



## Synthesis, Characterization and Semi-empirical Study of Di-nuclear Mixed-Ligands Complexes of Ru(II)

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### ABSTRACT

The dimeric complexes of  $\text{Ru}(\text{phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  prepared from the condensation product obtained by reacting diacetyldihydrazone with 2-acetylpyridine (DDACP) was characterized using microanalyses, infrared and UV-Vis spectra,  $^1\text{H}$ NMR, mass spectra and the molar conductivity. The elemental analyses data and the mass spectra fragmentation patterns are supportive of the formation of the dimeric mixed-ligand complexes,  $[\text{Ru}(\text{phen})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  and  $[\text{Ru}(\text{bipy})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ . The molar conductances determined, revealed the complexes to be 1:4 electrolytes with values  $562 \text{ mho cm}^2\text{mol}^{-1}$  and  $575 \text{ mho cm}^2\text{mol}^{-1}$  for the complexes respectively. Semi-empirical method has been used to calculate the binding and stabilization energies of the two complexes which suggested that  $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$  is more favoured thermodynamically. Mulliken charges on nitrogen atoms that are involved in coordination show that electrons are transferred from ligands to the Ru(II) ion during coordination.

**Key words:** Dimeric, complexes, Mixed – ligand, Fragmentation patterns, Semi-empirical method.

### INTRODUCTION

The chemistry of polynuclear transition metal complexes has been of immense current interest, due to the fascinating and versatile properties exhibited by them<sup>1</sup>. Transition metal complexes containing polypyridyl-type ligands exhibit attractive electrochemical and photophysical properties<sup>2-9</sup>. The ligand 2, 2', 6', 2''-terpyridine has been used widely in the preparation of molecular systems with diverse chemical properties<sup>9</sup>. In the ligand, the position of the nitrogen atom of each pyridine ring allows tridentate and meridian coordination to Ru, Os and Ir<sup>10-11</sup>. The synthesis of

the ligand can be applied to the preparation of derivatives containing an additional functional group which can be used as a bridge to connect two or more different metal centers to produce symmetrical and unsymmetrical metal complexes<sup>11</sup>. In addition, much work has been devoted to the bridged bi- and poly-nuclear ruthenium complexes particularly in their mixed valence states<sup>10</sup>. The short-bridging ligands such as pyrazine, tert-butylmalonitrile, dinitrogen, cyanogen or 4,4'-dithiodipyridine provide often a strong enough coupling between ruthenium – amine centers to allow complete electronic delocalization in the mixed – valence (MV) state<sup>10</sup>.

Polynuclear complexes of ruthenium(II) are valuable sensitizers for the conversion of light into chemical or electrical energy as they are efficient MLCT chromophores in which the absorption maximum can be tuned to almost any wavelength of the visible spectrum<sup>10</sup>. In order to ensure a potentially good charge separation from the excited state in a donor-chromophore-acceptor triad, it is good to aim at linear, rigid assembly<sup>12</sup>.

Herein, we report the synthesis and characterization of the  $\text{Ru}(\text{phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  with the condensate of diacetyldihydrazone with 2-acetylpyridine and the semi-empirical study of the complexes investigated.

## EXPERIMENTAL

### Materials and Method

#### Reagents

Reagent grade  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , 1,10-phenanthroline, LiCl, DMF, diethyl ether, 2,2'-bipyridyl, diacetyl, hydrazine hydrate, glacial acetic acid, 2-acetylpyridine,  $\text{NaClO}_4$  were purchased from the British Drug House Chemicals Ltd (BDH) and Aldrich Chemicals Co., and were used without further purification.

#### Preparation of the DDACP

0.456g (1mmole) diacetyldihydrazone<sup>13</sup> was transferred into 100mL round-bottom flask, 20mL methanol and 0.90mL 2-acetylpyridine added. The mixture stirred with calcium chloride guard-tube fixed to the flask. The bright-yellow solution obtained was stirred for 4hrs, after which the solution was left overnight. The yellow compounds obtained was filtered by suction and dried in the air (0.620g, 48%).

