Chapter 4

DISCUSSION

The ruthenium polypyridyl complexes had interesting properties. It had been reviewed previously. In this work, the $[Ru(phen)_2L]^{2+}$ complexes were synthesized which L were better π-acceptors than bidentate ligands such as 2-(phenylazo)pyridine (azpy) (Krause and Krause, 1980). The azpy molecule contained one nitrogen on pyridine and one on the azo moiety. The 2-(phenylazo)pyrimidine (azpym) had similar structure of azpy ligand but they had two nitrogen on pyrimidine ring. Pyrimidine was higher π-acid than pyridine. Thus, the derivatives of azpy and azpym ligands were synthesized and the chemistry of these ligands in the $[Ru(phen)_2L]^{2+}$complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) had been considered. From these results led to compare with the $[Ru(phen)_3]^{2+}$complex. In each ligand gave the difference results.

The $[Ru(phen)_2L]^{2+}$ (L = phen, azpy, dmazpy, deazpy, azpym and deazpym) complexes were synthesized as shown in equation (1)

$$[Ru^{II}(phen)_2Cl_2] + L \xrightarrow[EtOH:H_2O = 3:1]{AgNO_3,\ reflux} [Ru^{II}(phen)_2L]^{2+} + AgCl \qquad (1)$$

The reaction between $[Ru^{II}(phen)_2Cl_2]$, L = azpy, dmazpy, deazpy, azpym and deazpym ligands under refluxing afforded $[Ru^{II}(phen)_2L]^{2+}$. The role of $AgNO_3$ was to get rid of chloride atoms in starting materials. Then, the NH_4BF_4 or NH_4PF_6 were added in the complex solution to precipitate these complexes. In this work, the complexes were characterized by spectroscopic methods such as ES mass spectrometry, FAB mass spectrometry, UV-Visible spectroscopy, Infrared spectroscopy and NMR spectroscopy.

4.1 Electrospray and the FAB mass spectrometry

The electrospray (ES) and the FAB mass spectrometry are the techniques to confirm the molecular weight of molecule. In ligands, the parent peaks of each ligand gave 100% relative abundance. It was molecular weight of ligand with one protonation.

Each complex showed different patterns. The $[Ru(phen)_3](BF_4)_2$ complex showed the most intense peak at m/z 729, which was assigned to $[Ru(phen)_3]^{2+}$ (100%). The two tetrafluoroborate ion were lost from the complex. The $[Ru(phen)_2$ azpy$](BF_4)_2$, $[Ru(phen)_2$dmazpy$](PF_6)_2$ and $[Ru(phen)_2$deazpy$](PF_6)_2$ complexes gave the intense peak of $([Ru(phen)_2azpy]^{2+})^{2+}$ (m/z 322.8; 100%) $([Ru(phen)_2dmazpy]^{2+})^{2+}$ (646.4; 100%) and $([Ru(phen)_2deazpy]^{2+})^{2+}$ (358.0; 100%) species (double charge). Whereas, the $[Ru(phen)_2azpym](PF_6)_2$ and $[Ru(phen)_2deazpym](PF_6)_2$ complexes showed the most parent peaks at m/z 646 and 689. Which confirmed the molecular weight of $[Ru(phen)_2azpym]^{2+}$ (100%) and $[Ru(phen)_2deazpym]^{2+}$ (100%) species.

4.2. Infrared spectroscopy

All of ligands and complexes displayed many characteristic frequencies in the range 4000-370 cm^{-1}. The important functional groups such as C=N stretching, C=C stretching and N=N stretching modes. Krause and Krause reported that the N=N (azo) stretching mode occurred in range 1600-400 cm^{-1}. From Infrared spectroscopic data, azpy ligands showed the N=N stretching vibration at 1421 cm^{-1}. Whereas, the N=N stretching mode of dmazpy and deazpy ligand appeared at lower frequency (1402 and 1399 cm^{-1}, respectively). These results indicated that the N=N bond order in dmazpy and deazpy ligands was weaker than the azpy ligand because the dmazpy and deazpy had the substituent groups, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$, which were electron

donating groups. The electrons delocalized into the π^* orbital of azo function. The N=N bond order was decreased therefore, the N=N vibrational frequencies of dmazpy and deazpy occurred at lower energies than that of azpy ligand. In the same way, the N=N bond of free azpym ligand was stronger than deazpym ligand. It appeared at 1392 and 1379 cm^{-1}, respectively.

