0.1 M) supporting electrolyte.

lapping multiplets in support of the presence of isomers in the mixture. In the complexes, imidazole 4-H and 5-H appear as doublets at 6.7–6.8 ppm and 6.5–6.6 ppm, respectively. Aryl protons (7-H–11-H) are particularly perturbed by the substituent, 9-R and the signal movement is in accordance with the electronic effect of the group.²² The protons 8,10 (8',10')-H are particularly perturbed because of the direct influence of R at the *ortho*-position. Four sets of bpy protons are assigned as a,a'; b,b'; c,c'; d,d'. They appear at the most down-field region and are assigned on comparison with the reported results.^{18–20}

Electrochemistry and correlation with electronic spectra

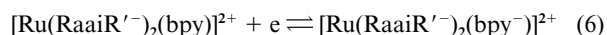
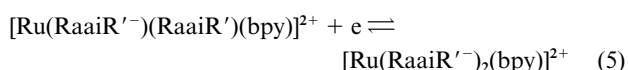
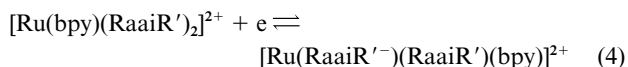
The electrochemical properties of the complexes have been examined cyclic voltammetrically at a glassy carbon working electrode in MeCN and the potentials are expressed with reference to the potential of SCE. The voltammograms display the Ru(III)/Ru(II) couple at positive potentials and the ligand reductions negative potentials compared to SCE. The potentials are summarised in Table 3 and a representative voltammogram is shown in Fig. 4. In the potential range +2.0 to –2.0 V at a scan rate of 50 mV s^{-1} four redox couples are observed; one of them is oxidative in nature at a potential positive to SCE and is quasireversible as is evident from the peak-to-peak separation value, $\Delta E_p > 110 \text{ mV}$. This process can

be described by the redox reaction shown in eqn. (3) and the $E_{1/2}$ values lie at 1.6–1.7 V.



The potential is expectedly higher than $\text{Ru}(\text{RaaiR}')_2\text{Cl}_2^{21}$ and $[\text{Ru}(\text{bpy})_2(\text{RaaiR}')](\text{ClO}_4)_2$.²⁴ The one electron nature of the redox process in eqn. (3) is supported by the i_{pa}/i_{pc} ratio (i_{pa} = anodic peak current and i_{pc} = cathodic peak current) which varies from 0.90–1.04 and in one case by coulometric analysis. The controlled potential coulometric oxidation at 1.85 V in dry MeCN for $[\text{Ru}(\text{bpy})(\text{MeaiiEt})_2](\text{ClO}_4)_2$ (**2b**) corroborates with the one-electron stoichiometry of the couple ($n = Q/Q' = 0.93$ where Q' is the calculated coulomb count after exhaustive electrolysis). The ruthenium(III) congener shows an identical response but reductive in nature. The dark brown solution changed to orange-red after electrolysis.

Three redox couples at potentials negative to SCE are due to reductions of the ligand. Both RaaiR' and bpy are π -acidic ligands. Arylazoimidazoles can accommodate two electrons at the LUMO which is mostly azo in character.^{21–27,35} The first two couples may be due to a azo⁻/azo redox reaction of two co-ordinated RaaiR' and the third response is due to the bpy⁻/bpy reaction (eqn. (4)–(6)).



The redox couples are symmetrically shifted to more positive potential by 0.2–0.3 V from the similar couples of $[\text{Ru}(\text{bpy})_2(\text{RaaiR}')_2]^{2+}$.²⁴ Both Ru(III)/Ru(II) and azo⁻/azo redox couples follow the potential order $\text{Ru}(\text{RaaiR}')_2\text{Cl}_2^{21} < [\text{Ru}(\text{bpy})_2(\text{RaaiR}')](\text{ClO}_4)_2^{24} < [\text{Ru}(\text{RaaiR}')_2(\text{bpy})](\text{ClO}_4)_2$. This is certainly due to the π -acidity order^{11,12} of the ligands: $\text{Cl}^- < \text{bpy} < \text{RaaiR}'$. The redox potential is sensitive to the substituent in the aryl ring and is linearly related with the Hammett σ values of the substituent. It is observed that the MLCT absorption energies ($\tilde{\nu}_{\text{CT}}$ for 517–528 nm) for $[\text{Ru}(\text{bpy})(\text{RaaiR}')_2]^{2+}$ show a linear correlation (eqn. (7)) with the difference in potential $\{\Delta E^0 = E_{1/2}^{\text{M}}(\text{eqn. (3)}) - E_{1/2}^{\text{L}}(\text{eqn. (4)})\}$.