#### Reaction of $\text{Ru}(\text{phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}^{14}$ with DDACP

0.114g (0.2mmole)  $\text{Cis-Ru}(\text{phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}^{14}$  was transferred to a 100mL two-neck round bottom flask, 1:1 MeOH- $\text{H}_2\text{O}$  mixture (20mL) added and degassed. To this 0.064g (0.2mmole) DDACP was added and the mixture refluxed under  $\text{N}_2$  gas for 6hrs. It was then cooled to room temperature and filtered. To the filtrate, 0.246g (2mmole)  $\text{NaClO}_4$  solution in 5mL distilled water was added dropwisely with constant stirring. The red precipitate obtained immediately was stirred for 30mins before it was filtered by suction, washed

with 15mL diethyl ether and then dried in the vacuo. Yield: 0.07g (20%)  $[\text{Ru}(\text{phen})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  Anal. Cal.  $\text{C}_{66}\text{H}_{60}\text{N}_{14}\text{O}_{20}\text{Cl}_4\text{Ru}_2$  (M.M: 1712.718): C, 46.24; H, 3.53; N, 11.45. Found: C, 46.73; H, 3.37; N, 11.40. FTIR:  $\nu/\text{cm}^{-1}$ : 1601 (C=N); 3063 (C-H aromatic); 625s, 1090vs ( $\text{ClO}_4$ ). UV-Vis:  $\text{cm}^{-1}$  22.756; 38.487; 45.274. ESI-MS ( $\text{CH}_3\text{CN}$ ) m/z: 391.02 (28%  $\{\text{Ru}(\text{phen})_2\text{L}\}^{2+}$ ), 310.14 (20%  $\{\text{Ru}_2(\text{phen})_4\text{L}\}^{4+}$ ), 324.51 (25%  $\{\text{Ru}_2(\text{phen})_4\text{L}\}^{4+} \cdot 3\text{H}_2\text{O}$ ), 560.99 (20%  $\{\text{Ru}_2(\text{phen})_4(\text{ClO}_4)_2\}^{2+}$ ).  $^1\text{H}$  NMR:  $\delta/\text{ppm}$ : 2.17(3H,  $\text{CH}_3\text{-C-C-CH}_3$ ), 3.13(3H,  $\text{CH}_3\text{-C=N}$ ), 7.20 – 8.91 (40H, aromatic).  $\delta_M/\text{mho cm}^2\text{mol}^{-1}$  562( $\text{CH}_3\text{CN}$ ) (1:4 electrolyte).

#### Reaction of $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}^{15}$ with DDACP

0.104g (0.2mmole)  $\text{cis-Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}^{15}$  dissolved in 10mL MeOH –  $\text{H}_2\text{O}$  mixture (1:1) and degassed for 30mins. To this 0.064 g (0.2mmole) DDACP was added and the mixture refluxed for 6hrs under  $\text{N}_2$  gas. It was then cooled to room temperature and filtered. 0.246g (2mmole)  $\text{NaClO}_4$  solution distilled water (5mL) was added dropwisely with constant stirring. The red precipitate obtained immediately was stirred for 30mins before it was filtered by suction, washed with 15mL diethyl ether and dried in the vacuo. Yield: 0.062g, (20%)  $[\text{Ru}(\text{bipy})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  Anal. Cal.  $\text{C}_{58}\text{H}_{56}\text{N}_{14}\text{O}_{18}\text{Cl}_4\text{Ru}_2$  (M.M: 800.28): C, 44.03; H, 3.57; N, 12.41. Found: C, 43.98; H, 3.67; N, 12.40. FTIR:  $\nu/\text{cm}^{-1}$ : 1600 (C=N); 3070 (C-H aromatic); 2972 (C-H aliphatic); 625s, 1090vs ( $\text{ClO}_4$ ). UV-Vis:  $\text{cm}^{-1}$  22.437; 23.915sh; 35.452; 39.828sh; 41.787. ESI-MS ( $\text{CH}_3\text{CN}$ ) m/z: 286.84 (25%  $\{\text{Ru}_2(\text{bipy})_4\text{L}\}^{4+}$ ), 288.82 (28%  $\{\text{Ru}(\text{bipy})\text{L}\}^{2+}$ ), 366.91 (32%  $\{\text{Ru}(\text{bipy})_2\text{L}\}^{2+}$ ), 445.82 (18%  $\{\text{Ru}(\text{bipy})_3\text{L}\}^{2+}$ ), 674.27  $\{\text{Ru}_2(\text{bipy})_4\text{L}(\text{ClO}_4)_2\}^{2+}$ .  $^1\text{H}$  NMR:  $\delta/\text{ppm}$ : 2.17(3H,  $\text{CH}_3\text{-C-C-CH}_3$ ), 2.62 ( $\text{CH}_3\text{-C=N}$ ), 7.49 – 8.84 (40H, aromatic).  $\delta_M/\text{mho cm}^2\text{mol}^{-1}$  575 ( $\text{CH}_3\text{CN}$ ) (1:4 electrolyte).

