Chapter 4

DISCUSSION

The interesting properties of $[Ru(bpy)_2L]^{2+}$ complexes, where L is 2,2′-bipyridine (bpy) ligand, lead to synthesize ruthenium complexes with other bidentate ligands which are better π-acceptors than bpy, such as 2-(phenylazo)pyridine (azpy) (Krause and Krause, 1980) and 2-(phenylazo)pyrimidine (azpym) (Ghos, *et al.*, 1983 and Ghos, *et al.*, 1984). Azpy consisting of one pyridine ring with a pendent nitrogen donor atom from an azo function has been employed in development of transition metal coordination chemistry. Azpym consists of one pyrimidine ring with a pendent nitrogen donor atom from an azo function. Due to unsymmetric N-donor sites in the azoimine function, -N=N-C=N-, isomeric complexes in ruthenium and osmium have been extensively studied (Misra, *et al.*, 1998).

In this present work, the chemistry of ruthenium(II) complexes with new azoimine ligands of azpy and azpym which have the substituents as electron-donating groups ($-NR_2$; R = $-CH_3$, $-CH_2CH_3$). The objectives of this work are to study the chemical properties of $[Ru(bpy)_2L]^{2+}$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym), compared to those of the $[Ru(bpy)_3]^{2+}$ complex.

4.1 Electrospray and FAB mass spectrometric techniques

The electrospray and FAB mass spectrometry are basic techniques to determine the molecular weight of molecule.

The electrospray mass spectra of dmazpy, deazpy, azpym and deazpym ligands showed the parent peaks of each ligand which gave 100% relative abundance, the molecular weight of ligand with one protonation.

Fragmentation characters of complexes showed different patterns. The parent peak, which gave 100% relative abundance, was molecular weight of each complex. The positive ion FAB mass spectrum of $[Ru(bpy)_2azpy](BF_4)_2$ showed the parent peak at m/z = 684, corresponding to $[Ru(bpy)_2azpy](BF_4)^+$ ion (Figure 37). The mass spectra in case of $[Ru(bpy)_2L](BF_4)_2$ complexes, where L = dmazpy, deazpy and azpym showed the intense peaks at m/z = 727, 755.2 and 685 which were due to a dissociation of BF_4^- molecule. For the parent peaks at m/z = 640, 333.9 and 598 were identified to the species of $[Ru(bpy)_2dmazpy]^+$, the doubly charged ions $([Ru(bpy)_2deazpy]^+)^{2+}$ in electrospray mass spectrum and $[Ru(bpy)_2azpym]^+$ ion (Figure 38-40), respectively. The spectrum of the $[Ru(bpy)_2deazpym](BF_4)_2$ complex (Figure 41) showed the intense peak at m/z = 669, corresponding to losing of two BF_4^- molecules. This peak was assigned to $[Ru(bpy)_2deazpym]^+$. The parent peak exhibited at m/z = 641. It may be come from the fragmentation of the species of m/z 669 to lose the ethylene molecule.

This method could be used to confirm the formula and molecular mass of ligands and complexes as expected.

4.2 Infrared spectroscopic technique

Infrared spectra of free ligands and $[Ru(bpy)_2L](BF_4)_2$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) showed the important peaks in the range 1,600-400 cm^{-1}. The objective in studying the IR spectra were to locate the important functional groups such as C=N stretching, N=N stretching, C=C stretching and C-H bending of para disubstituted benzene

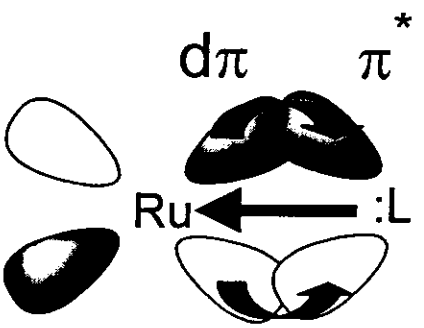
The N=N stretching vibrations of free dmazpy, deazpy, azpym and deazpym have been observed at 1400, 1397, 1392 and 1379 cm^{-1}, respectively. Whereas, N=N stretching frequency of azpy ligand appeared at 1421 cm^{-1}, higher energy than those found in dmazpy, deazpy, azpym and deazpym. This could be explained that the substituents, $-NR_2$ (R = $-CH_3$, $-C_2H_5$) of dmazpy deazpy and deazpym donated electrons to the phenyl ring. These electrons can delocalize into the pyridine and pyrimidine rings. Because of the delocalization of π-electrons, the N=N bond strength is decreased. Therefore, the substituted ligands showed the stretching frequencies of N=N(azo) bond at lower frequencies. Since the azo modes in dmazpy and deazpy appeared at closed frequencies, it indicated that the electron donating abilities of methyl and ethyl groups are comparable. Furthermore, the N=N bond of azpym occurs at lower frequencies than azpy ligand. The decreasing of the N=N bond strength attributes to inductive effect of the nitrogen atom in pyrimidine ring.

