Inorganica Chimica Acta 362 (2009) 5170–5174

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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Syntheses and properties of new metal–carbon bonded heteroleptic complexes of ruthenium(II) containing terpyridine coligand

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ARTICLE INFO

Article history:
Received 28 July 2009
Received in revised form 4 September 2009
Accepted 8 September 2009
Available online 12 September 2009

Keywords:
2-(Arylazo)aniline
Terpyridine
Cycloruthenation
Redox

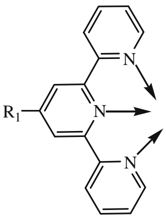
ABSTRACT

Reactions of 2-(arylazo)aniline, HL [H represents the dissociable protons upon orthometallation and HL is p-$RC_6H_4N=NC_6H_4$–NH_2; R = H for HL^1; CH_3 for HL^2 and Cl for HL^3] with Ru(R_1-tpy)Cl_3 (where R_1-tpy is 4′-(R_1)-2,2′,6″,2″-terpyridine and R_1 = H or 4-*N*,*N*-dimethylaminophenyl or 4-methylphenyl) afford a group of complexes of type [Ru(L)(R_1-tpy)]·ClO_4 each of which contains *C*,*N*,*N* coordinated L^- as a tridentate ligand along with a terpyridine. Structure of one such complex has been determined by X-ray crystallography. All the Ru(II) complexes are diamagnetic, display characteristic ^1H NMR signals and intense $d\pi(Ru^{II}) \rightarrow \pi^*(tpy)$ MLCT transitions in the visible region. Cyclic voltammetric studies on [Ru(L)(R_1-tpy)]·ClO_4 complexes show Ru(II)–Ru(III) oxidation within 0.63–0.67 V versus SCE.

1. Introduction

The chemistry of Ru(II) complexes incorporating polypyridyl ligands has expanded significantly in recent years. Particular attention has been focused on the complexes of Ru(II) with 2,2′,6′,2″-terpyridine (*tpy*) and 2,2′-bypyridine (*bpy*) ligands [1–9]. Homoleptic and heteroleptic *tpy* complexes have been prepared using (tpy)$RuCl_3$ precursors [1–6]. Often, reaction of tridentate ligands with (tpy)$RuCl_3$, during the preparation of *bis* heteroleptic complex of the type $[Ru(L)(tpy)]^{n+}$, resulted in formation of intractable mixtures, and in particular when drastic reaction condition was required [1–6]. Although there are abundant reports on the synthesis of $[Ru(L)(tpy)]^{n+}$ type of complexes where L is tridentate but the reports are scarce where L binds to Ru centre with Ru–C(aryl) bond [10–13]. Therefore, from our interest on the design and synthesis of ligands, suitable for orthometallation, we intended to prepare $[Ru(L)(tpy)]^{n+}$ complexes where L is tridentate with M–C(aryl) bond.

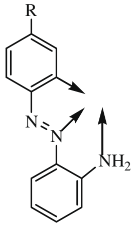
Herein we report the synthesis of $[Ru(L)(tpy)]^+$ complexes using three kinds of substituted *tpy* ligands and three types of substituted HL as given in the structures **1** and **2**. The complex formations have been authenticated on the basis of X-ray studies and ^1H NMR spectroscopy. The redox property of the new Ru(II) cyclometallates have been studied electrochemically. A plausible description of redox orbitals have been ascribed on the basis of single point DFT calculations.



R_1-tpy

1

R_1 = H for tpy,
4-methylphenyl
4-N,N-dimethylaminophenyl



HL

2

R = H for HL^1 (**2a**),
CH_3 for HL^2 (**2b**),
Cl for HL^3 (**2c**)

2. Results and discussion

2.1. Syntheses

Reaction of one equivalent 2-(arylazo)aniline (HL) **2** with Ru(R_1-tpy)Cl_3, in refluxing methanol and subsequently upon treatment with $NaClO_4$, afforded [Ru(L)(R_1-tpy)]·ClO_4, **3**. The composition of diamagnetic [Ru(L)(R_1-tpy)]·ClO_4 complexes matched well with the analytical data and total proton count in ^1H NMR spectrum (*vide infra*). Orthometallation of HL, substituting the *ortho* aryl hydrogen of aryl ring, has been established from spectral (^1H NMR) data (see below) and confirmed by X-ray studies. Seven complexes have been prepared varying the *tpy* moiety and HL as given in Scheme 1.