#### 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 syntronics (India) conductivity meter (model 306) in acetonitrile and 300MHz NMR spectra on a Bruker DPX300 Spectrometer in deuterated dimethylsulphoxide ( $\text{DMSO-d}_6$ ).

**RESULTS AND DISCUSSION**

The complexes were obtained by refluxing the Ru(phen)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O and Ru(bipy)<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O with DDACP in MeOH-H<sub>2</sub>O mixture under N<sub>2</sub>. The red precipitates obtained were found to have low yields probably due to the formation of dinuclear Ru(II) complexes in which the L acts as a bridge between

two [Ru(phen)<sub>2</sub>]<sup>2+</sup>. The microanalyses data for these complexes gave satisfactory results. The colours of the compounds were consistent with those of similar systems<sup>9,16</sup>.

The infrared spectra of the complexes revealed the -C=N stretching frequencies at 1601cm<sup>-1</sup> and 1600cm<sup>-1</sup> respectively for the 1,10-

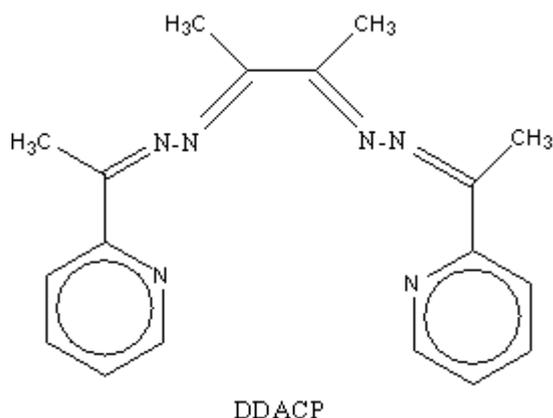
**Table 1: Ru-N bond distances for the two di-nuclear Ru(II) complexes**

Bond distance (Å)	[Ru <sub>2</sub> (bipy) <sub>4</sub> L] <sup>4+</sup>	[Ru <sub>2</sub> (phen) <sub>4</sub> L] <sup>4+</sup>
Ru1-N1/Ru2-N1'	2.049/2.052	2.044/2.061
Ru1-N2/Ru2-N2'	2.061/2.070	2.063/2.056
Ru1-N3/Ru2-N3'	2.060/2.067	2.044/2.027
Ru1-N4/Ru2-N4'	2.053/2.058	2.058/2.071
Ru1-N5/Ru2-N5'	2.089/2.087	2.098/2.083
Ru1-N6/Ru2-N6'	2.054/2.083	2.058/2.078
Av. Ru <sub>1</sub> -N/Ru <sub>2</sub> -N	2.061/2.068	2.061/2.063