Table 28 The N=N stretching mode of free ligands and $[Ru(bpy)_2L](BF_4)_2$ (L = azpy, dmazpy, deazpy, azpym and deazpym)

Ligand	$\nu_{(N=N)}$,cm^{-1}	
	Free ligand	$[Ru(bpy)_2L](BF_4)_2$
Azpy	1421	1330
Dmazpy	1400	1289
Deazpy	1397	1291
Azpym	1392	1304
Deazpym	1379	1263

The N=N stretching modes in $[Ru(bpy)_2L](BF_4)_2$ complexes were shifted to lower frequencies approximately to 100 cm^{-1} than that in free ligands (Table 28). This was the strong evidence for the most π-back bonding from ruthenium to azo, $t_{2g} \rightarrow \pi^*$ (azo) (Scheme I). The N=N stretching vibration for azpy complex showed a strong absorption at 1330 cm^{-1}. This band shifted to lower energy for the dmazpy, deazpy, azpym and deazpym complexes which occurred at 1289, 1291, 1304 and 1263 cm^{-1}, respectively. The azpy complex displayed the N=N stretching modes at higher energy than in dmazpy and deazpy complexes because dmazpy and deazpy accepted electrons from both Ru(II) center and substituent groups. Therefore, the N=N bond order in dmazpy and deazpy complexes were decreased.

In the azpym and deazpym complexes, $\nu_{(N=N)}$ were red shifted by 25 and 65 cm^{-1} from the azpy complex, respectively. Results of these studies suggested that decreasing of N=N bond order in azpym complex involed π-backbonding from Ru(II) center to π^* orbital of azo function and inductive effect of the nitrogen atom in pyrimidine ring. The deazpym complex showed the N=N stretching mode at lower energy than in azpy and azpym complexes it suggested that deazpym accepted electrons from both Ru(II) and substituent groups. Then the N=N bond order in deazpym complex is reduced. The $[Ru(bpy)_2L](BF_4)_2$ complexes also showed bands in the range 1000-1100 cm^{-1} due to the tetrafluoroborate anion.

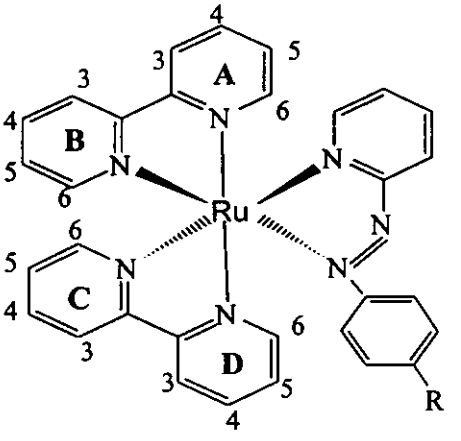


Scheme I

4.3 Nuclear Magnetic Resonance spectroscopic technique

^{1}H NMR spectroscopy is an important technique to determine molecular structure because different protons in a molecular structure will show different chemical shifts. Furthermore, ^{1}H NMR spectra exhibited the proportionation of protons in each complex, and their chemical shifts are related to their positions in complexes. In addition, they showed the number of protons in each peak corresponding to the formula structure which are assigned from ^{1}H-^{1}H COSY spectra. The ^{13}C NMR signals showed the number of carbon atoms in each complex corresponding to the formula structure which are assigned from HMQC spectra.

The structure of $[Ru(bpy)_2L](BF_4)_2$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) are elucidated by using 1D and 2D NMR spectroscopic techniques. The ^{1}H NMR spectra of $[Ru(bpy)_2L](BF_4)_2$ complexes in acetone-d_6 showed characteristic peaks of bpy and L ligands. The four pyridine rings in the bpy ligands are magnetically non-equivalent position, because they are in different shielding environments. The structures of these complexes are not a symmetric molecules. The slight difference between the shielding environments of the four pyridine rings in an bipyridine ligands could be seen more clearly in this Figure.