The results of the $[Ru(phen)_2L]^{2+}$ (L = phen, azpy, dmazpy, deazpy, azpym and deazpym) complexes are shown in Table 31. Intense vibrational frequency was observed at 1084 and 847 cm^{-1} due to the presence of BF_4^- and PF_6^- salt, respectively.

Table 31 The N=N (azo) stretching vibrational frequencies of ligands and complexes

Compound	$\nu_{N=N}$, cm^{-1}
azpy	1421
$[Ru(phen)_2azpy](BF_4)_2$	1304
dmazpy	1402
$[Ru(phen)_2dmazpy](PF_6)_2$	1294
deazpy	1399
$[Ru(phen)_2deazpy](PF_6)_2$	1293
azpym	1392
$[Ru(phen)_2azpym](PF_6)_2$	1300
deazpym	1379
$[Ru(phen)_2deazpym](PF_6)_2$	1260

The N=N stretching mode in complexes occurred at lower frequency than that in free ligand, ca. 40-110 cm^{-1}, due to $t_{2g} \rightarrow \pi^*$ (azo) donation (π-back bonding). The bond order of N=N (azo) decreased, then The N=N stretching mode of free

ligands occurred at higher frequency than complexes. The N=N stretching mode of the azpy complex occurred at higher frequency than the dmazpy and deazpy complexes. Because dmazpy and deazpy ligands accepted electrons from the substituent groups. The π-back bonding of dmazpy and deazpy complexes less than azpy complex. Therefore, the N=N (azo) stretching of dmazpy and deazpy complexes were weaker than azpy complexes. Similarly, the N=N stretching mode of the azpym complex appears at higher frequency than the deazpym complexes.

4.3 UV-Visible absorption spectroscopy

Absorption spectra of ligands and complexes were recorded in the range 200-800 nm in various solvents. The absorption bands of ultraviolet and visible regions were in the range 200-400 nm and 400-800 nm, respectively.

In ligands, the azpy and azpym ligands, the absorption bands in UV region was assigned to $\pi \rightarrow \pi^*$ transitions but visible region is assigned to $n \rightarrow \pi^*$ transitions. In the case of dmazpy, deazpy and deazpym ligands showed intense bands in UV and visible region were assigned to $\pi \rightarrow \pi^*$ transitions, because the substituent (methyl and ethyl groups) in dmazpy, deazpy and deazpym at para position on benzene ring were electrons donating groups. They increase π-electron density in molecule. It leads to increase the HOMO level closed to LUMO level, the energy transition was decreased. The $\pi \rightarrow \pi^*$ transitions was shifted to lower energy and gave more intense band than azpy and azpym ligands. Furthermore, the substituents were auxochrome which have effect to the absorption of bonded chromophores. Consequently, the colors of dmazpy, deazpy and deapym were different.

The absorption spectra of $[Ru(phen)_2L]^{2+}$ (L = phen, azpy, dmazpy, deazpy, azpym and deazpym) complexes showed in the range 200-300 nm (two bands) were

assigned to intraligand transition of phen ligand and the range 300-400 nm was assigned to intraligand transition of third ligand. In visible region, each complexes was attributed to the metal-to-ligand charge tranfer (MLCT) transition (d(Ru)$\rightarrow\pi^*$ (ligand)). The phen, azpy and azpym complexes had one MLCT band but the dmazpy, deazpy and deazpym complexes had two MLCT bands. The maximum wavelength was the most intense band. These results are summarized in Table 32 in case of acetronitrile solvent.