$$\tilde{\nu}_{\text{CT}} = 1.742\Delta E^0 + 0.312 \quad (7)$$

The results are comparable with the other examples of ruthenium(II) with π -acidic ligands *e.g.*, 2,2'-bipyridine,^{41,42} 2-(arylaazo)pyridines,¹⁰ 2-(arylaazo)imidazoles²¹ and 2-aryl-(2-pyridylmethylene)amine.³⁸

Electrochemical parameterization of the Ru(III)/Ru(II) redox potential of arylazoimidazole complexes of ruthenium(II)

Several complexes of 1-alkyl-2-(arylaazo)imidazoles of ruthenium(II) belong to $\text{RuCl}_2(\text{RaaiR}')_2$,^{21,22} $[\text{Ru}(\text{bpy})_2(\text{RaaiR}')](\text{ClO}_4)_2$ ²⁴ and $[\text{Ru}(\text{bpy})(\text{RaaiR}')_2](\text{ClO}_4)_2$ have been characterised by spectroscopic and electrochemical techniques. The electrochemical data used in this work are additive with respect to ligand substitution.^{11,12,43}

Data are restricted to electrochemically reversible/quasi-reversible redox couples involving Ru(III)/Ru(II) and recorded in MeCN solution using $[\text{Bu}_4\text{N}][\text{ClO}_4]$ (0.1 M) supporting electrolyte. A ligand electrochemical parameter, $E_{\text{L}}(\text{L})$, based upon the Ru(III)/Ru(II) redox potential as an electrochemical standard was introduced by Lever.⁴³ He proposed a relationship

Table 5 Electrochemical potential and calculated/experimental Ru(III)/Ru(II) potential of ruthenium(II) complexes

Ligand(L)	$E_L(L)^a$ (V vs. NHE)		$[\text{Ru}(\text{bpy})_2(\text{RaaiR}')^{2+}]^{2+}$		$[\text{Ru}(\text{bpy})(\text{RaaiR}')_2]^{2+}$	
	<i>tcc</i> -RuCl ₂ (RaaiR') ₂	<i>ctc</i> -RuCl ₂ (RaaiR') ₂	$E_{\text{calcd.}}^b$	$E_{\text{expt.}}^{b,c}$	$E_{\text{calcd.}}^b$	$E_{\text{expt.}}^{b,c}$
Haaime	0.334	0.375	1.528	1.470	1.768	1.680
Meaime	0.326	0.367	1.512	1.450	1.736	1.660
OMeime	0.321	0.361	1.502	^e	1.714	^e
Claiime	0.347	0.382	1.542	1.480	1.798	1.720
NO ₂ aime	0.372	0.403	1.604	^e	1.918	^e
HaaieEt	0.333	0.368	1.514	1.490	1.740	1.690
MeaieEt	0.329	0.356	1.490	1.460	1.692	1.660
OMeieEt	0.318	0.351	1.496	^e	1.702	^e
ClaiieEt	0.346	0.383	1.544	1.500	1.800	1.730
NO ₂ aieEt	0.378	0.418	1.616	^e	1.942	^e
Haaich ₂ Ph	0.343	0.381	1.544	1.500	1.792	1.720
Meaich ₂ Ph	0.333	0.370	1.518	1.480	1.748	1.680
OMeich ₂ Ph	0.328	0.366	1.576	^e	1.742	^e
Claiich ₂ Ph	0.381	0.387	1.552	1.53	1.818	1.750
NO ₂ aich ₂ Ph	0.403	0.411	1.666	^e	2.042	

^a $E_L(L)$ values were calculated following eqn. (8) with additional data from ref. 24. ^b Values are expressed in V vs. SCE. ^c From ref. 24. ^d Present work. ^e Not available.