R = H, $N(CH_3)_2$ and $N(C_2H_5)_2$

The four sets of proton on bipyridine ligands are identified by the symbol A, B, C and D. The pyridine ring A is trans to another pyridine ring D, while ring A and ring D are in different shielding environments. The pyridine ring B is trans to nitrogen atom on the azo function of L ligand and pyridine ring C is trans to pyridine ring of L ligand. Thus the protons on pyridine ring A, B, C and D are magnetically non-equivalent. As a result there should be sixteen distinct signals in the ^{1}H NMR spectra for the bipyridine ligands. According to the coupling scheme of 2,2′-bipyridine, sixteen of these resonances are predicted to be doublet of doublet of doublets. Due to long-range coupling on the order of 1.0-2.0 Hz. These splitting patterns are clearly seen in the ^{1}H NMR spectra of all complexes in Figure 52, 56, 60, 64 and 68. The spectrum of bipyridine ligands in each complex should be pointed out that the four sets of protons on pyridine ring are identified by the symbol A, B, C and D. However, an unequivocal assignment of a set of signals to A or B or C or D could not be distinguished. However, within each set the assignment is supported by a ^{1}H-^{1}H COSY spectrum.

Table 29 showed the proton chemical shifts of $[Ru(bpy)_2L]^{2+}$ complexes, where L were bpy, azpy, dmazpy, deazpy, azpym and deazpym. The spectrum of $[Ru(bpy)_3]^{2+}$complex appeared four signals corresponding to 24 protons. It was symmetrical structure of the complex. The four signals 8.86 (ddd), 8.23 (ddd), 8.06 (ddd) and 7.60 (ddd) ppm could be assigned to H3, H4, H6 and H5, respectively, by comparison with those already reported (Constable and Seddon, 1982 and Watts, 1983). The chemical shifts of H_3 were lower field than the orther protons.

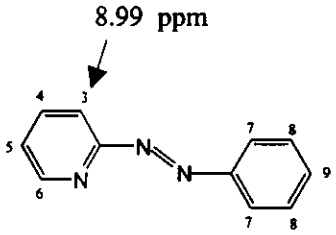
In comparison with the NMR data of $[Ru(bpy)_3]^{2+}$, the spectra of $[Ru(bpy)_2L]^{2+}$complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) showed characteristic peaks of both bpy and L ligands with systematic variation of H3, H4, H5 and H6.

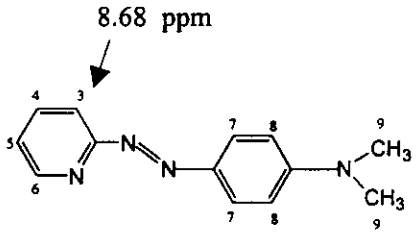
Table 29 ^{1}H NMR chemical shifts of $[Ru(bpy)_2L]^{2+}$ in acetone-d_6 solution

Compound	δ(ppm) of pyridine ring					
	bpy				L	
	H3	H4	H5	H6	H3 (pyridine)	H4 (pyrimidine)
$[Ru(bpy)_3]^{2+}$ [a]	8.50	8.05	7.39	7.73	-	-
this work	8.86	8.23	8.06	7.60		
$[Ru(bpy)_2azpy]^{2+}$	8.97	8.35	7.73	8.32	8.99	-
	8.95	8.32	7.70	7.99		
	8.64	8.10	7.68	7.96		
	8.50	8.10	7.54	7.66		
$[Ru(bpy)_2dmazpy]^{2+}$	8.95	8.32	7.70	8.28	8.68	-
	8.94	8.31	7.65	8.10		
	8.74	8.28	7.64	7.94		
	8.70	8.21	7.60	7.55		
$[Ru(bpy)_2deazpy]^{2+}$	8.93	8.31	7.70	8.28	8.64	-
	8.92	8.30	7.65	8.10		
	8.73	8.28	7.63	7.93		
	8.70	8.21	7.60	7.56		
$[Ru(bpy)_2azpym]^{2+}$	8.98	8.38	7.77	8.34	-	9.33
	8.96	8.36	7.73	7.95		
	8.66	8.35	7.69	7.93		
	8.52	8.12	7.56	7.82		
$[Ru(bpy)_2deazpym]^{2+}$	8.92	8.35	7.73	8.33	-	9.13
	8.91	8.32	7.68	8.08		
	8.77	8.30	7.63	7.90		
	8.75	8.23	7.62	7.75		

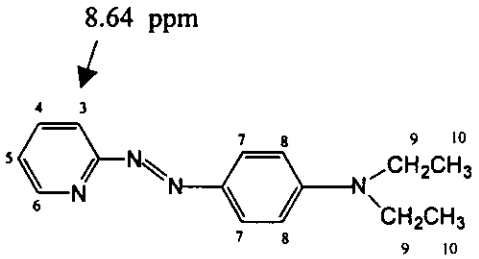
[a] Yang, *et al.*, 2001 (in DMSO solution)

The properties of the third ligands are effected to each proton on bpy ligands which showed the different chemical shifts. The proton chemical shifts for H3 of the third ligands in complexes, it found that the chemical shift of azpy complex is lower field than dmazpy and deazpy complexes. This may be due to the fact that the H3 of deazpy and dmazpy complexes have more electron density than azpy complex.