Table 32 The lowest energies of MLCT absorption bands of complexes in acetonitrile solvent

Complexes	λ_{max} nm,(ε^aX10^{-4} $M^{-1}cm^{-1}$)
$[Ru(phen)_3]^{2+}$	446 (1.0)
$[Ru(phen)_2\ azpy]^{2+}$	496 (0.9)
$[Ru(phen)_2dmazpy]^{2+}$	577 (2.7)
$[Ru(phen)_2\ deazpy]^{2+}$	587 (3.2)
$[Ru(phen)_2azpym]^{2+}$	494 (7.4)
$[Ru(phen)_2deazpym]^{2+}$	616 (2.5)

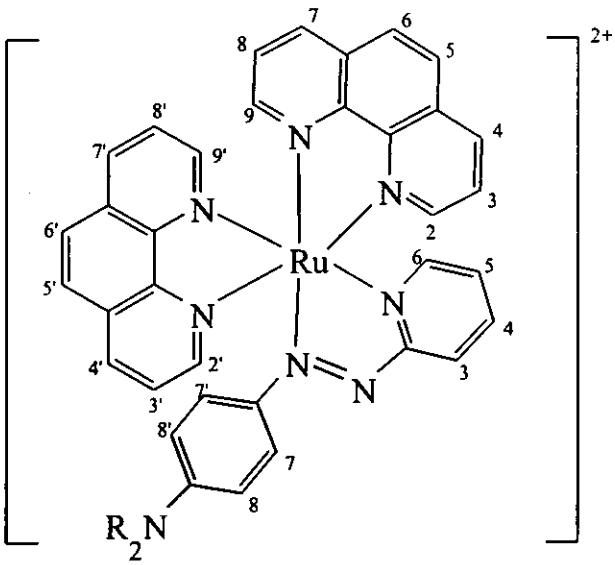
[a]Molar Extinction coefficient

From the Table 32, the MLCT band of deazpy complex appeared at lower energy than the dmazpy and azpy complexes, respectively. Similarly, the MLCT band of deazpym complex appeared at lower energy than that in the azpym complex. $[Ru(phen)_2L]^{2+}$ (L = azpy, dmazpy, deazpy, azpym and deazpym) complexes had MLCT bands at lower energy than $[Ru(phen)_3]^{2+}$ complexes. Thus, it was expected that the third ligands would stabilize the Ru better than phen ligand.

4.4 Nuclear magnetic resonance spectroscopy

The ^{1}H NMR spectroscopic data of ligands showed similarly data. The H6 was located next to nitrogen atom on pyridine ring in azpy, dmazpy and deazpy ligands showed the lowest field chemical shift. The H6 appeared doublet of doublet of doublet (ddd) peaks. While azpym and deazpym ligands, the H6 and the H4, which were equivalent protons, appeared doublet (d) peaks at the lowest field. The protons of substituent group occurred at upfield in range 3.6-1.2 ppm.

In the complexes, from the results of ^{1}H NMR and ^{1}H-^{1}H COSY data could be used to determine a roughly structure. The numbers of protons in each complex corresponded to the structural formula. The aromatic protons of ligands in compounds displayed multiplets peaks in range 9.4-6.0 ppm. Two sets of NMR signal were observed. One set in each complex corresponded to the phen ligand. The other set corresponded to the third ligands (Zhen, *et al.*, 2000). Because asymmetric molecule in complexes had different environments. The protons on phenanthroline ring lied in magnetically nonequivalent position (Yang, *et al.*, 2001). Thus, the chemical shifts of these protons appeared in adjacent position.

