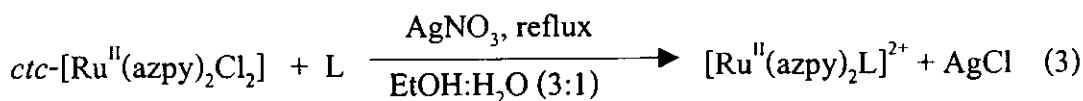# Chapter 4

DISCUSSION

The chemistry of ruthenium(II) complexes containing azoimine (-N=C-N=N-) and imine (-N=C-C=N-) functional groups showed interesting properties. The advantage of the azoimine functional unit was to stabilize low valent metal redox state, such as Ru(II), Os(II). The ligands, 2-(phenylazo)pyridine (azpy), 2-(phenylazo) pyrimidine (azpym), has azoimine function. These ligands were bidentated ligands which has strong π-acceptor properties and donor atom was nitrogen. Azpy consisted of one nitrogen from pyridine ring with a pendant nitrogen donor atom from azo function. Azpym had similar structure but there were two nitrogen on the pyrimidine ring. Pyrimidine was higher π-acidity than pyridine (Santra, *et al.*, 1999).

The 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands were polypyridine ligands which consisted of imine (-N=C-C=N-) functional group. The objectives of this works were synthesis and studied the chemistry of $[Ru(azpy)_2L]^{2+}$ complexes (where L= azpy, azpym, bpy and phen) by spectroscopic techniques.

The convenient synthetic routes used for the preparation of $[Ru(azpy)_2L]^{2+}$ complexes are shown in equation (3)

$$ctc\text{-}[Ru^{II}(azpy)_2Cl_2] \ + \ L \ \xrightarrow[\text{EtOH:H}_2\text{O (3:1)}]{\text{AgNO}_3,\ \text{reflux}} \ [Ru^{II}(azpy)_2L]^{2+} + AgCl \quad (3)$$

The reaction of the ctc-$[Ru(azpy)_2Cl_2]$ complex, L = azpy, azpym, bpy and phen ligands and AgNO$_3$ were refluxed in EtOH:H$_2$O mixture to produce the complexes of $[Ru^{II}(azpy)_2L]^{2+}$. Then, the $[Ru^{II}(azpy)_2L]^{2+}$ complexes were precipitated by NH$_4$PF$_6$ and NH$_4$BF$_4$.

In this work, these complexes were identified by spectroscopic studies : FAB mass spectrometry, UV-visible absorption spectroscopy, Infrared spectroscopy, and NMR spectroscopy and the structures of $[Ru(azpy)_2L]^{2+}$ (L = azpy, bpy and phen) were determined by X-ray crystallography.

4.1 FAB mass spectrometry

The FAB mass spectra of $[Ru(azpy)_3](PF_6)_2$, $[Ru(azpy)_2azpym](PF_6)_2$ and $[Ru(azpy)_2bpy](PF_6)_2$ showed the most intense peak at m/z 651, 652 and 624 which confirmed the molecular weight of $[Ru(azpy)_3]^{2-}$ (100%), $[Ru(azpy)_2azpym]^{2+}$(100%), and $[Ru(azpy)_2bpy]^{2+}$(100%), respectively. The two hexafluorophosphate ions which were counter ion easily lost from the complexes. In the case of the $[Ru(azpy)_2phen]$ $(BF_4)_2$ complex, the maximum molecular peak was observed at m/z 648 corresponding to the molecular ion $[Ru(azpy)_2phen]^{2+}$ (100%), resulting from losing of two tetrafluoroborate ions from the molecule.

4.2 Infrared spectroscopy

Infrared spectroscopy was sensitive to the presence of chemical functional group in a sample. All of ligands and complexes were carried out in the range of 4000-370 cm^{-1}. Each $[Ru(azpy)_2L]^{2+}$ complexes showed many vibrations of different intensities below 1600 cm^{-1}. The important functional groups in these complexes were C=N, C=C and N=N stretching modes.

In free azpy, there were bands at 790, 738 and 688 cm^{-1}. These bands together indicated the existence of a mono-substituted benzene ring.