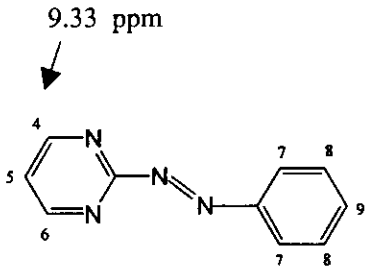


dmazpy

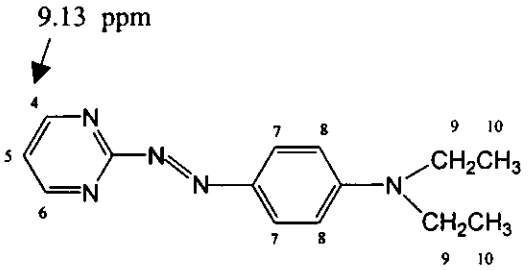


deazpy

The properties of the third ligands in azpym and deazpym complexes are effected to each proton on bpy ligands. The proton chemical shifts for H4 of the third ligands, it found that the chemical shift of azpym complex is lower field than deazpym complex. This may be due to the fact that the H4 of deazpym complex has more electron density than azpym complex.



azpym



deazpym

In addition, the chemical shifts of H3 and H4 in azpy, azpym and deazpym ligands are lower field than H3 onto the pyridine ring of bpy ligands in complexes. Whereas, the chemical shifts of H3 onto the pyridine ring of bpy ligands are lower field than H3 as the third ligands are dmazpy and deazpy in complexes. The electron-donating groups ($-N(CH_3)_2$ and $-N(C_2H_5)_2$) at the para position on benzene ring in dmazpy, deazpy and deazpym complexes led to a significant upfield shift of H3 in pyridine ring of dmazpy and deazpy ligands and H4 in pyrimidine ring of deazpym ligand.

In the case of free ligands, the H6 are located on pyridine or pyrimidine rings next to nitrogen atom which gave signals at the most downfield. Whereas, the H3 in complexes were lower field than H6 which was a good indication of N-coordination.

4.4 UV-Visible absorption spectroscopic technique

UV-Visible absorption spectroscopy is the technique to study the electronic transitions of the ligands and complexes.

The absorption spectra of ligands and complexes were recorded in both ultraviolet (200-400 nm) and visible regions (400-800 nm). The UV-Vis spectra of the complexes are shown in Figure 78.