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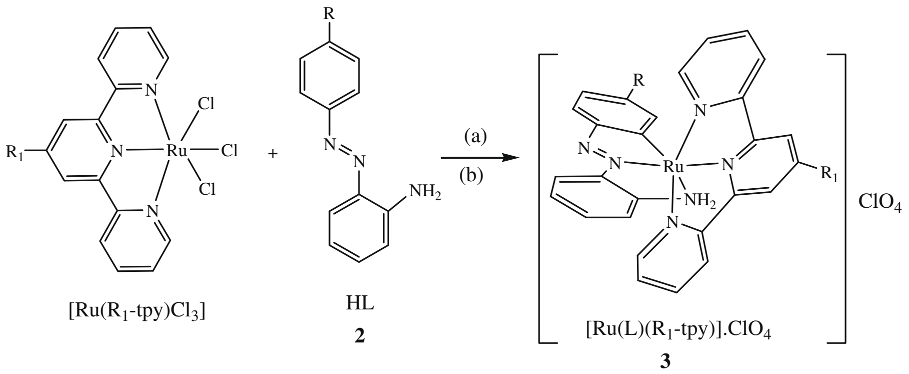
doi:10.1016/j.ica.2009.09.024



	R	R_1
3a	H	4-methylphenyl
3b	CH_3	4-methylphenyl
3c	Cl	4-methylphenyl
3d	H	4-N,N-dimethylaminophenyl
3e	Cl	4-N,N-dimethylaminophenyl
3f	CH_3	H
3g	Cl	H

Scheme 1. Synthesis of [Ru(L)(R_1-tpy)]·ClO_4, **3**. (a) MeOH, (b) $NaClO_4$.

2.2. Characterization

All the complexes **3a–g**, are soluble in common organic solvents furnishing pink solutions. UV–Vis spectra of the complexes have been recorded in dichloromethane solutions. All the complexes displayed several absorptions in the visible and ultraviolet regions. The absorptions near 500 nm has been assigned to the MLCT transition *i.e.* $d\pi(Ru^{II}) \rightarrow \pi^*(tpy)$ consistent with DFT results (see below). An absorption near 1050 nm of lower intensity was observed for all the complexes in contrast to the reported *tpy* complexes of ruthenium [1–6]. A representative spectrum of **3a** is shown in Fig. 1. The UV–Vis spectral data are given in Section 4.

The IR spectra of the complexes (Figs. S8–S14 in the Supplementary material) in solid KBr support ν_{NH2} appeared as broad band within the ranges 3261–3210 cm^{-1}. The $\nu_{N=N}$ of the ligands (~1455–1474 cm^{-1}) shifted to lower frequency upon complexation (1382–1409 cm^{-1}), consistent with coordination of the azo nitrogen [14–22]. Ruthenium complexes exhibited a broad band near 1090 cm^{-1}, characteristic of uncoordinated ClO_4^-. The IR data are collected in Section 4.

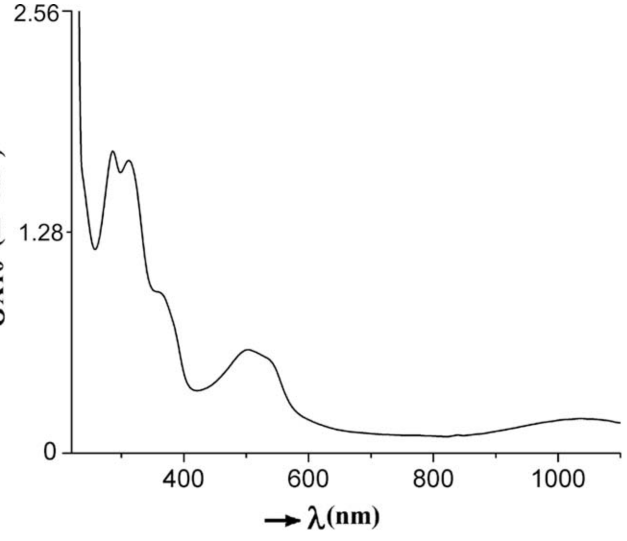


Fig. 1. UV–Vis spectrum of [Ru(L^3)(4-methylphenyl-tpy)]·ClO_4 in dichloromethane.