In free azpym, the best indication for the presence of a benzene ring in this molecule was the out-of-plane C-H bending at 816, 766 and 690 cm^{-1}. These bands also established the benzene ring as being mono-substituted.

The N=N stretching frequency in free azpy occurred at 1421 cm^{-1} and free azpym appeared at 1393 cm^{-1}. The N=N stretching frequencies of azpym occurred at lower energies than azpy ligand.

The results of N=N(azo) stretching vibration frequencies of ligands and complexes are shown in Table 33. The very broad structureless band was observed at 1084 and 847 cm^{-1}. It was due to the present of BF_4^- and PF_6^- salts, respectively.

Table 33 The N=N (azo) stretching vibration frequencies of ligands and complexes

Compound	$V_{N=N}$, cm^{-1}
azpy	1421
azpym	1393
α-[Ru(azpy)$_2$Cl$_2$]	1322
[Ru(azpy)$_3$](PF$_6$)$_2$	1360
[Ru(azpy)$_2$azpym](PF$_6$)$_2$	1358
[Ru(azpy)$_2$bpy](PF$_6$)$_2$	1351
[Ru(azpy)$_2$phen](BF$_4$)$_2$	1354

The ability of azpy and azpym as a strong π-acceptor towards electron rich metal center was well documented. The diagnostic test for this interaction was the shift of V(N=N) to lower frequencies than in free ligands compared to its complex. It was due to the strong $d\pi$(Ru^{II})$\rightarrow\pi$*(L) back bonding.

In the precursor complex, *ctc*-Ru(azpy)$_2$Cl$_2$, the N=N stretching frequencies appeared at 1322 cm^{-1} which lower energies than of mixed ligand complexes, [Ru(azpy)$_2$ L]$^{2+}$. Besides, [Ru(azpy)$_3$](PF$_6$)$_2$ and [Ru(azpy)$_2$azpym](PF$_6$)$_2$ complexes contained higher azo stretching frequencies than those of the [Ru(azpy)$_2$bpy](PF$_6$)$_2$ and [Ru(azpy)$_2$phen](BF$_4$)$_2$ complexes. These may be due to better π-acceptor properties of azpy and azpym than bpy and phen. It resulted in less π-back-donation to the azo function.

4.3 UV-Visible absorption spectroscopy

The electronic spectra of complexes solutions were recorded in various solvents in the UV-Visible region (200-800 nm).

The electronic spectra of the azpy, azpym, bpy and phen ligands were studied as well. Only azpy and azpym were colored. Free azpy displayed absorption bands in acetonitrile solution at ~ 314 nm ($\varepsilon \approx$ 15000 M^{-1}cm^{-1}) and at ~ 442 nm ($\varepsilon \approx$ 600 M^{-1}cm^{-1}) these were respective assigned to $\pi \longrightarrow \pi^*$ and n $\longrightarrow \pi^*$ transitions. The absorption spectrum of azpym ligand was similar to azpy ligand which the bands occurred at ~ 299 nm ($\varepsilon \approx$ 16000 M^{-1}cm^{-1}) and at ~ 446 nm ($\varepsilon \approx$ 600 M^{-1}cm^{-1}) these were attributed to $\pi \longrightarrow \pi^*$, n$\longrightarrow \pi^*$ transitions, respectively. The bpy and phen ligands had only two $\pi \longrightarrow \pi^*$ transitions in the UV region.

The spectra of all the [Ru(azpy)$_2$L]$^{2+}$ complexes in the ultraviolet region were dominated by the two intense bands of the ligands. In visible region, all the complexes exhibited one transition near 500 nm. On the basis of their high intensities this band

was assinged to charge-transfer in nature. The spectral data are summarized in Table 34 in the case of using acetonitrile as the solvent solvent.

