



# Mixed ligand complexes of Ru(II) complexes with 5,6-dimethyl -3-pyridin-2-yl-[1,2,4]triazine: Synthesis, Characterization and Quantum Chemical Study using Semi-empirical PM 3 and *Ab initio* Methods

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## ABSTRACT

The condensation product between 2,6-diacetylpyridinedihydrazone and pyridine-2-aldehyde were prepared and this was reacted with *cis*-Ru(phen)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O and *cis*-Ru(bipy)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O to form two mixed – ligand complexes. The complexes were characterized using elemental analyses, infrared and electronic spectra, mass spectra, <sup>1</sup>H NMR, and the molar conductances determined. The elemental analyses data is satisfactory with the formation of the prepared complexes which conformed to the electrocyclisation of the introduced ligand. The mass spectra data is consistent with the molecular structural patterns of the complexes. The conductivity measurement revealed that the complexes were 1:2 electrolytes. Quantum chemical methods are used to calculate the binding and stabilization energies of the two complexes which suggested that binding and stabilization energies of [Ru(phen)<sub>2</sub>L]<sup>2+</sup> are thermodynamically more favourable compared to [Ru(bipy)<sub>2</sub>L]<sup>2+</sup>.

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## Introduction

A number of polypyridyl Ru<sup>2+</sup> complexes are useful non-radioactive probes for the structural elucidation of nucleic acids [1]. These compounds have also been found to have valuable photoluminescence properties with large molar absorption coefficients in the visible region [2,3]. They are known to have the potential to insert and stack between the DNA base pairs and further develop into photochemical probes of DNA structures as well as anticancer drugs [4-7]. The interactions of CT-DNA with transition metal complexes containing planar polycyclic groups have been investigated extensively [1]. The increase in interest in the study of the interaction between polypyridylruthenium(II) complexes and DNA has been as a result of the employment of the various modifications of 2,2'-bipyridine and 1,10-phenanthroline to address different issues [6]. The easily constructed rigid chiral structures spanning all three dimensions and a rich photophysical repertoire have contributed to considerable attraction to these complexes [8]. Herein we report the synthesis and characterization of two mixed –ligand complexes of *cis*-Ru(phen)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O and *cis*-Ru(bipy)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O with the condensation product of 2,6-diacetylpyridinedihydrazone and pyridine-2-aldehyde (DDAP).

## Experimental

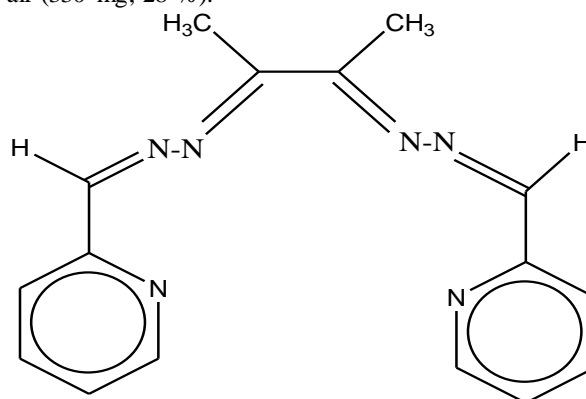
### Materials and method

#### Reagents

Reagent grade RuCl<sub>3</sub>.3H<sub>2</sub>O, 1,10-phenanthroline, LiCl, DMF, diethyl ether, acetone, 2,2'-bipyridyl, diacetyl, hydrazine hydrate, glacial acetic acid, pyridine-2-aldehyde, NaClO<sub>4</sub> were purchased from the British Drug House Chemicals Ltd (BDH) and Aldrich Chemicals Co. were used without further purification.

## Preparation of the DDAP

456 mg (1mmole) diacetylpyridinedihydrazone [9] was transferred into 100 mL round-bottom flask, 20 mL methanol and 0.76 mL pyridine-2-aldehyde added. The mixture was stirred with a calcium chloride guard-tube on the flask for 4 hrs. Few minutes of stirring produced a bright –yellow solution which became turbid as stirring continued. The bright –yellow compound obtained after 4hrs of stirring was filtered by suction and dried in the air (330 mg, 28 %).