The compositions of **3a**–**g** matched well with the C, H, N analytical data and ^1H NMR spectral data. The ^1H NMR spectra (Supplementary Figs. S15–S21) of the complexes were recorded in $CDCl_3$. The well resolved ^1H NMR spectra of [Ru(L)(R_1-tpy)]·ClO_4, **3**, complexes are consistent with their structures. The significant features that have been taken into consideration to elucidate the structures are as follows: (i) The NH_2 resonance of [Ru(L)(R_1-tpy)]·ClO_4, **3**, appeared as a singlet in the range of δ 5.28–4.56 for two proton; (ii) the total count of aromatic protons matched well with the total number of protons (data are given in Section 4); (iii) a sharp singlet appeared in the range of δ 6.10–4.99 for the **3b**, **3c** and **3e**–**g** (where $R = CH_3$ or Cl) indicating the orthometallation on the substituted phenyl ring of HL.

2.3. X-ray structure

Suitable crystals of [Ru(L^2)(4-methylphenyl-tpy)]·ClO_4, **3b**, were grown by slow diffusion of dichloromethane solution into petroleum ether. A perspective view of the molecule has been shown in Fig. 2 and selected bond distances and angles are collected in Table 1. The monoanionic $(L^2)^-$ ligand bind to the ruthenium metal in *C,N,N*-tridentate fashion along with 4′-(4-methyl phenyl)-2,2′,6′,2″-terpyridine (4-methylphenyl-tpy). Two tridentate ligands are meridionally bound to the Ru(II) centre in the cationic complex $[Ru(L^2)(4\text{-methylphenyl-tpy})]^+$. The crystal consists of a cluster of $[Ru(L^2)(4\text{-methylphenyl-tpy})]^+$, $[ClO_4]^-$ and dichloromethane solvent in 3:3:2 stoichiometry in asymmetric unit. All the units of [Ru(L^2)(4-methylphenyl-tpy)]·ClO_4 in the asymmetric unit are equivalent having similar bond parameters. The RuN_5C coordination sphere is distorted octahedral. The Ru1–N5 (central pyridine nitrogen of terpyridine) distance [Ru1–N5, 1.967(5) Å] is shorter than the terminal Ru1–N (pyridine) distances [Ru1–N4, 2.056(4) Å; Ru1–N6, 2.064(4) Å] like other ruthenium terpyridine

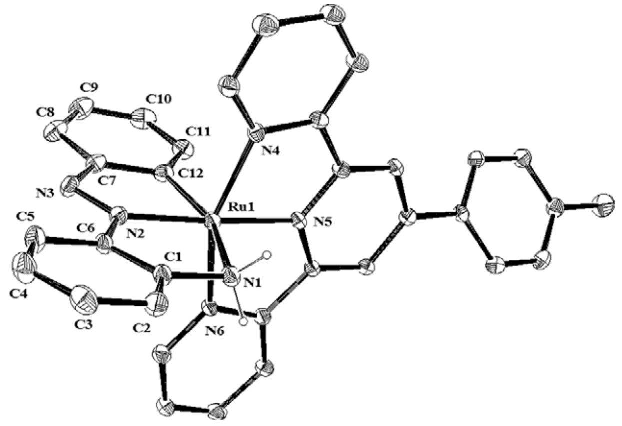


Fig. 2. Molecular structure of $[Ru(L^2)(4\text{-methylphenyl-tpy})]^+$, (except ClO_4) with atom numbering scheme. The hydrogen atoms excepting on N(1) of the amino groups have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for compound **3b**.

Distances	
Ru1–N1	2.218(5)
Ru1–N2	1.966(5)
Ru1–N4	2.056(4)
Ru1–N5	1.967(5)
Ru1–N6	2.064(4)
N1–C1	1.448(9)
N2–N3	1.298(7)
N2–C6	1.419(9)
N3–C7	1.386(10)
Ru1–C12	2.000(5)
Angles	
N1–Ru1–N2	79.8(2)
N1–Ru1–N4	90.25(18)
N1–Ru1–N5	105.14(18)
N1–Ru1–N6	91.92(16)
N1–Ru1–C12	158.1(2)
N2–Ru1–N4	100.6(2)
N2–Ru1–N5	175.02(18)
N2–Ru1–N6	102.51(19)
N2–Ru1–C12	78.3(2)
N4–Ru1–N5	78.98(19)
N4–Ru1–N6	156.9(2)
N4–Ru1–C12	93.6(2)
N5–Ru1–N6	78.21(18)
N5–Ru1–C12	96.8(2)