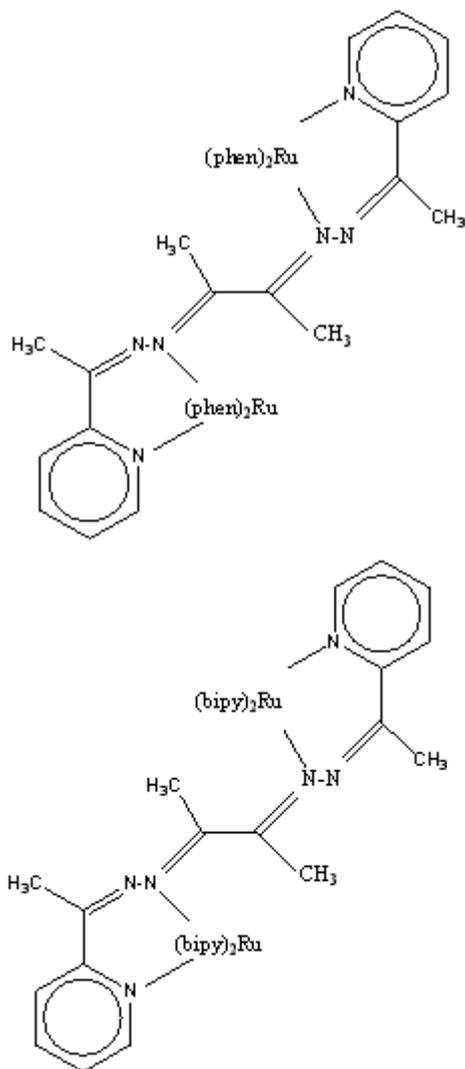
**Table 2: Frontier molecular energies, heat of formation, Mulliken charges, binding and stabilization energies**

	[Ru <sub>2</sub> (bipy) <sub>4</sub> L] <sup>4+</sup>	[Ru <sub>2</sub> (phen) <sub>4</sub> L] <sup>4+</sup>
HOMO (eV)	-17.80	-17.15
LUMO (eV)	-9.80	-9.59
E <sub>HOMO</sub> -E <sub>LUMO</sub> (eV)	8.00	7.56
Dipole moment (Debye)	0.52	1.75
PSA (Å <sup>2</sup> )	53.517	55.049
H <sub>f</sub> (kJ/mol)	3547.53	3587.40
Total energy (au)	-10072.38	-10365.27
Binding energy (kJ/mol)	-270.85 (-279.01)*	-330.16 (-342.94)*
Stabilization energy (kJ/mol)	-726.82	-785.01
Mulliken charges		
N1/N1'	0.506/0.504	0.484/0.490
N2/N2'	0.472	0.488/0.483
N3/N3'	0.457/0.440	0.457/0.437
N4/N4'	0.487/0.484	0.477/0.460
N5/N5'	0.302/0.457	0.477/0.460
N6/N6'	0.482/0.467	0.319/0.494
Av. N/N' bonded to Ru (II)	0.541/0.471	0.457/0.474
<sup>a</sup> N7/N7'	-0.032/-0.273	-0.041/-0.223
Ru1/Ru2	-1.038	-1.033/-1.048

\*binding energy from HF/3-21G\* calculation and a Mulliken charges on nitrogen atom that did not participate in coordination



**Fig. 1: The structure of the DDACP**



**Fig. 2: The proposed structure of the complexes**

phenanthroline and 2,2'-bipyridine complexes<sup>9</sup>. The aromatic  $-C-H$  of both complexes appeared at  $3063\text{cm}^{-1}$  and  $3070\text{cm}^{-1}$  respectively for  $[\text{Ru}(\text{phen})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  and  $[\text{Ru}(\text{bipy})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ . The strong bands at ca  $625\text{cm}^{-1}$  and  $1090\text{cm}^{-1}$  observed in both complexes correspond to the  $-\text{ClO}_4$  stretching frequencies<sup>17</sup>.

The single spin-allowed d-d transition from the ground term  $^5T_{2g}$  to  $^5E_g$ <sup>18</sup> was at  $22,756\text{cm}^{-1}$  and  $22,437\text{cm}^{-1}$  with a shoulder  $23,915\text{cm}^{-1}$  respectively for  $[\text{Ru}(\text{phen})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  and  $[\text{Ru}(\text{bipy})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ . The ligand transitions in the complexes were observed between the range  $35,452\text{cm}^{-1}$ -  $45,274\text{cm}^{-1}$  in the two complexes.