DDAP

## Fig.1: The structure of the DDAP Reaction of Ru(phen)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O[10]with DDAP

To a suspension of *cis*-Ru(phen)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O (114 mg, 0.2 mmole) in 20 mL (1:1) MeOH – H<sub>2</sub>O mixture and N<sub>2</sub> gas bubbled through for 30 mins. To this 58 mg (0.2 mmole) DDAP was added and the mixture refluxed for 6hrs under N<sub>2</sub> gas, after which the mixture was cooled to room temperature, before it was filtered by gravity. To the filtrate, 246 mg NaClO<sub>4</sub> solution in 5 mL distilled water was added with constant stirring, the red

precipitate obtained immediately was stirred for 30 mins before it was filtered by suction, washed with 15 mL diethyl ether and then dried in the vacuo. Yield: 66 mg, (37 %) Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O Anal. Cal. C<sub>34</sub>H<sub>32</sub>N<sub>8</sub>O<sub>10</sub>Cl<sub>2</sub>Ru (M.M: 884.312): C, 46.15; H, 3.65; N, 12.67. Found: C, 46.89; H, 3.51; N, 12.26. FTIR: ν/cm<sup>-1</sup>: 1412m (N=N); 1245s (C-N); 1601m (C=N); 3420m (O-H of H<sub>2</sub>O); 623s, 1088vs (ClO<sub>4</sub>).UV-Vis: cm<sup>-1</sup> 22,644; 34,780sh; 38,466; 45,259. ESI-MS (CH<sub>3</sub>CN) m/z: 323.95(100% {Ru(phen)<sub>2</sub>L}<sup>2+</sup>). <sup>1</sup>H NMR: δ/ppm: 2.40 (6H, methyl), 7.10 – 8.93(12H, aromatic). Λ<sub>M</sub>/mho cm<sup>2</sup>mol<sup>-1</sup>323 (CH<sub>3</sub>CN) (1:2 electrolyte).

#### Reaction of Ru(bipy)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O[11] with DDAP

104 mg (0.2 mmole) Ru(bipy)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O was transferred to a 100 mL two-neck round bottom flask, 10 mL methanol – water mixture (1:1) added and N<sub>2</sub> gas passed for 30 mins. To this 58 mg (0.2 mmole) DDAP was added and the mixture refluxed for 6 hrs under N<sub>2</sub> gas. After which it was cooled to room temperature before it was filtered by gravity. 246 mg NaClO<sub>4</sub> solution in 5 mL distilled water was added with stirring, the red precipitate obtained immediately was stirred for 30 mins before it was filtered by suction, washed with 15 mL diethyl ether and then dried in vacuo. Yield: 65 mg, (41%) Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> Anal. Cal. C<sub>30</sub>H<sub>28</sub>N<sub>8</sub>O<sub>8</sub>Cl<sub>2</sub>Ru (M.M: 800.28): C, 44.98; H, 3.53; N, 14.00. Found: C, 45.16; H, 3.46; N, 13.65. FTIR: ν/cm<sup>-1</sup>:1364m (N=N); 1246s (C-N); 1603s (C=N); 3420m (O-H of H<sub>2</sub>O); 623s, 1092vs (ClO<sub>4</sub>). UV-Vis: cm<sup>-1</sup> 22,166; 24,184; 35,525; 39,920; 41,637; 47,964.323 (CH<sub>3</sub>CN) (1:2 electrolyte). ESI-MS (CH<sub>3</sub>CN) m/z: 300.15 (100% {Ru(bipy)<sub>2</sub>L}<sup>2+</sup>). Λ<sub>M</sub>/mho cm<sup>2</sup>mol<sup>-1</sup> 302 (CH<sub>3</sub>CN) (1:2 electrolyte).<sup>1</sup>H NMR: δ/ppm: 2.33 (6H, methyl), 7.45 – 8.83 (14H, aromatic).