complexes [23–26]. The Ru1–C12 (2.000(5) Å), Ru1–N2(azo) (1.966(5) Å) bond lengths of $[Ru(L^2)(4\text{-methylphenyl-tpy})]^+$ are within the normal range [27–29]. The [Ru1–N1(amine) (2.218(5) Å) is longer than the other amine complexes [27–29] due to the trans effect of aryl carbon [18]. In the crystal lattice the perchlorate ions are held between two $[Ru(L^2)(p\text{-methylphenyl-tpy})]^+$ through hydrogen bond interaction with the amino protons. The dichloromethane solvents are held in the crystal lattice through non bonded interactions. The relevant packing diagram has been given in Fig. S29 (Supplementary material).

2.4. Electrochemistry

$[Ru(L)(R_1\text{-tpy})]\cdot ClO_4$ complexes exhibit one electron quasi reversible oxidative cyclic voltammetric responses in the range of 0.63–0.67 V versus SCE in acetonitrile solution. A representative cyclic voltammogram of **3c** is shown in Fig. 3 and data are given in Section 3. The oxidation has been assigned according to the couple of Eq. (1) where $[Ru(L)(R_1\text{-tpy})]^{2+}$ is the Ru(III) analogue of $[Ru(L)(R_1\text{-tpy})]^+$.

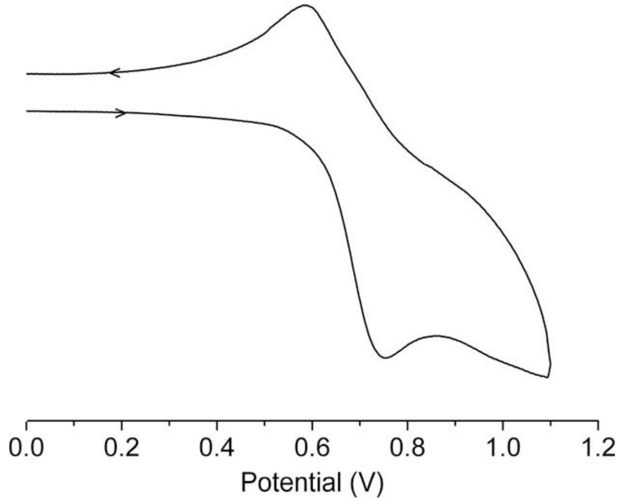


Fig. 3. Cyclic voltammogram of the $[Ru^{II}(L^3)(4\text{-methylphenyl-tpy})]\cdot ClO_4$ complex in acetonitrile solution (0.1 M TBAP) at scan rate of 50 mV s^{-1}.

$$[Ru(L)(R_1\text{-tpy})]^+ - e \rightarrow [Ru(L)(R_1\text{-tpy})]^{2+} \qquad (1)$$

According to the DFT results the composition of HOMO (Fig. 4a) of $[Ru(L)(R_1\text{-tpy})]^+$ is Ru centered indicating the oxidation to be metal centered. The LUMO (Fig. 4b) is primarily concentrated on the *tpy* ligand. Therefore the HOMO → LUMO MLCT transition is consistent with the assignment of UV–Vis spectra.

3. Concluding remarks

Quite a number of reports are there on Ru(II) terpyridine complexes incorporating tridentate coligands. But the examples on the corresponding organometallic analogues are limited. The new organometallic heteroleptic *bis* complexes have been prepared utilising the strategy of orthometallation. A series of such Ru(II) complexes have been prepared containing tridentate *C,N,N* donor ligands along with a terpyridine analogue. Therefore, we believe that the methods of preparation and properties of orthometallated Ru(II) complexes in presence of polypyridyl ligands may prove to be useful in future.

4. Experimental

4.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedure [30]. Ruthenium trichloride was purchased from Johnson Matthey, India. $Ru(R_1\text{-tpy})Cl_3$ was synthesized following the reported procedure [31]. The ligands 2-(phenylazo)aniline (HL^1), 2-(4-methylphenylazo)aniline (HL^2), and 2-(4-chlorophenylazo)aniline (HL^3) were prepared following the reported procedures [15–17].