The fragmentation patterns observed in the complexes is also an indication that DDACP acts as a bridge between two of the starting Ru(II) compounds.

In the  $[\text{Ru}(\text{phen})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  complex, peaks at  $m/z = 391.02$ ,  $310.14$ ,  $324.51$  and  $560.99$  correspond to  $\{\text{Ru}(\text{phen})_2\text{L}\}^{2+}$ ,  $\{\text{Ru}_2(\text{phen})_4\text{L}\}^{4+}$ ,  $\{\text{Ru}_2(\text{phen})_4\text{L}\}^{4+} \cdot 3\text{H}_2\text{O}$ ,  $\{\text{Ru}_2(\text{phen})_4(\text{ClO}_4)_2\}^{2+}$  respectively. The peaks at  $m/z = 286.84$  and  $m/z = 288.82$  were assigned to  $\{\text{Ru}_2(\text{bipy})_4\text{L}\}^{4+}$  and  $\{\text{Ru}(\text{bipy})\text{L}\}^{2+}$  respectively in  $[\text{Ru}(\text{bipy})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$  while the other peaks in the complex at  $m/z = 366.91$ ,  $m/z = 445.82$  and  $m/z = 674.27$  stand for  $\{\text{Ru}(\text{bipy})_2\text{L}\}^{2+}$ ,  $\{\text{Ru}(\text{bipy})_3\text{L}\}^{2+}$  and  $\{\text{Ru}_2(\text{bipy})_4\text{L}(\text{ClO}_4)_2\}^{2+}$  respectively. The fragmentation patterns observed in these complexes have molecular weights which were consistent with the expected values.

The  $^1\text{H}$  NMR of the complexes showed the three methyl protons of  $(\text{CH}_3-\text{C}-\text{C}-\text{CH}_3)$  at  $2.17\text{ppm}$  for both of them and while the three methyl protons of  $\text{CH}_3-\text{C}=\text{N}-$  at  $3.13\text{ppm}$  and  $2.62\text{ppm}$  respectively. The aromatic protons were observed in the complexes between  $7.20\text{ppm}$  and  $8.91\text{ppm}$ . The number of the aromatic protons in each case indicated that the 1,10-phenanthroline and 2,2'-bipyridine rings in the starting Ru(II) compounds are present in the mixed-ligand complexes coupled with the aromatic ring of the introduced ligand, L. The molar conductance of  $562\text{mho cm}^2\text{mol}^{-1}$  was obtained for the  $[\text{Ru}(\text{phen})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$  complex while that of  $[\text{Ru}(\text{bipy})_2]_2\text{L}(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$  is at  $575\text{mho}$

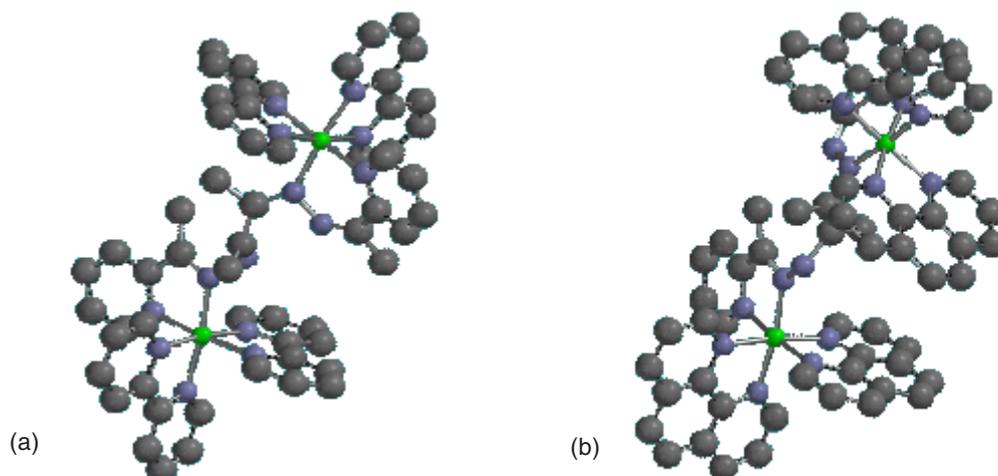


Fig. 3: Optimized Ru(II) complexes at PM3; (a) =  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and (b) =  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$