#### Physical measurements

Microanalyses were performed by a Perkin-Elmer 2400II CHNS analyzer. UV/VIS spectra were recorded on a Perkin-Elmer Lambda 950 spectrophotometer, FTIR spectra (KBr) on a Shimadzu FTIR-8400S spectrometer and ESI mass spectra on a Waters Qtof Micro YA263 Spectrometer. Molar conductances were measured by a Sytronics (India) conductivity meter (model 306) in acetonitrile and 300MHz NMR spectra on a Bruker DPX300 spectrometer in deuterated dimethylsulphoxide (DMSO-d<sub>6</sub>).

#### Results and Discussion

The complexes, Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O and Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> were obtained from MeOH-H<sub>2</sub>O (1:1) mixture refluxed under N<sub>2</sub> gas. They were isolated by reacting DDAP and Ru(phen)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O and Ru(bipy)<sub>2</sub>Cl<sub>2</sub>.2H<sub>2</sub>O in a 1:1 ratio and 2 mmole NaClO<sub>4</sub> added. Both complexes were analyzed for C,H,N and satisfactory analyses were obtained in each of the cases which revealed that the ligand electrocyclicised to give L. The percentage yields of the complexes were found to be appreciable. The compounds showed colours that are consistent with similar systems [12].

In the infrared spectra of the complexes, the stretching vibration due to the ν (C=N) was observed at 1601 cm<sup>-1</sup> and 1603 cm<sup>-1</sup> respectively, while the ν (C-N) appeared at 1245 cm<sup>-1</sup> and 1246 cm<sup>-1</sup> respectively for the compounds. In the two complexes, the electrocyclicisation of the ligand on complexation was confirmed by the presence of the band due to ν(N=N) at 1412 cm<sup>-1</sup> and 1364 cm<sup>-1</sup> for Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O and Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> respectively.

The UV-Visible spectra of the Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O showed the higher energy transitions at 34,780sh cm<sup>-1</sup> (288 nm)

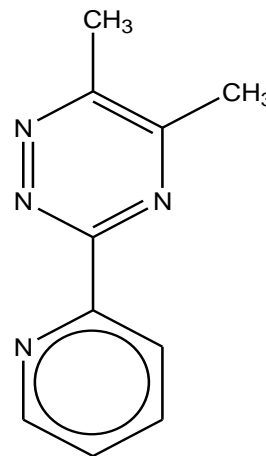
and 38,466 cm<sup>-1</sup> (259 nm) which are phenanthroline -based intramolecular π →π\* transitions [13,14]. The Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> exhibited an intense band at a higher energy absorption band centered at 35,529 cm<sup>-1</sup>(282 nm) with other bands at 39,920 cm<sup>-1</sup>(251 nm) , 41,637 cm<sup>-1</sup>(240 nm) and 47,963 cm<sup>-1</sup>(209 nm). These were due to bipyridine-based intraligand π →π\* transitions [13,14].

The visible region of the UV-Visible the complexes revealed the single spin-allowed transition from <sup>5</sup>T<sub>2g</sub> →<sup>5</sup>E<sub>g</sub>. This was observed at 22,644cm<sup>-1</sup> for the Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O and at 22,166cm<sup>-1</sup>with a shoulder at 24,184cm<sup>-1</sup> for the Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> complex.

In the mass spectra of the Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O, the peak at m/z = 323.95 stand for {Ru(phen)<sub>2</sub>L}<sup>2+</sup>and the peak at m/z = 300.15 for {Ru(bipy)<sub>2</sub>L}<sup>2+</sup> in the Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> complex. These fragmentation patterns were consistent with the expected values for these compounds.