4.2. Syntheses of complexes

4.2.1. $[Ru(L)(R_1\text{-tpy})]\cdot ClO_4$

The $[Ru(L)(R_1\text{-tpy})\cdot ClO_4]$ complexes were obtained by following a general procedure. Specific details are given below for a particular complex.

4.2.1.1. $[Ru(L^1)(4\text{-methylphenyl-tpy})]\cdot ClO_4$ ***3a***. HL^1 (0.043 g, 0.22 mmol) was dissolved in methanol (40 mL) and to it were added $[Ru(4\text{-methylphenyl-tpy})Cl_3]$ (0.0 g, 0.22 mmol). The

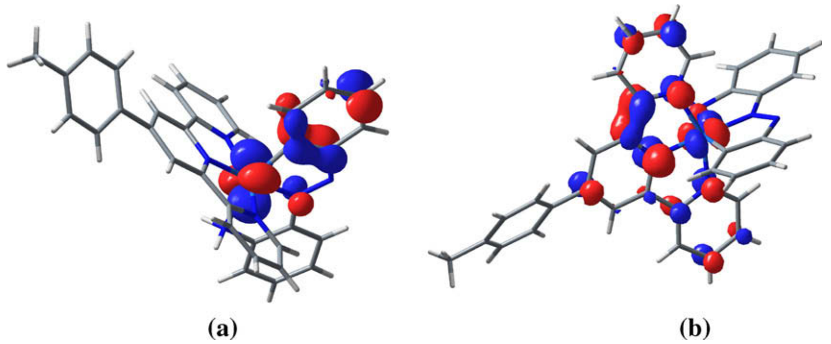

(a) (b)

Fig. 4. (a) HOMO of $[Ru(L^2)(4\text{-methylphenyl-tpy})]^+$ and (b) LUMO of $[Ru(L^2)(4\text{-methylphenyl-tpy})]^+$.

mixture was then refluxed for 4 h, when a pink solution was obtained. Evaporation of these solutions afforded a dark solid which was washed with petroleum ether several times to remove excess ligands, and then it was purified by thin layer chromatography on silica plate with toluene/acetonitrile (20:80) as the eluent. A pink band separated and the complex was extracted from it with methanol and $NaClO_4$. The pure crystals, obtained upon evaporation of the solvent, was recrystallised from dichloromethane-petroleum ether to afford $[Ru(L^1)((4\text{-methylphenyl-tpy})]\cdot ClO_4$ as a crystalline dark solid. Yield: 60%. *Anal.* Calc. for **3a**: C, 56.70; H, 3.78; N, 11.67. Found: C, 56.64; H, 3.87; N, 11.74%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1040 (3200), 495 (6300), 365 (8125), 310 (17100), 290 (18300). IR (KBr pellets, cm^{-1}): ν_{NH2} 3260, 3234, $\nu_{N=N}$ 1404, ν_{Cl-O} 1089. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.75 (d, 1H); 8.74 (s, 2H); 8.27 (d, 2H); 8.16 (d, 1H); 7.81 (d, 2H); 7.70 (t, 2H); 7.60–7.57 (m, 1H); 7.52 (d, 1H); 7.49–7.43 (m, 3H); 7.41 (d, 2H); 7.01 (t, 2H); 6.91–6.87 (m, 1H); 6.65–6.62 (m, 1H); 6.15 (d, 1H); 4.62 (s, 2H); 2.84 (s, 3H). $E_{1/2}$ [V]: 0.63.

4.2.1.2. [Ru(L²)(4-methylphenyl-tpy)]·ClO₄ **3b**.

4.2.1.2. $[Ru(L^2)(4\text{-methylphenyl-tpy})]\cdot ClO_4$ ***3b***. Yield: 60%. *Anal.* Calc. for **3b**: C, 57.26; H, 3.98; N, 11.45. Found: C, 57.34; H, 4.02; N, 11.58%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1090 (5350), 500 (9800), 360 (14450), 310 (25560), 285 (27840). IR (KBr pellets, cm^{-1}): ν_{NH2} 3258, 3238, $\nu_{N=N}$ 1405, ν_{Cl-O} 1089. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.70 (d, 1H); 8.49 (s, 2H); 8.27 (d, 2H); 8.04 (d, 1H); 7.85–7.81 (m, 2H); 7.73–7.68 (m, 2H); 7.55–7.34 (m, 7H); 7.00 (t, 2H); 6.68 (d, 1H); 5.89 (s, 1H); 4.56 (s, 2H); 2.47 (s, 3H); 1.91 (s, 3H). $E_{1/2}$ [V]: 0.66.