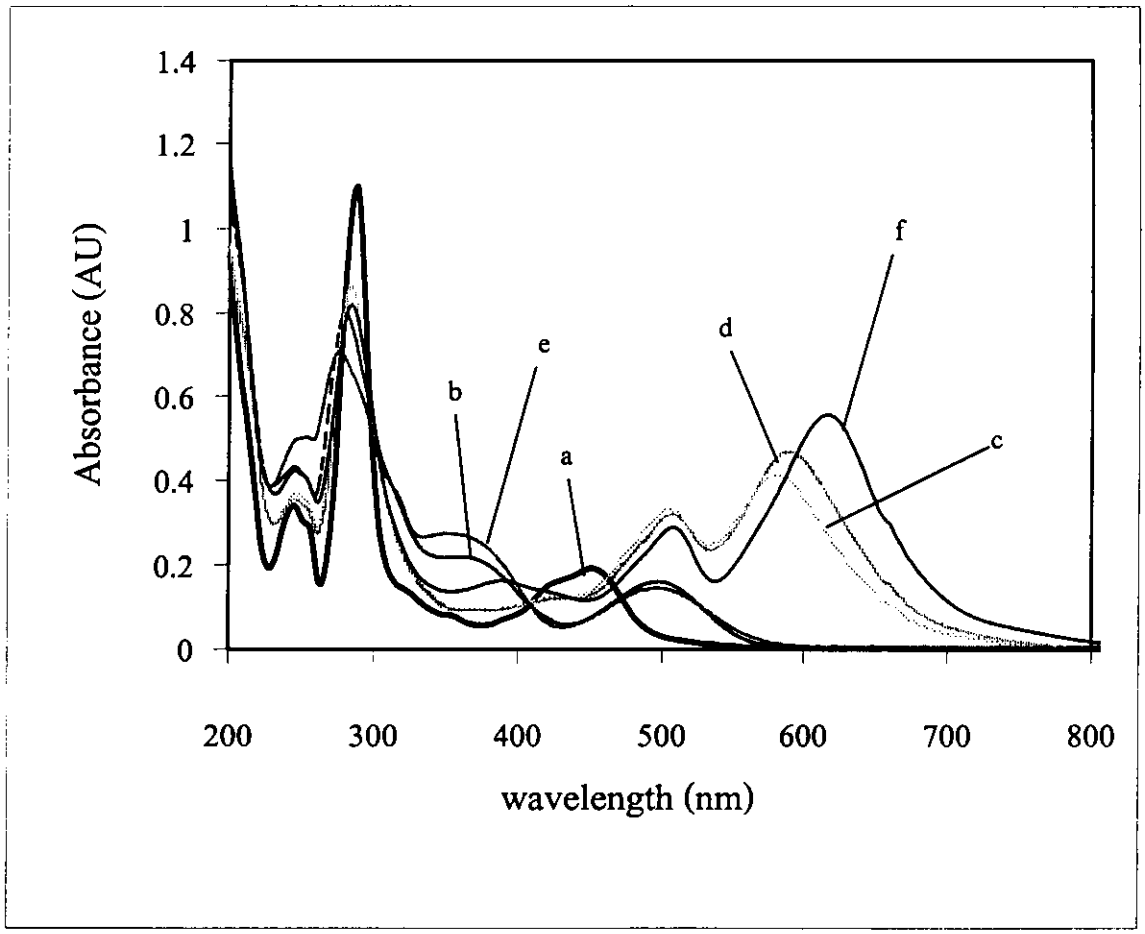


Figure 78 UV-Vis spectra of the ruthenium complexes in acetonitrile solution :
(a) $[Ru(bpy)_3](BF_4)_2$; (b) $[Ru(bpy)azpy](BF_4)_2$;
(c) $[Ru(bpy)dmazpy](BF_4)_2$; (d) $[Ru(bpy)deazpy](BF_4)_2$;
(e) $[Ru(bpy)azpym](BF_4)_2$; (f) $[Ru(bpy)deazpym](BF_4)_2$

The spectra of $[Ru(bpy)_2L]^{2+}$ complexes, where L are azpy (curve b), dmazpy (curve c), deazpy (curve d), azpym (curve e) and deazpym (curve f), are very similar to that of its parent compound $[Ru(bpy)_3]^{2+}$ (curve a). According to literature, the strong absorptions in the 240-290 nm region are generally assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions, the absorption in the visible region is assigned to MLCT transition as observed in ruthenium polypyridyl complexes (Felix, *et al.*, 1980, Kober and Meyer, 1982 and Rillema, *et al.*, 1982). For the mixed-ligand complexes of the type $[Ru(bpy)_2L]^{2+}$ (L= azpy, dmazpy, deazpy, azpym and deazpym), very intense UV bands characteristically occur at ~240 and ~290 nm, which have been assigned to $\pi \rightarrow \pi^*$ electronic transitions associated with the bipyridine ligands. There are also intense bands in the visible spectra assigned to $d\pi(Ru) \rightarrow \pi^*$ transitions. This transition is absent in the free ligands.

The absorption process corresponds to a MLCT, which formally involves the transfer of an electron from the metal to the third ligand, that result from the energy level of $\pi \rightarrow \pi^*$ transitions of azpy, dmazpy, deazpy, azpym and deazpym ligands shift to lower energy than bpy ligand. According to MLCT bands in visible region of the azpy and azpym complexes, only one absorption band in each complex is observed in the visible region. In contrast, the complexes of dmazpy, deazpy and deazpym show two absorption bands which correspond to $d\pi \rightarrow \pi^*$ transitions. The position of the MLCT band maxima are related to the degrees of π delocalization in ligands. As the number of ligand π systems interacting with the metal center increases, the energy of the $d\pi \rightarrow \pi^*$ transition shifts to the red.

The positions of the electronic absorption maxima and the extinction coefficients for the complexes $[Ru(bpy)_2L]^{2+}$ and free ligands are given in Table 30.

Table 30 UV-Visible data of free ligands and $[Ru(bpy)_2L]^{2+}$ (L = bpy, azpy, dmazpy, deazpy, azpym and deazpym) in acetonitrile solution

Compound	λ_{max}, nm (ε x 10^{-4}, $M^{-1}cm^{-1}$)			
	$\pi \rightarrow \pi^*$ (bpy)	$\pi \rightarrow \pi^*$ (L)		MLCT
		Free ligand	Complex	
$[Ru(bpy)_3]^{2+}$ [a]	250 (2.5) 285 (8.7)	[b]283 (4.0)	285 (8.7)	451 (1.4)
this work	244 (2.6) 288 (8.3)	282 (1.2)	288 (8.3)	450 (1.4)
$[Ru(bpy)_2azpy]^{2+}$	246 (2.3) 280 (4.4)	314 (1.8)	362 (1.2)	498 (0.9)
		[c]448 (0.05)		
$[Ru(bpy)_2dmazpy]^{2+}$	246 (2.5) 284 (5.9)	423 (3.7)	430 (0.9) sh	504 (2.3)
				580 (2.8)
$[Ru(bpy)_2deazpy]^{2+}$	246 (2.5) 284 (6.1)	431 (3.4)	434 (0.8) sh	506 (2.2)
				588 (3.3)
$[Ru(bpy)_2azpym]^{2+}$	254 (2.8) 276 (3.9)	298 (1.6)	310 (2.7) sh	496 (0.8)
		[c]439 (0.04)	350 (1.5)	
$[Ru(bpy)_2deazpym]^{2+}$	246 (3.0) 284 (5.8)	431 (2.9)	390 (1.1)	508 (2.0)
				616 (3.9)