The <sup>1</sup>H NMR of the complexes showed six (6) methyl <sup>1</sup>H at 2.40 for the Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O complex while the six (6) methyl <sup>1</sup>H for the Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> complex was observed at 2.33. The proton attached to the C=N in DDAP was absent in the NMR spectra of the complexes and the reduction in the number of the aromatic protons from 14 <sup>1</sup>H and 16 <sup>1</sup>H for the Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O and Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> respectively to 12 <sup>1</sup>H and 14 <sup>1</sup>H respectively. The molar conductances of the complexes in acetonitrile, CH<sub>3</sub>CN (10<sup>-3</sup>mol L<sup>-1</sup>) are 323 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>and 302 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>respectively for Ru(phen)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>. 3H<sub>2</sub>O and Ru(bipy)<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub> . The value of the conductance of the solutions of the complexes confirmed that the compounds are 1:2 electrolytes.

Two mixed-ligand Ru<sup>II</sup> complexes with L were successfully synthesized and characterized. It was observed that the ligand electrocyclicised upon complexation, this was confirmed by the elemental analyses, the infrared spectra and the <sup>1</sup>H NMR also supported it.



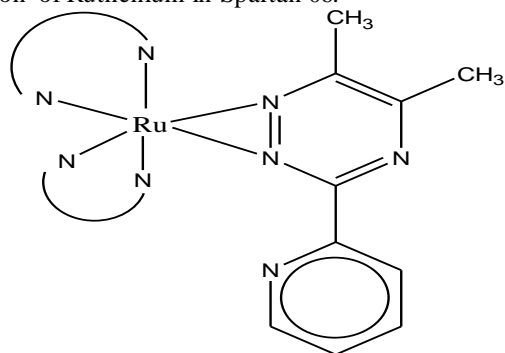
L

#### 5,6-Dimethyl-3-pyridin-2-yl-[1,2,4]triazine

**Fig. 2: The structure of the ligand after electrocyclicization Computational Details**

Quantum chemical methods (Semi-empirical, PM3 and *ab initio*, HF/3-21G\*) were used for the calculations of geometries, heat of formation, binding energy and thermodynamics parameters for the two mixed-ligand Ru<sup>II</sup> complexes using a Spartan 06 computational software package. The methods (PM3

and HF/3-21G\*) are only available methods for parameterization of Ruthenium in Spartan 06.



= 1,10-phenanthroline and 2,2'-bipyridine  
**Fig. 3: The proposed structure of the complexes**

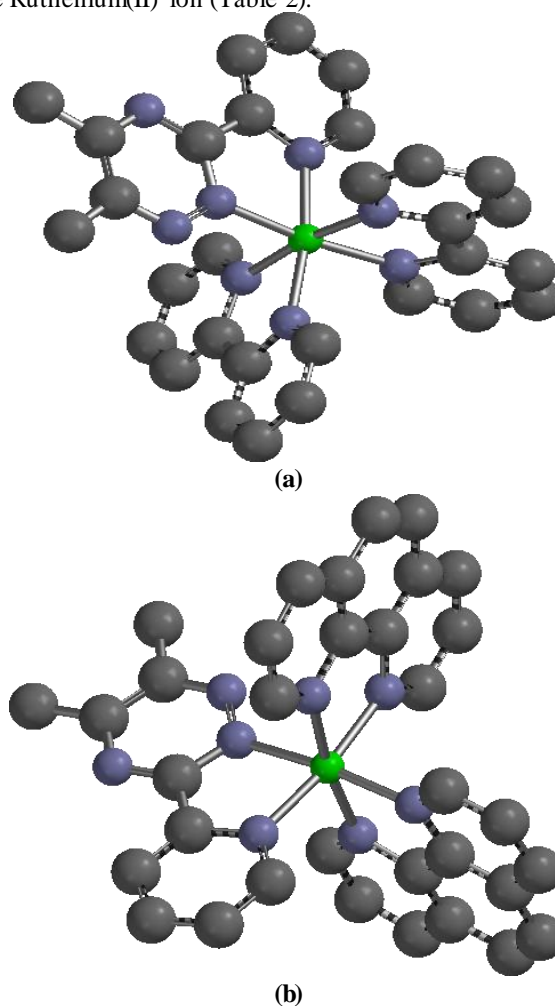
The average Ru-N bond distance calculated at PM3 and *ab initio* is 2.062 and 2.184 for  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  and 2.059 and 2.179 for  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  respectively. The Ru-N bond distances calculated at HF/3-21G\* were longer than that of semi-empirical method, however it has been reported that geometrical parameters from PM3 calculation for transition metal complexes are more accurate than that of *ab initio* methods [15]. The bond distance calculated at PM3 are closer to the similar Ru(II) complex reported by Kundu et al., using DFT [16].