4.2.1.3. $[Ru(L^3)(4\text{-methylphenyl-tpy})]\cdot ClO_4$ ***3c***. Yield: 60%. *Anal.* Calc. for **3c**: C, 54.11; H, 3.47; N, 11.14. Found: C, 54.21; H, 3.42; N, 11.23%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1040 (2000), 500 (5920), 365 (9150), 310 (16780), 285 (17840). IR (KBr pellets, cm^{-1}): ν_{NH2} 3244, 3210, $\nu_{N=N}$ 1382, ν_{Cl-O} 1087. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.70 (d, 1H); 8.49 (s, 2H); 8.27 (d, 2H); 8.07 (d, 1H); 7.82 (d, 2H); 7.78–7.72 (m, 2H); 7.57–7.40 (m, 7H); 7.02 (t, 2H); 6.87 (d, 1H); 6.10 (s, 1H); 4.66 (s, 2H); 2.49 (s, 3H). $E_{1/2}$ [V]: 0.67.

4.2.1.4. $[Ru(L^1)(4\text{-}N,N\text{-dimethylaminophenyl-tpy})]\cdot ClO_4$ ***3d***. Yield: 60%. *Anal.* Calc. for **3d**: C, 56.11; H, 4.03; N, 13.09. Found: C, 56.23; H, 4.12; N, 13.11%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1070 (4550), 517 (20000), 365 (27560), 315 (42440), 290 (38300). IR (KBr pellets, cm^{-1}): ν_{NH2} 3247, 3215, $\nu_{N=N}$ 1406, ν_{Cl-O} 1085. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.73 (d, 1H); 8.46 (s, 2H); 8.23 (d, 2H); 8.15 (d, 1H); 7.82 (d, 2H); 7.69 (t, 2H); 7.57–7.51 (m, 3H); 7.45 (d, 3H); 6.98 (t, 2H); 6.90–6.84 (m, 3H); 6.64 (t, 1H); 4.64 (s, 2H); 3.10 (s, 6H). $E_{1/2}$ [V]: 0.64.

4.2.1.5. $[Ru(L^3)(4\text{-}N,N\text{-dimethylaminophenyl-tpy})]\cdot ClO_4$ ***3e***. Yield: 60%. *Anal.* Calc. for **3e**: C, 53.63; H, 3.73; N, 12.51. Found: C, 53.69; H, 3.82; N, 12.43%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1060 (2300), 515 (8460), 365 (12820), 315 (18820), 290 (16820). IR (KBr pellets, cm^{-1}): ν_{NH2} 3244, 3212, $\nu_{N=N}$ 1381, ν_{Cl-O} 1087. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.67 (d, 1H); 8.46 (s, 2H); 8.26 (d, 2H); 8.03 (d, 1H); 7.83 (d, 1H); 7.73–7.68 (m, 2H); 7.56–7.47 (m, 3H); 7.45–7.37 (m, 3H); 6.99–6.96 (m, 2H); 6.83–6.78 (m, 2H); 6.08 (s, 1H); 5.79–5.74 (m, 1H); 4.73 (s, 2H); 3.07 (s, 6H). $E_{1/2}$ [V]: 0.65.

4.2.1.6. $[Ru(L^2)(tpy)]\cdot ClO_4$ ***3f***. Yield: 60%. *Anal.* Calc. for **3f**: C, 52.22; H, 3.60; N, 13.05. Found: C, 52.16; H, 3.67; N, 12.98%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1035 (1400), 525 (10430), 370 (17230), 315 (24860), 275 (27820), 235 (28850). IR (KBr pellets, cm^{-1}): ν_{NH2} 3261, 3242, $\nu_{N=N}$ 1383, ν_{Cl-O} 1087. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.67 (d, 1H); 8.34 (d, 2H); 8.19 (d, 2H); 8.01 (t, 2H); 7.69 (t, 2H); 7.57–7.49 (m, 3H); 7.47–7.41 (m, 2H); 6.99 (t, 2H); 5.81 (d, 1H); 5.45 (s, 1H); 5.28 (s, 2H); 1.90 (s, 3H). $E_{1/2}$ [V]: 0.63.