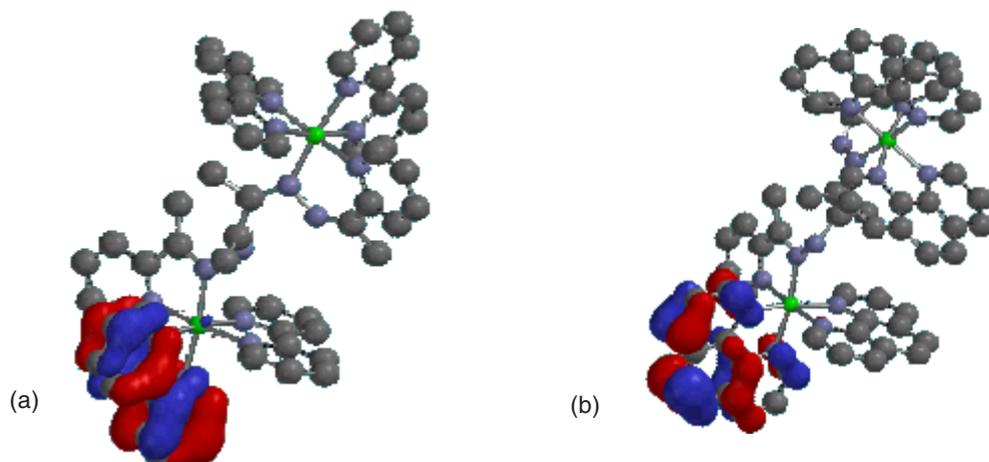


Fig. 4: The HOMO map at PM3; (a) =  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and (b) =  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$

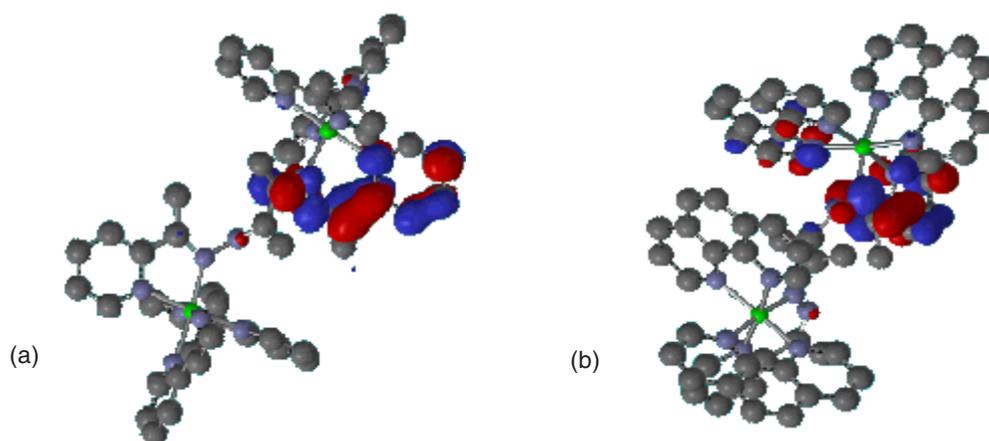


Fig. 5: The LUMO map at PM3; (a) =  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and (b) =  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$

$\text{cm}^2\text{mol}^{-1}$ . These values showed that the complexes are dimeric.

### Computational methods

Quantum chemical methods (Semi-empirical, PM3) was used for the optimization of the complex geometries. Heat of formation, binding energy for the two mixed-ligand binuclear Ru<sup>II</sup> complexes were also calculated using PM3 as implemented in Spartan' 06 computational software package. It has been reported that geometrical parameters from PM3 calculation for transition metal complexes are more accurate than that of *ab initio* methods<sup>19</sup>, however, HF/3-21G\* was used to calculate the stabilization energy for the two binuclear Ru(II) complexes. The average Ru1-N (Ru2-N) bond distance are 2.061 (2.068) and 2.061 Å (2.063 Å) for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  respectively (Table 1).