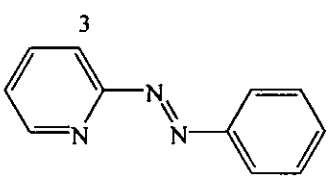


R = -N(CH$_3$)$_2$, -N(C$_2$H$_5$)$_2$

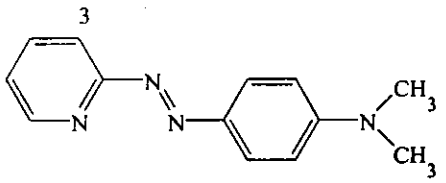
Figure 67 The structure of $[Ru(phen)_2L]^{2+}$ (L = azpy, dmazpy, deazpy ligands).

From the Figure 67, the phen protons were assigned in range 9.1-7.6 ppm. The H4 gave signal at the lowest field. The chemical shift of H4 approached to the H4'. The signal of both protons was doublet of doublet peaks.

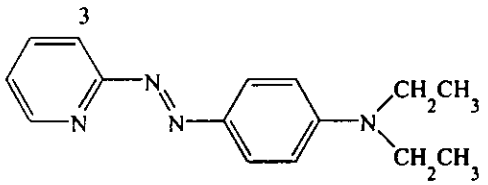
The chemical shifts of protons on the third ligands (azpy, azpym and deazpym complexes) were occurred at lower field than phen protons due to the anisotropic, inductive and resonance effects. In case of dmazpy and deazpy complexes, protons of the third ligands occurred at higher field than phen protons, because of the substituent groups. Azpy, dmazpy and deazpy complexes, the H3 (azpy, dmazpy and deazpy) were displayed chemical shifts in Figure 68.



azpy ligand → H3 = 9.02 ppm



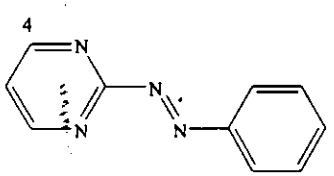
dmazpy ligand → H3 = 8.72 ppm



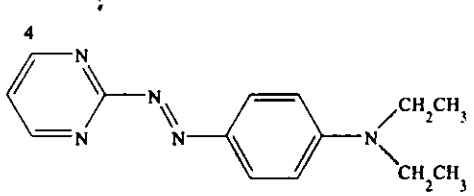
deazpy ligand → H3 = 8.69 ppm

Figure 68 The structures and chemical shifts of the H3 in azpy, dmazpy and deazpy ligands.

The azpym and deazpym complexes had H4 on pyrimidine ring, which displayed the most chemical shifts and there were shown in Figure 69.



azpym ligand → H4 = 9.31



deazpym ligand → H4 = 9.11 ppm

Figure 69 The structures and chemical shifts of the H4 in azpym and deazpym Ligands.

H4 on pyrimidine ring had more chemical shifts than H3 on pyridine ring because pyrimidine ring had two nitrogen atoms, which gave electron to metal center better than pyridine ring. Thus, H4 on pyrimidine ring appeared at downfield than H3 on pyridine ring.

The protons on benzene of the third ligands gave lower chemical shifts than proton on pyrimidine ring (inductive effect). The alkyl groups on substituents of dmazpy, deazpy and deazpym ligands in complexes appeared in range 3.6-1.2 ppm. The methyl protons ($-CH_3$) of dmazpy complex were singlet peak. The methyl protons of deazpy and deazpym complexes were triplet peaks as they were located next to methylene protons. The methylene protons (-CH2-) of deazpy and deazpym complexes were quartet.

4.5 Cyclic voltammetry

4.5.1 In the free ligands

Reduction range

The reduction peaks of ligands at scan rate 50 mV/s, the forward scan showed only one cathodic peak at –1.61 (azpy), -1.79 (dmazpy), -1.79 (deazpy), -1.32 (azpym) and –1.66 (deazpym) V. The anodic peaks of ligands showed anodic peak at –1.47 (azpy), -1.42 (dmazpy), -1.42 (deazpy), -1.05 (azpym) and –1.66 (deazpym) V. When the higher scan rate (100-1000 mV/s), the reduction (Figure 70 and 71, Appendix) and oxidation (Figure 72 and 73, Appendix) species could not give reversible couple. Then, the species in reduction range displayed irreversible couple. The reduction peak was two electrons transfer because it was believed that the azo function (-N=N-) was electron acceptor. It was showed that all ligands accepted two electrons into its lowest unoccupied molecular orbital (LUMO) which was primary azo