The bite angles N1-Ru-N2 (N1-Ru-N6) and N4-Ru-N5 (N5-Ru-N6) are 80.53 (172.02) and 173.67 (79.87) for  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  at PM3 respectively. These angles were calculated to be 77.68 (171.00) and 172.30 (76.02) for  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  at HF/3-21G\* method. For  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$ , N1-Ru-N2 (N1-Ru-N6) and N4-Ru-N5 (N5-Ru-N6) bite angles calculated at PM3 are 79.64 (171.61) and 173.36 (79.76) respectively. These bond angles were calculated to be 76.61 (170.76) and 172.08 (75.92) at HF/3-21G\*. These show that the two Ru(II) complexes have distorted octahedral geometries which may be as a result of steric effect occasioned by the bulkiness of the ligands twisting it out of coplanarity.

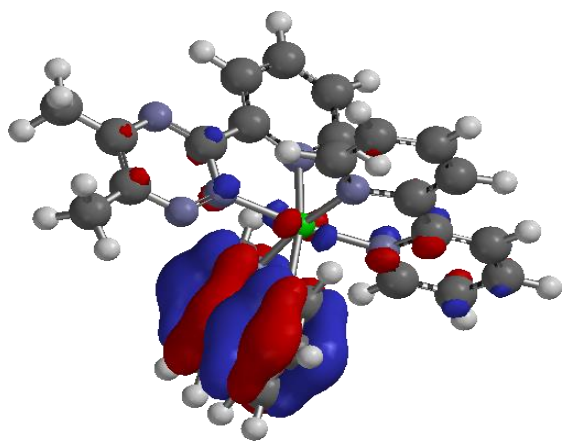
**Table 1: Selected bond distances (Å) and bond angles (°)**

	$[\text{Ru}(\text{phen})_2\text{L}]^{2+}$		$[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$	
	PM3	HF/3-21G*	PM3	HF/3-21G*
Ru-N1	2.056	2.176	2.050	2.166
Ru-N1	2.061	2.186	2.056	2.178
Ru-N3	2.061	2.188	2.056	2.181
Ru-N4	2.060	2.185	2.054	2.176
Ru-N5	2.075	2.204	2.075	2.167
Ru-N6	2.059	2.163	2.061	2.207
Average Ru-N	2.062	2.184	2.059	2.179
N1-Ru-N2	80.53	77.68	79.64	76.61
N1-Ru-N3	94.14	96.68	94.74	97.80
N1-Ru-N4	91.41	89.86	91.79	90.20
N1-Ru-N5	93.58	96.66	93.41	96.50
N1-Ru-N6	172.02	171.00	171.61	170.76
N2-Ru-N3	172.31	172.35	171.88	170.31
N2-Ru-N4	94.03	97.15	94.62	98.20
N2-Ru-N5	90.63	88.28	90.39	87.49
N2-Ru-N6	94.88	96.65	95.43	97.54
N3-Ru-N4	80.49	77.43	79.61	76.34
N3-Ru-N5	95.25	97.66	95.82	98.49
N3-Ru-N6	91.03	89.49	90.82	88.64
N4-Ru-N5	173.67	172.30	173.36	172.08
N4-Ru-N6	95.44	97.84	95.40	97.78
N5-Ru-N6	79.87	76.02	79.76	75.92