[a] Crutchley, 1982 (recorded in H_2O), sh = shoulder

[b] Recorded in EtOH

[c] $n \rightarrow \pi^*$ transition

UV-Visible data of $[Ru(bpy)_2L]^{2+}$ reveals that the lowest energy of MLCT band in the visible region decreases in the order $[Ru(bpy)_3]^{2+} > [Ru(bpy)_2azpy]^{2+} \approx [Ru(bpy)_2azpym]^{2+} > [Ru(bpy)_2dmazpy]^{2+} \approx [Ru(bpy)_2deazpy]^{2+} > [Ru(bpy)_2deazpym]^{2+}$. This result indicates that the energy level of $\pi \rightarrow \pi^*$ transitions decreases in the order bpy > azpy ≈ azpym > deazpy ≈ dmazpy > deazpym complexes. This is due to the effect of electron donating substituents, $-N(CH_3)_2$ and $-N(CH_2CH_5)_2$, which extend π conjugation of ligands then π^* levels are reduced.

4.5 Cyclic Voltammetric technique

4.5.1 Free ligands

Reduction range

Goswami and co-worker (1983) reported that the free 2-(phenylazo) pyridine ligand, displays two quasi-reversible couples in the negative potential region. It emerges that the azpy accept two electrons in its lowest unoccupied molecular orbital (LUMO) which is primary azo in character. In this study, the reduction potential of azpy, dmazpy, deazpy, azpym and deazpym ligands showed irreversible couples, which became clearly couples at higher scan rate (200-1000 mV/s). It was believed that the azo function, -N=N-, was electron acceptor.

The reduction potential exhibits the electron accepting ability of the ligand. The positive potential is the greater electron accepting ability. The negative potential values of azpy, dmazpy, deazpy, azpym and deazpym are compared and show that azpym (E_{pc} = -1.47 V) can accept the electron better than azpy (E_{pc} = -1.62 V) ≈ deazpym (E_{pc} = -1.66 V), and dmazpy (E_{pc} = -1.79 V) ≈ deazpy (E_{pc} = -1.82 V).

Oxidation range

Cyclic voltammogram of azpy and azpym ligands did not give any peaks in the range 0.0 to 1.4 V. However, the dmazpy, deazpy and deazpym ligands which have substituents on the phenyl ring (-NR_2, R = -CH_3 and -C_2H_5) showed two quasi-reversible couples in this region. The difference might be due to substituent effect in dmazpy, deazpy and deazpym molecules.

4.5.2 $[Ru(bpy)_2L](BF_4)_2$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym)

The electrochemical behavior of the complexes in acetonitrile was examined by cyclic voltammetry. The voltammogram displayed metal oxidations on the positive side and the ligand reductions on the negative with respect to ferrocene. It was well known that the electrochemical behavior of the ruthenium(II) polypyridyl complexes was usually observed as a metal-centered oxidation and a series of ligand-centered reductions.

Reduction range

In the reduction range –2.5 to 0.0 V, reduction responses were observed under similar conditions using a glassy carbon working electrode. The results are given in Table 31. The reduction responses are compared with the results for free ligands.

Santra and co-worker (1999) reported that the free azpym ligand displayed two quasi-reversible one-electron cyclic voltammetric responses with peak-to-peak separation (ΔE_p = 130 and 170 mV).

Polypyridyl ligands were also capable of accepting electrons. However, it was well documented in literature that the azopyridine ligands were better π-acceptors

and underwent easier reductions than those of the polypyridine ligands (Kruase and Krause, 1980).

The reference $[Ru(bpy)_3]^{2+}$ complex exhibited three reversible one-electron reductions to give $[Ru(II)(bpy)^{1-}_3]^-$. Such reduction waves were also reproduced in this work.