Table 34 The lowest energies of MLCT absorption bands of complexes in

acetonitrile

Complexes	λ_{max} nm, $(\varepsilon \times 10^{-4} M^{-1}cm^{-1})$
α-[Ru(azpy)$_2$Cl$_2$]	584 (1.2)
[Ru(azpy)$_3$](PF$_6$)$_2$	494 (1.3)
[Ru(azpy)$_2$azpym](PF$_6$)$_2$	487 (1.2)
[Ru(azpy)$_2$bpy](PF$_6$)$_2$	517 (1.1)
[Ru(azpy)$_2$phen](BF$_4$)$_2$	516 (1.1)

Results from the Table 34 showed that all the complexes appeared to be typical charge-transfer (CT) spectra with high values of the molar extinction coefficients of the lowest energy band $(10^4 M^{-1}cm^{-1})$. The absorption spectra of azpy, azpym, bpy and phen complexes showed intense bands at λ_{max} 494, 487, 517 and 516 nm, respectively. The MLCT bands for the complexes of [Ru(azpy)$_2$bpy](PF$_6$)$_2$ and [Ru (azpy)$_2$phen](BF$_4$)$_2$ were rather in the low energies value compared with those for the [Ru(azpy)$_3$](PF$_6$)$_2$ and [Ru(azpy)$_2$azpym](PF$_6$)$_2$ complexes. Owing to the azpy and azpym ligands were good π-acceptor ligand, back-bonding from Ru(II) to azpy or azpym results in stabilization of the dπ levels relative to π*(bpy, phen) and an increase in the MLCT band energy. A decrease in MLCT band energy (in bpy and phen complexes) was observed when ligand was a relatively good π-donor ligand (Sullivan and Salmon, 1979).

4.4 Nuclear Magnetic Resonance spectroscopy

^{1}H-NMR spectroscopy

The NMR spectrum of complexes were recorded in acetone-d_6 solvent. The chemical shifts of azpy in complexes are listed in Table 35.

The signal of proton H6 in azpy ligand occurred at the lowest field, because proton H6 located next to nitrogen atom on pyridine ring. The proton signal at 9.03 ppm in ^{1}H NMR spectrum of free azpym was assigned to proton H4 and H6 which were equivalent proton. These protons were appeared at the lowest field because it located next to nitrogen atoms on pyrimidine ring.

In the Ru(azpy)$_2$Cl$_2$ complex, the $tcc(\gamma)$ and $ctc(\alpha)$-isomers showed one set of azpy ligands, indicating that two equivalent azpy ligands. The ^{1}H NMR and ^{13}C NMR in six positions occurred at the lowest field caused by the influence of nitrogen atom on pyridine ring. In the ccc (β)-isomer, two azpy ligands were not equivalent then the ^{1}H NMR and ^{13}C NMR signals of each azpy displayed differently. The chemical shifts in the α-Ru(azpy)$_2$Cl$_2$ complexes shifted to lower field than free azpy.

The ^{1}H NMR spectrum of the [Ru(azpy)$_2$L]$^{2+}$ complexes, where L = bpy and phen, in acetone-d_6 displayed only one set of ligand peaks which was due to the symmetry induced equivalent nature of each half of the molecule. Whereas, the structure of azpy and azpym complexes were not a symmetric molecule. The Table 35 shows chemical shifts of azpy in the [Ru(azpy)$_2$L]$^{2+}$ complexes and Figure 85 shows molecular structure of complexes.
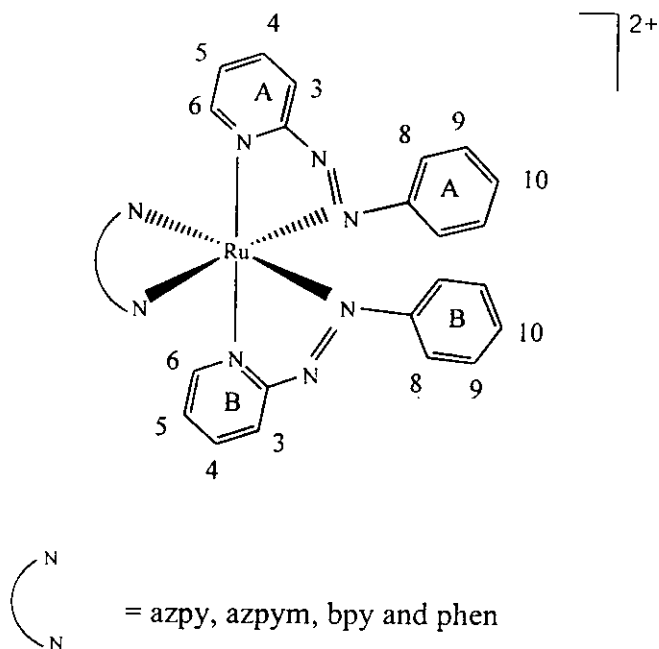
Figure 81 The molecular structure of $[Ru(azpy)_2L]^{2+}$ complex

From Figure 81, the pyridine ring A of one azpy ligand was trans to pyridine ring B of another azpy. If the third ligand had symmetry (bpy and phen) the molecule could be symmetric and the signals of azpy would show only one set. Table 35 shows the proton chemical shifts of azpy in $[Ru(azpy)_2L]^{2+}$ in acetone-d_6.