in character (Goswami, *et al.*, 1983). In this works, all ligands expected two electrons transfer in reduction range. If the positive potential of ligands were high, there were the greater electron accepting ability. The reduction potential species of ligands were compared and showed that azpy accepted the electron better than dmazpy and deazpy. And then, azpym ligand accepted the electron better than deazpym ligand. This corresponded to infrared spectroscopic data.

Oxidation range

Dmazpy, deazpy and deazpym ligands showed irreversible and quasi-reversible couples of substituent groups whereas, azpy and azpym showed no peaks in oxidation range. Irreversible couple showed the anodic peak at +0.57 (dmazpy), +0.55 (deazpy) and +0.60 (deazpym) V and quasi-reversible couple showed +0.81 (dmazpy), +0.83 (deazpy) and +0.89 (deazpym) V.

4.5.2 In the complexes

The cyclic voltammogram of the $[Ru(phen)_2L]^{2+}$ (L = phen, azpy, dmazpy, deazpy, azpym and deazpym ligands) complexes showed the redox of ligands and Ru (II/III) with respect to ferrocene.

Reduction range

The cyclic voltammograms of $[Ru(phen)_3]^{2+}$ were shown one couple at -1.72 V and Ep_a value at -1.89 V (Figure 76, Appendix), which it occurred desorption spike on reverral (Tokel-Takvoryan, *et al.*, 1973). The reduction range of the $[Ru(phen)_2L]^{2+}$ (L = azpy, dmazpy, deazpy, azpym and deazpym ligands) complexes gave two complete reversible couples of the thrid ligands and the phen ligands gave one complete reversible couple and other was quasi-reversible couple (Figure 74 and 75,

Appendix for $[Ru(phen)_2azpy]^{2+}$). The couples of the third ligands were occurred at lower potential than phen ligand and they was shifted to less potential in complexes when compared with free ligands. The data of complexes in reduction range are shown in Table 33.

Table 33 Summary of reduction potential of complexes

Complexes	$E_{1/2}$, V (ΔE_p, mV)			
	L		phen	
	I	II	III	IV
$[Ru(phen)_3](BF_4)_2$	-	-	-1.72(105)	-1.89[a]
$[Ru(phen)_3azpy](BF_4)_2$	-0.88(80)	-1.61(75)	-2.05(65)	-2.33(125)
$[Ru(phen)_3dmazpy](PF_6)_2$	-0.60(70)	-1.76(70)	-2.04(70)	-2.27(100)
$[Ru(phen)_3deazpy](PF_6)_2$	-0.93(68)	-1.77(74)	-2.03(80)	-2.27(130)
$[Ru(phen)_3azpym](PF_6)_2$	-0.92(65)	-1.71(85)	-2.25(65)	-2.57(115)
$[Ru(phen)_3deazpym](PF_6)_2$	-0.88(53)	-1.63(60)	-2.01(60)	-2.26(120)

L = The third ligand, a = E_{pc}

From couple I, azpy had $E_{1/2}$ less than dmazpy and deazpy, similarly azpym had $E_{1/2}$ less than dmazpy in complexes. Azpy ligand accepted electron than dmazpy and deazpy in complexes. While, azpym ligand accepted electron than deazpym ligand. Phen ligand accepted bad electron when compared with all ligand in complexes. This result, azpy was better π-acceptor than dmazpy and deazpy. Azpym was better π-acceptor than deazpym but azpym had $E_{1/2}$ less than azpy. Then azopyrimidine ligands (azpym and deazpym) were better π-acceptor than azopyridine ligands (azpy, dmazpy and deazpy) and phen ligand.