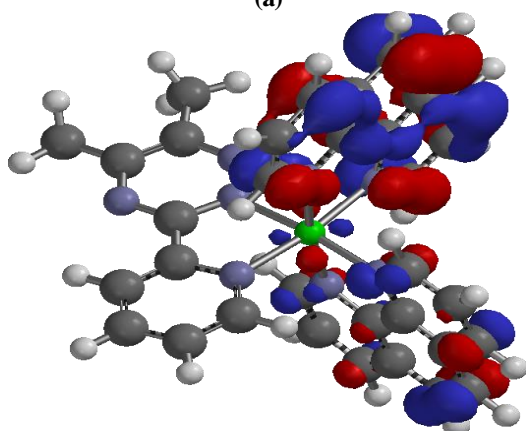
Optimized geometries of forming the HOMO and LUMO of  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  and  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  complex ions are shown in Figures 4, 5 and 6 respectively. The HOMO revealed that the  $\pi$ -electrons of the system dwell mainly on one unit of 1,10-phenanthroline and 2,2'-bipyridine ligands of  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  and  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  respectively (Figure 4). The LUMOs are localized on 6-Dimethyl-3-pyridin-2-yl-[1,2,4]triazine of the two complexes. This shows that in the ruthenium(II) complexes, the unoccupied molecular orbitals are located on 6-Dimethyl-3-pyridin-2-yl-[1,2,4]triazine moiety. The HOMO and LUMO energies calculated at PM3 (HF/3-21G\*) are -14.52 (-13.73) and -6.52 eV (-3.90 eV) for  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  respectively, however in  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  the HOMO and LUMO energies are -15.03 and -7.03 eV for PM3 and -14.30 and -3.97 eV for HF/3-21G\* calculation. The dipole moment (D.M) and polar surface area (PSA) are some important parameters to be considered in solute-solvent interactions, therefore D.M and PSA calculated at both semi-empirical and *ab initio* methods show that  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  may exhibit more complex-solvent interactions. The Mulliken charges on nitrogen atoms involved in the coordination and Ru(II) show transfer of charges (electrons) from nitrogen atoms to the Ruthenium(II) ion (Table 2).



**Figure 4: Optimized Ru(II) complexes at PM3; (a) =  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  and (b) =  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$**

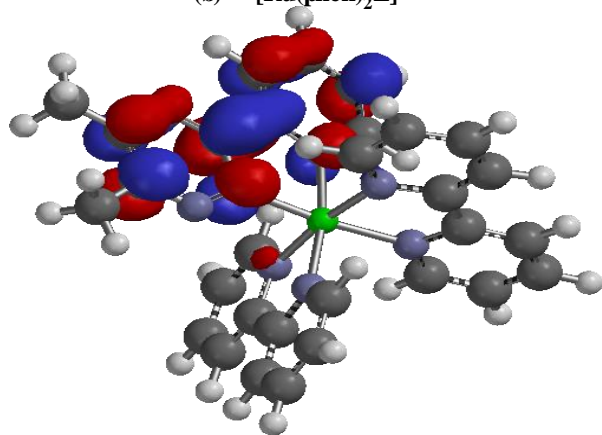


(a)

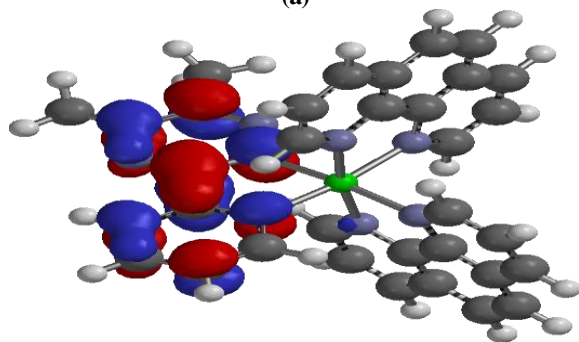


(b)