4.2.1.7. $[Ru(L^3)(tpy)]\cdot ClO_4$ ***3g***. Yield: 60%. *Anal.* Calc. for **3g**: C, 48.80; H, 3.03; N, 12.65. Found: C, 48.65; H, 3.09; N, 12.74%. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), dichloromethane): 1040 (1020), 525 (6800), 365 (11650), 320 (18250), 275 (19450), 235 (19850). IR (KBr pellets, cm^{-1}): ν_{NH2} 3255, 3244, $\nu_{N=N}$ 1382, ν_{Cl-O} 1088. ^{1}H NMR ($CDCl_3$ + 1 drop DMSO-d$_6$, ppm): δ 8.69 (d, 1H); 8.35 (d, 2H); 8.20 (d, 2H); 8.10–8.00 (m, 2H); 7.76–7.67 (m, 2H); 7.58–7.51 (m, 2H); 7.49–7.44 (m, 2H); 7.05–6.99 (m, 2H); 6.85–6.81 (m, 1H); 6.01 (d, 1H); 4.99 (s, 1H); 4.66 (s, 2H). $E_{1/2}$ [V]: 0.64.

4.3. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin–Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin–Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1601 PC spectrophotometer. ^{1}H NMR spectra were obtained on Brucker DPX 400 and Brucker 500 RPX NMR spectrometers in $CDCl_3$ with 1 drop DMSO-d$_6$ using TMS as the internal standard. Electrochemical measurements were made under dinitrogen atmosphere using a PAR model VARSASTAT-II potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical

Table 2
Crystallographic data for **3b**.

Chemical formula	**3**($C_{34}H_{27}N_6Ru$), **3**(ClO_4), **2**(CH_2Cl_2)
Formula weight	2330.26
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	16.681(2)
b (Å)	18.454(5)
c (Å)	18.852(4)
α (°)	76.589(12)
β (°)	63.794(8)
γ (°)	86.571(12)
λ (Å)	0.71073
V (Å^3)	5058.7(19)
$F(0\,0\,0)$	2364
Z	2
T (K)	293
D (mg/m$^{-3)}$	1.530
μ (mm^{-1})	0.698
R_1 (all data)	0.0602
wR_2 [$I > 2\sigma(I)$]	0.1618
Goodness-of-fit (GOF)	1.02

data were collected at 298 K and are uncorrected for junction potentials.

4.4. DFT calculations

Using the X-ray coordinates of the [Ru(L^2)(4-methylphenyl-tpy)]·ClO_4 complex, ground state electronic structure calculations have been carried out using DFT [32] methods with the GAUSSIAN 03 program [32]. Becke' hybrid function [33] with the Lee–Yang–Parr (LYP) correlation function [34] was used throughout the study. LANL2DZ valence and effective core potential functions were used. All energy calculations were performed using the self-consistent field "tight" option of the GAUSSIAN 03 program to ensure sufficiently well converged values for the state energies.

4.5. Crystallography

Single crystals of [Ru(L^2)(4-methylphenyl-tpy)]·ClO_4 were grown by slow diffusion of a dichloromethane solution into petroleum ether at 298 K. Data were collected by ω-scan technique on a Bruker Smart CCD diffractometer with Mo Kα radiation monochromated by graphite crystal. Structure solution was done by direct method with SHELXS-97 program [35]. Full matrix least square refinements on F^2 were performed using SHELXL-97 program [36]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. All hydrogens were included at calculated positions. The data collection parameters and relevant crystal data are collected in Table 2.

Acknowledgements

We are thankful to the DST (New Delhi) for funding under DST-SERC (SR/S1/IC-0026/2007) project. JP is thankful to the CSIR (New Delhi) for his fellowship (No. 09/106(0097)2K8-EMR-I). We are thankful to Dr. G. Saha (Chembiotek). The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, University of Kalyani. The support of DST under FIST and UGC SAP program to the Department of Chemistry, University of Kalyani is acknowledged.

Appendix A. Supplementary material

CCDC 740067 [(L^2)Ru(4-methylphenyl-tpy)]·ClO_4, **3b** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.09.024.

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