Optimized geometries, HOMO and LUMO of  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  complex ions are shown in Figures 3, 4 and 5 respectively. The highest occupied molecular orbital (HOMO) representing  $\pi$ -electrons of the complexes are localized on one unit of 1,10 phenanthroline and 2,2'-bipyridine ligands for  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  and  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  respectively (Figure 4). The lowest unoccupied molecular orbital (LUMO) is mainly on (1-pyridin-2-yl-ethylidene) -hydrazine subunit of DDACP for the two complexes (Figure 5). The HOMO and LUMO energies calculated are -17.80 and -9.80 eV for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and -17.15 and -9.59 eV for  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  respectively. The  $E_{\text{HOMO}} - E_{\text{LUMO}}$  energy presenting  $\pi - \pi^*$  main transitions in the complexes are 8.00 and 7.56 eV for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  respectively. The dipole moment (D.M) and polar surface area (PSA) are some important parameters to be considered in solute-solvent interactions which have overall effect on the reactivity, therefore D.M and PSA calculated at Semi-empirical method show that  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  may exhibit more complex-solvent interactions. The Mulliken charges on nitrogen atoms involved in the coordination are all positive and the average charge on these nitrogen atoms are 0.541/0.471 e for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and 0.457/0.474 e for  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  as compared to -0.032/-0.273 e and -0.041/-0.223 e on N7/N7' for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  respectively. These show that electrons are

transferred from ligands to the Ru(II) ion during coordination (Table 2).

To evaluate the effect of DDACP on dinuclear Ru(II) complexes, binding energy (BE) and stabilization energy were calculated from the energy involved in the dissociation processes as shown in equations 1 and 2.

$$\text{Binding energy (B.E)} = [\text{Ru}_2\text{X}_4\text{L}]^{4+} - 2\text{E}[\text{RuX}_2]^{2+} - \text{EL} \quad \dots(1)$$

$$\text{Stabilization energy (S.E)} = \text{E}[\text{Ru}_2\text{X}_4\text{L}]^{4+} - 2\text{ERu}^{2+} - 4\text{EX} - \text{EL} \quad \dots(2)$$

where X = 1,10-phenanthroline or 2,2'-bipyridine and L = DDACP and E = energy of each species.

The calculated binding energy and stabilization energy as presented in Table 2 were carried out only for the ground states of the complex ions. The BE calculated for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  are -270.85 and -279.01 kJ/mol for PM3 and HF/3-21G(d) calculations respectively. These are calculated to be -330.16 and -342.94 kJ/mol for  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  at PM3 and HF/3-21G(d) levels. The stabilization energies calculated at HF/3-21G(d) level are -726.82 and -785.01 kJ/mol for  $[\text{Ru}_2(\text{bipy})_4\text{L}]^{4+}$  and  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  respectively. Comparison of the binding energies and stabilization energies suggest that  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  is more favoured thermodynamically. The higher binding energy and lower stabilization energy in the  $[\text{Ru}_2(\text{phen})_4\text{L}]^{4+}$  may be attributed to the availability of more  $\pi$ -electrons on phenanthroline moiety of the compound.

### CONCLUSION

The formation of the bridged mixed – ligand dimeric complexes was supported by the microanalyses, fragmentation pattern in the mass spectra, and the conductivity measurements. The <sup>1</sup>HNMR and infrared spectra in conjunction with other analytical data all lends credence to the formation of the compounds.

Furthermore, the quantum chemical methods (Semi-empirical, PM3) used for the

optimization of the complex geometries have the HOMO map localized on 1,10-phenanthroline and 2,2'-bipyridine and LUMO is mainly on (1-pyridin-2-yl-ethylidene)-hydrazine subunit of DDACP for the two complexes. The binding and stabilization energies calculated for the two mixed-ligand dinuclear Ru<sup>II</sup> complexes revealed that [Ru<sub>2</sub>(phen)<sub>4</sub>L]<sup>4+</sup> ion is more stable thermodynamically.

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