Table 31 Reduction potentials data of $[Ru(bpy)_2L]^{2+}$ in 0.1 M TBAH acetonitrile at scan rate 100 mV/s (ferrocene as an internal standard)

Complex	$E_{1/2}$,V (ligand reduction)			
	L		bpy	
	I	II	III	IV
$[Ru(bpy)_3]^{2+}$	-1.74	-1.93	-2.17	-
$[Ru(bpy)_2azpy]^{2+}$	-0.87	-1.61	-2.07	-2.40
$[Ru(bpy)_2dmazpy]^{2+}$	-1.02	-1.75	-2.07	-2.27
$[Ru(bpy)_2deazpy]^{2+}$	-1.04	-1.76	-2.07	-2.23
$[Ru(bpy)_2azpym]^{2+}$	-0.67	-1.48	-2.04	-2.38
$[Ru(bpy)_2deazpym]^{2+}$	-0.86	-1.64	-2.04	-2.25

The cyclic voltammogram of the $[Ru(bpy)_2L]^{2+}$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) display four electron reductions (Figure 73-77). The data (Table 31) reveal that the first and the second (Figure 86-89, Appendix A) of these reductions occurred at more positive potentials relative to the reduction of azo function of L while the third and the fourth reductions are related to the reduction of

the bpy ligand (Sullivan, *et al.*, 1979) with one electron transfer in each equation (1) - (4).

$$[Ru^{II}(bpy)_2L]^{2+} + e^- \leftrightarrows [Ru^{II}(bpy)L^{1-}]^{+} \quad (1)$$

$$[Ru^{II}(bpy)_2L^{1-}]^{+} + e^- \leftrightarrows [Ru^{II}(bpy)L^{2-}]^{0} \quad (2)$$

$$[Ru^{II}(bpy)_2L^{2-}]^{0} + e^- \leftrightarrows [Ru^{II}(bpy)^{1-}(bpy)L^{2-}]^{1-} \quad (3)$$

$$[Ru^{II}(bpy)^{1-}(bpy)L^{2-}]^{1-} + e^- \leftrightarrows [Ru^{II}(bpy)^{1-}(bpy)^{1-}L^{2-}]^{2-} \quad (4)$$