Figure 5: The HOMO map at PM3; (a) =  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  and (b) =  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$



(a)



(b)

Figure 6: The LUMO map at PM3; (a) =  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  and (b) =  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$

To evaluate the effect of 5,6-Dimethyl-3-pyridin-2-yl-[1,2,4]triazine on  $\text{RuX}^{2+}$  complexes, binding energy (BE) was calculated from the energy involved in the dissociation process (equation 1) and stabilization energy are as given in equation 2:

$$\text{Binding energy (B.E)} = E[\text{RuX}_2\text{L}]^{2+} - E[\text{RuX}_2]^{2+} - E\text{L} \quad (1)$$

$$\text{Stabilization energy (S.E)} = E[\text{RuX}_2\text{L}]^{2+} - E(\text{Ru}^{2+} + 2\text{X} + \text{L}) \quad (2)$$

where X = 1,10-phenanthroline or 2,2'-bipyridine and L = 5,6-Dimethyl-3-pyridin-2-yl-[1,2,4]triazine and E = energy of each species.

Calculations of the binding energy as presented in Table 2 were carried out only for the ground states of the complex ions. Heat of formation  $\Delta H_f$  at PM3 method for  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  and  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  are -111.75 and -110.81 Kcal/mol respectively, this shows that the heat of formation for the two complexes were exothermic in nature. The binding and stabilization energies calculated for  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  at HF/3-21G\* are -117.83 and -483.31 Kcal/mol respectively, whereas these were calculated to be -113.90 and -464.27 Kcal/mol for  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$  as presented in Table 2. Comparison of the binding energies and stabilization energies suggest that  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  is thermodynamically and more favourable, this may be due to the availability of more  $\pi$ -electrons on phenanthroline.

Table 2: The total energy, heat of formation ( $H_f$ ), HOMO, LUMO, Dipole moment, Mulliken charges, binding and stabilization energies.

	$[\text{Ru}(\text{phen})_2\text{L}]^{2+}$		$[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$	
	PM3	HF/3-21G (d)	PM3	HF/3-21G (d)
$H_f$ (kJ/mol)	1534.34	-6149.19*	1488.67	-5998.52*
HOMO (eV)	-14.52	-13.73	-15.03	-14.30
LUMO (eV)	-6.52	-3.90	-7.03	-3.97
$E_{\text{HOMO}}$	8.00	9.83	8.00	10.33
$E_{\text{LUMO}}$ (eV)	2.20	1.12	2.94	0.67
D.M (Debye)				
Mullikan charges	0.483	-0.881	0.484	-0.859
	-	-0.317/-	-	-0.319/-
$N^a$	0.154/0.015	0.731	0.155/0.018	0.731
N7/N8	-1.045	1.229	-1.035	1.246
Ru	-111.75	-	-110.81	-
$\Delta H_f$ (Kcal/mol)	-	-117.83	-	-113.90
		-483.31		-464.27
B. E (Kcal/mol)				
S. E (Kcal/mol)				

<sup>a</sup>average Mulliken charges on six nitrogen atoms that bonded to Ruthenium(II) and \*total energy in au

### Conclusion

The electrocyclisation of the ligand and formation of the mixed-ligand complexes of  $\text{Ru}(\text{phen})_2\text{L}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ru}(\text{bipy})_2\text{L}(\text{ClO}_4)_2$  were confirmed by the  $^1\text{H}$ NMR, infrared spectra, the UV-Vis spectra and mass fragmentation patterns all gave data that support the formation of the mixed-ligand complexes. The Semi-empirical (PM3) and *ab initio* (HF/3-21G\*) methods used for the calculations of the geometries, heat of formation, binding energy and thermodynamics parameters for the two mixed-ligand  $\text{Ru}^{\text{II}}$  complexes, support that the  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  is thermodynamically stable than the  $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$ . This may be attributed to the availability of more  $\pi$ -electrons on phenanthroline.

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