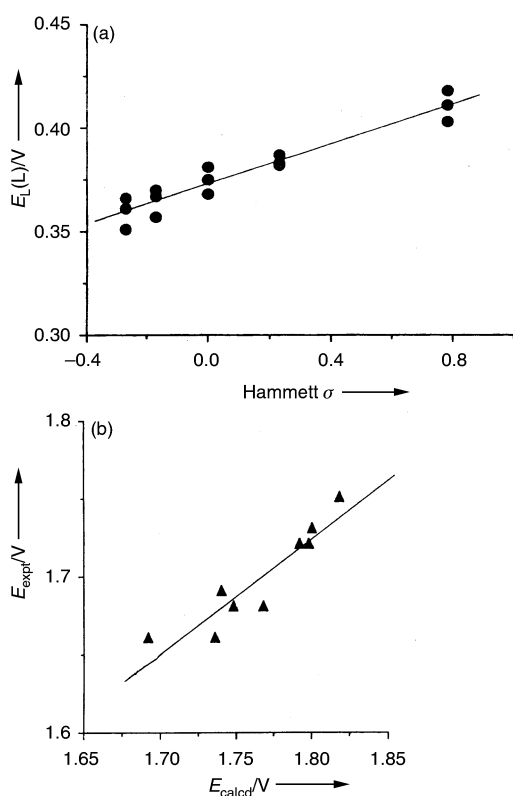


Fig. 5 (a) Plot of $E_L(L)/V$ (with reference to NHE) vs. Hammett σ constants of the substituent at RaaiR' in *ctc*-RuCl₂(RaaiR')₂; (b) correlation between the calculated (E_{calcd}) and experimental (E_{expt}) potential of Ru^{III}/Ru^{II} (with reference to SCE) of $[\text{Ru}(\text{bpy})_n(\text{RaaiR}')_2](\text{ClO}_4)_2$.

between $E_L(L)$ and E_{obs} for a series of complexes $[\text{Ru}(\text{bpy})_n\text{L}_{6-2n}]^{m+}$ ($n=0-3$; L may be monodentate, bidentate LL, tridentate LLL) and is named here as Lever's equation (eqn. (8)).

$$E_{\text{obs}}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = 2n \times 0.255 + (6 - 2n) E_L(L) \quad (8)$$

The plot of $E_L(L)$ versus Hammett σ values exhibit a good linear correlation⁴⁴ and follows the equation (eqn. (9), Fig. 5a) (only $E_L(L)$ values of *ctc*-Ru(RaaiR')₂Cl₂ are used).

$$E_L(L) = 0.0485 \sigma + 0.373 \quad (9)$$

Herein L refers to 1-alkyl-2-(arylo)imidazoles (RaaiR'). The equation (8) and data from ligand electrochemical series proposed by Lever have been used^{43,44} to calculate $E_L(L)$ for RaaiR'. It is observed that $E_L(L)$ values are dependent on the stereochemistry of the complexes; $E_L(L)$ for *tcc*-RuCl₂(RaaiR')₂ is less than that of *ctc*-RuCl₂(RaaiR')₂.

The $E_L(L)$ values have been used to calculate Ru(III)/Ru(II) potentials for $[\text{Ru}(\text{bpy})_2(\text{RaaiR}')^{2+}]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{RaaiR}')_2]^{2+}$ and the theoretical and experimental values are compared in Table 5 (Fig. 5b). Based on a similar argument we may expect that the theoretical potential of Ru(III)/Ru(II) for $[\text{Ru}(\text{RaaiR}')_3]^{2+}$ will lie in the range 1.9–2.2 V vs. SCE. The plots of potential $E_{1/2}^M(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$ in $[\text{Ru}(\text{bpy})_n(\text{MeaaiMe})_{3-n}]^{2+}$ versus number of bpy is linear and the intercept ($n=0$) predicts $E^M(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$ for $[\text{Ru}(\text{MeaaiMe})_3]^{2+}$ as 2.202 V vs. NHE.

Conclusion

This work describes the isolation of hetero-tris-chelates $[\text{Ru}(\text{bpy})(\text{RaaiR}')_2](\text{ClO}_4)_2$ (bpy = 2,2'-bipyridine; RaaiR' = 1-alkyl-2-(arylo)imidazole) and their spectral and electrochemical characterisation. The X-ray structure determination suggests formation of a *trans-cis* isomer out of the three different geometrical isomeric forms: *trans-cis*, *cis-trans* and *cis-cis* with reference to coordination pairs of N(imidazole) and N(azo). Complexes exhibit intense MLCT transitions and the energy of transition is linearly related with difference in potential of Ru(III)/Ru(II) and the first bound ligand reduction. Electrochemical parametrization of Ru(III)/Ru(II) redox potential has been carried out using Lever's method and the calculated ligand potential $E_L(L)$ has been used to predict Ru(III)/Ru(II) redox potentials in the complexes.

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References

- 1 J. Reedijk, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty eds., Pergamon Press, Oxford, 1987, vol. 2, p. 73.
- 2 W.-T. Wong, *Coord. Chem. Rev.*, 1994, **131**, 45.