Oxidation range

In the oxidation range showed the redox property of both metal center (RuII/III) and substituent groups of ligand.

The substituent couple of ligand was occurred at less positive potential at +0.84 (ΔE_p= 80 mV) for $[Ru(phen)_3dmazpy](PF_6)_2$, +0.70 ($\Delta E_p$= 75 mV) for $[Ru(phen)_3deazpy](PF_6)_2$ and +0.74 (ΔE_p= 60 mV) for $[Ru(phen)_3deazpym](PF_6)_2$ complexes (Figure 76, Appendix). The shift of substituent couple was due to greater conjugation in ligands. This led to lower the π^* level. As a result, the redox potential of phenyl ring occurred at lower potential than that of free ligand.

The redox potential of Ru(II/III) in $[Ru(phen)_3](BF_4)_2$ and $[Ru(phen)_3azpy](BF_4)_2$ complexes were found to be reversible couple. Their redox potentials are shown in Figure 78 (Appendix). Other complexes, the redox potentials were not observed within solvent window. The data of both couple are shown in Table 34.

Table 34 Summary of couple V (ligand) and redox potential of complexes

Complexes	$E_{1/2}$, V (ΔE_p, mV)	
	Substituent couple	Ru(II/III) couple
$[Ru(phen)_3](BF_4)_2$	-	+0.89(75)
$[Ru(phen)_3azpy](BF_4)_2$	-	+1.38(63)
$[Ru(phen)_3dmazpy](PF_6)_2$	+0.85[a]	-
$[Ru(phen)_3deazpy](PF_6)_2$	+0.70(75)	-
$[Ru(phen)_3azpym](PF_6)_2$	-	-
$[Ru(phen)_3deazpym](PF_6)_2$	+0.74(60)	-

a = E_{pa}

The following data, the Ru(II/III) potential of the $[Ru(phen)_3azpy](BF_4)_2$ complex shifted to more positive potential than $[Ru(phen)_3](BF_4)_2$. The third ligands could stabilize the Ru(II/III) in complexes better than phen.

4.6 X-ray Diffractometer

X-ray crystallography is the most precise and comfortable technique for determination of the actual structure. The single crystals of [protonated 2-(phenylazo) pyridine and protonated 2-(4-hydroxyphenylazo)pyridine (3:1)]tetrafluoroborate were studied.

The azpy molecule contains one nitrogen on pyridine and one on the azo moiety. They are acting as the donor atoms to metal ions. In acidic solution, both nitrogens can react with protons. From X-ray data, the molecular structure was shown that azpy ligands reacted with the Co, N(1) and N(3) bonded to Co ion. This mean that N(1) is more basic than N(2) and should be protonated. The difference-Fourier map showed a big electron density near N(1). The results from X-ray data indicated that the protonation occurred at the azo nitrogen (N1) and it was more strongly basic than the pyridine nitrogen (N3). In addition, N(1)-N(2) distance, which was similar to that of the azobenzene, was 1.248(4) $Å^3$. The benzene ring and pyridine rings were almost planar and their interplanar angle was $9.3(1)^\circ$. The azo bond was not in the same plane as the benzene ring with the torsion angle N2-N1-C1-C6 being $5.0(4)^\circ$; meanwhile, that of N1-N2-C7-N3 was $-13.8(4)^\circ$. This implies that the pyridine ring was slightly distorted. This could be due to the repulsion between N1 and N3 besides the hydrogen bond interaction between N3 and H1(N1). The crystal structure was stabilized by intramolecular N-H N hydrogen bonds and van der Waals forces. In addition, some oxidation products of the azpy compounds were observed as 25% of the total products. This was similar to the oxidation of aromatic compound, used air as the oxidant and

Co(III) salts as catalyst. However, the mechanism to produce such products was too complicated and was not investigated further. All the H-atoms (except the hydroxy group) were fixed geometrically and refined using constraints with isotropic temperature factor (Panneersel, *et al.*, 2000).