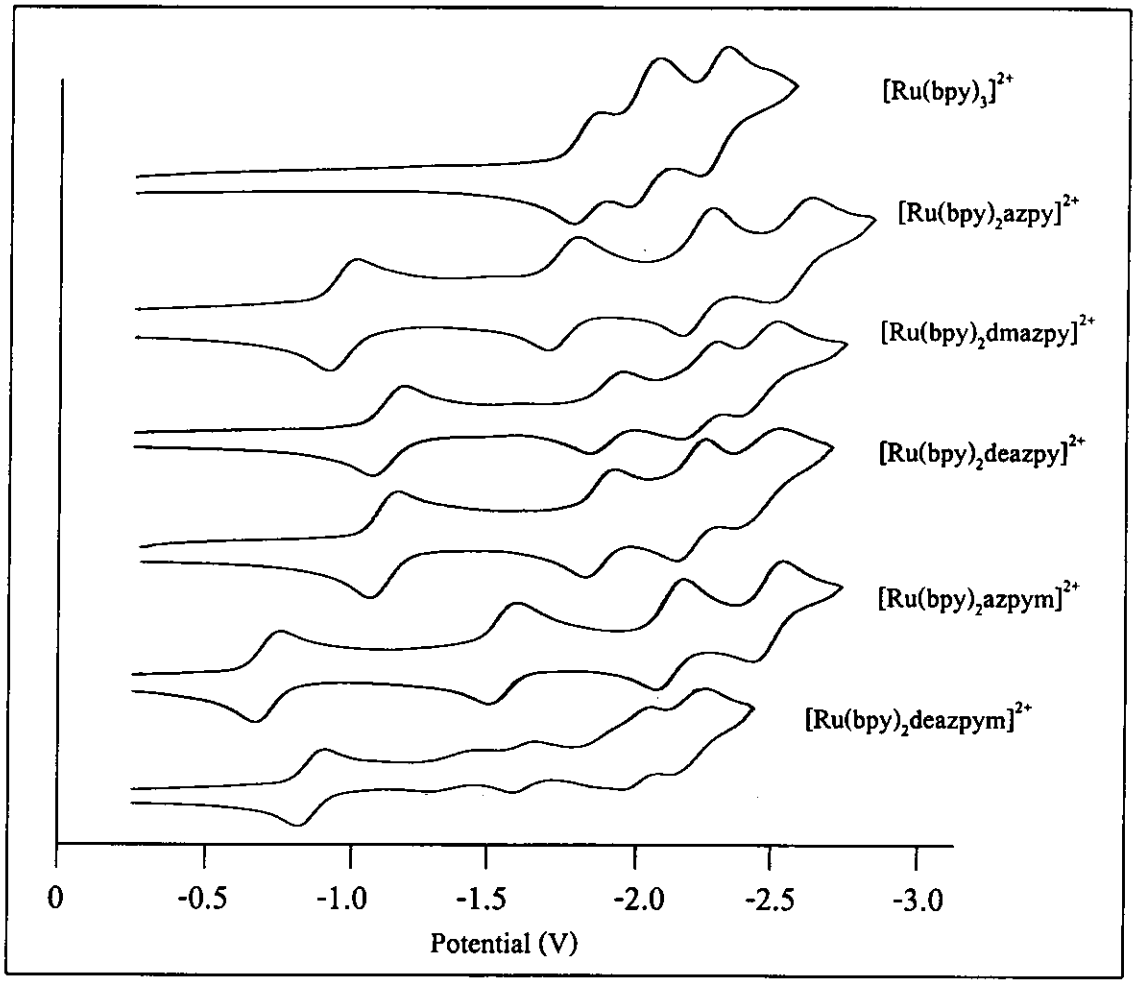


Figure 79 Cyclic voltammograms for successive one-step reductions of each bidentate ligand bound to ruthenium(II)

In comparison with the $[Ru(bpy)_3]^{2+}$ complex, the first and the second reductions of $[Ru(bpy)_2L]^{2+}$ complexes, (where L = azpy, dmazpy, deazpy, azpym and deazpym ligands) occurred easiler than the first reduction step of $[Ru(bpy)_3]^{2+}$. These results could be due to the nature of the third ligands. Whereas, the third and the fourth reduction waves are attributed to the bpy ligands.

The negative potential values of $[Ru(bpy)_3L]^{2+}$complexes are compared and it shows the azpym ligand is the best π-acceptor among these ligands. Therefore, the $[Ru(bpy)_2azpym]^{2+}$ complex accepts electron better than $[Ru(bpy)_2azpy]^{2+} \approx [Ru(bpy)_2deazpym]^{2+}$ and $[Ru(bpy)_2dmazpy]^{2+} \approx [Ru(bpy)_2deazpy]^{2+}$ complexes. This was in accord with the π-acidity order (Yamamoto, *et al.*, 1996) of the ligands : azopyrimidine > azopyridine > bipyridine.

Oxidation range

Generally, redox reduction of metal were observed in the oxidation range. In addition, in some complexes the redox properties of ligand center were also observed.

Table 32 Oxidation potentials data of $[Ru(bpy)_2L]^{2+}$ in 0.1 M TBAH acetonitrile at scan rate 100 mV/s (ferrocene as an internal standard)

Assignment couple	$E_{1/2}$,V (Oxidation potential of L in complexes)					
	bpy	azpy	dmazpy	deazpy	azpym	deazpym
Ligand with substituents	-	-	+0.71	+0.74	-	+0.77
Ru (II/III)	+0.91	+1.20	-	-	-	-

In comparison with $[Ru(bpy)_3]^{2+}$complex (+0.91 V), the metal-centered oxidation potential of $[Ru(bpy)_2azpy]^{2+}$complex at +1.02 V is shifted to the more positive potential, whereas the other complexes cannot be observed the Ru(III)/Ru(II) couples within experimental condition. The redox potential of $[Ru(bpy)_2azpym]^{2+}$, $[Ru(bpy)_2dmazpy]^{2+}$, $[Ru(bpy)_2deazpy]^{2+}$ and $[Ru(bpy)_2deazpym]^{2+}$ complexes are expected to occur at higher potential than that in $[Ru(bpy)_3]^{2+}$ complex. This results could be understood considering the nature of the third ligands. The ruthenium oxidation potential is affected by the nature of the ligands. For closely related ligands, the azopyridine ligands thus stabilize ruthenium(II) better than bipyridine in equation (5).

$$Ru(bpy)_2L^{3+} + e^- \rightleftarrows Ru(bpy)_2L^{2+} \qquad (5)$$

The ligand with substituents in complexes are occurred at less positive at +0.71 V (ΔE_p = 70 mV) for $[Ru(bpy)_2dmazpy]^{2+}$, +0.74 V (ΔE_p = 75 mV) for $[Ru(bpy)_2deazpy]^{2+}$and +0.77 V (ΔE_p = 90 mV) $[Ru(bpy)_2deazpym]^{2+}$. The shift of this couple is due to conjugation in ligands. This led to lower the π^* energy level. Therefore, the redox potential of phenyl rings occurred at low potential than that in free ligand.

The following data give the Ru(III)/Ru(II) oxidation potential in order azopyrimidine > azopyridine > pyridine. The dmazpy, deazpy and deazpym ligands could stabilize the Ru(II) in complexes better than other bidentate ligands. The substituents, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$, could donate electron to the molecule and increased the strength of σ bonding at pyridine (for dmazpy and deazpy ligand) and pyrimidine (for deazpym ligand) toward Ru(II).