- 3 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
- 4 K. Kalyanasundaram, S. M. Zakeeruddin and Md. K. Nazeeruddin, *Coord. Chem. Rev.*, 1994, **132**, 259.
- 5 V. Balzani and L. de Cola, eds. *Supramolecular Chemistry*, Kluwer, Dordrecht, 1992.
- 6 M. Haga, M. M. Ali, H. Maegawa, K. Nozaki, A. Yoshimura and T. Ohno, *Coord. Chem. Rev.*, 1994, **132**, 99.
- 7 H. E. Toma and K. Araki, *Coord. Chem. Rev.*, 2000, **196**, 307.
- 8 M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121.
- 9 C. J. da Curha, E. S. Dodsworth, M. A. Monteiro and A. B. P. Lever, *Inorg. Chem.*, 1999, **38**, 5399.
- 10 B. K. Ghosh and A. Chakravorty, *Coord. Chem. Rev.*, 1982, **46**, 159.
- 11 H. Masui, A. L. Freda, M. C. Zerner and A. B. P. Lever, *Inorg. Chem.*, 2000, **39**, 141.
- 12 G. Wolfbauer, A. M. Bond, G. B. Deacon, D. R. MacFarlane and L. Spiccia, *J. Am. Chem. Soc.*, 2000, **122**, 130.
- 13 Z. Q. Lei, *React. Funct. Polym.*, 2000, **43**, 139.
- 14 N. C. Pramanik and S. Bhattacharya, *Transition Met. Chem.*, 1997, **22**, 524.
- 15 L. K. Stultz, M. H. V. Huynh, R. A. Binstead, M. Curry and T. J. Meyer, *J. Am. Chem. Soc.*, 2000, **122**, 5984.
- 16 E. Alessio, E. Iengo, S. Zorzet, A. Bergamo, M. Coluccia, A. Boccarelli and G. Sava, *J. Inorg. Biochem.*, 2000, **79**, 173.
- 17 J. Luo, K. B. Reddy, A. S. Salameh, J. F. Wishart and S. S. Isied, *Inorg. Chem.*, 2000, **39**, 2321.
- 18 S. Baitalik, U. Florke and K. Nag, *Inorg. Chem.*, 1999, **38**, 3296.
- 19 F. Basuli, S.-M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2000, **39**, 1120.
- 20 D. Heseck, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda and M. G. B. Drew, *Inorg. Chem.*, 2000, **39**, 308.
- 21 T. K. Misra, D. Das, C. Sinha, P. Ghosh and C. K. Pal, *Inorg. Chem.*, 1998, **37**, 1672.
- 22 T. K. Misra and C. Sinha, *Transition Met. Chem.*, 1999, **24**, 161.
- 23 S. Pal, T. K. Misra and C. Sinha, *Transition Met. Chem.*, 2000, **25**, 333.
- 24 S. Pal, T. K. Misra, C. Sinha, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 2000, **19**, 1925.
- 25 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 2246.
- 26 E. T. Bell-Loncella and C. A. Bessel, *Inorg. Chim. Acta*, 2000, **303**, 199.
- 27 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1982, **21**, 2737.
- 28 B. J. Coe, C. I. McDonald, S. M. Couchman, J. C. Jeffery, L. H. Rees, S. J. Coles, T. Gelbrich and M. B. Hursthouse, *Polyhedron*, 2000, **19**, 1193.
- 29 S. Goswami, A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1982, 1288.
- 30 P. Majumder, S. Goswami and S.-M. Peng, *Polyhedron*, 1999, **18**, 2543.
- 31 G. M. Sheldrick, SHELXL-Plus, Siemens, Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, 1990.
- 32 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 33 G. M. Sheldrick Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
- 34 A. Seal and S. Ray, *Acta Crystallogr., Sect. C*, 1984, **40**, 929.
- 35 P. K. Santra, T. K. Misra, D. Das, C. Sinha, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1999, **18**, 2869.
- 36 D. Das, Ph.D. Thesis, Burdwan University, Burdwan, India, 1998.
- 37 K. Motoda, H. Sakiyama, N. Matsumoto, H. Okawa and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1995, 3419.
- 38 S. Choudhuri, A. K. Deb. and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 1994, 1305.
- 39 E. C. Johnson, B. P. Sullivan, D. J. Salmon, S. A. Adeyemi and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 2211.
- 40 E. M. Kober and T. J. Meyer, *Inorg. Chem.*, 1982, **21**, 3967.
- 41 S. Chakrabarty, P. Munshi and G. K. Lahiri, *Polyhedron*, 1999, **18**, 1437.
- 42 D. Bhattacharayya, S. Chakrabarty, P. Munshi and G. K. Lahiri, *Polyhedron*, 1999, **18**, 2951.
- 43 A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 1271.
- 44 H. Masui and A. B. P. Lever, *Inorg. Chem.*, 1993, **32**, 2199.