The proton on pyridine ring appeared at lower field than phenyl ring, due to the electron withdrawing, N atom on pyridine. All the complexes of $[Ru(azpy)_2L]^{2+}$ showed signal of proton H3 in azpy ligand at lower field than other protons. This may be dued to the proton H3 having less electron density an than other positions. These assignments were made on the basis of ^{1}H-^{1}H COSY NMR spectra.

The $[Ru(azpy)_3]^{2+}$ complexes showed the signals of proton which were not equivalent. Three azpy ligands in this complex exhibited three set of peaks proton. One

pyridine ring among three azpy ligands in complexes was occurred at low field. Owing to this pyridine ring was trans to electron withdrawing group, azo(N=N).

Table 35 ^{1}H NMR chemical shift azpy in $[Ru(azpy)_2L]^{2+}$ in acetone-d_6

Compound	δ (ppm) of azpy in $[Ru(azpy)_2L]^{2+}$						
	pyridine ring				phenyl ring		
	H3	H4	H5	H6	H8	H9	H10
Free azpy	7.80	8.06	7.57	8.76	8.04	7.64	7.64
ctc-Ru(azpy)$_2$Cl$_2$	8.61	8.22	7.77	9.37	6.93	7.23	7.36
$[Ru(azpy)_3]^{2+}$	9.28	8.70	7.99	8.81	7.34	7.54	7.56
	8.75	8.56	7.99	8.36	7.37	7.45	7.60
	8.71	8.45	7.92	8.63	7.02	7.31	7.52
$[Ru(azpy)_2azpym]^{2+}$	9.31	8.71	8.06	8.86	7.42	7.53	7.63
	8.78	8.58	8.01	8.40	7.02	7.35	7.56
azpym ligand	-	9.52	8.03	8.62	7.00	7.29	7.52
$[Ru(azpy)_2bpy]^{2+}$	8.99	8.43	7.84	8.41	7.37	7.42	7.58
$[Ru(azpy)_2phen]^{2+}$	8.83	8.36	7.65	8.16	7.43	7.46	7.60

The complex of $[Ru(azpy)_2azpym]^{2+}$ was similar to azpy complex but proton on pyrimidine, the third ligand (azpym), occurred at 9.52 (H4) which was downfield than proton H3 on pyridine. Because the fact that pyrimidine contained two nitrogen atoms in the ring which gave electron to metal center better than pyridine ring.

The NMR spectrum of $[Ru(azpy)_2bpy]^{2+}$ complex in acetone-d_6 displayed only one set of ligand peaks which was due to the symmetry of the molecule. The signals of pyridine ring in complex appeared only two pyridine rings (one from bpy and another one from azpy). The pyridine ring from bpy ligand occurred at lower field than pyridine ring from azpy ligand. Owing to pyridine ring from bpy was trans to electron withdrawing group, azo (N=N).

In the same way, the NMR spectrum of $[Ru(azpy)_2phen]^{2+}$ complex was similar to $[Ru(azpy)_2bpy]^{2+}$ complex. The pyridine signals of azpy showed upfield than phen ligand which was trans to electron withdrawing group, azo (N=N).

^{13}C NMR spectroscopy

The ^{13}C NMR data of the compound in acetone-d_6 were summarized in Table 22 to 25. The number of carbon atoms in each complex corresponds to the formula structure which assigned from ^{1}H-^{13}C HMQC spectra. The chemical shifts were downfield from the free ligand position. In contrast to ^{1}H NMR spectra, there was little evidence of through-space shielding effects in operation. The free azpy displayed 7 resonance signals in aromatic region. In the precursor complex, ctc-Ru(azpy)$_2$Cl$_2$, displayed distinct seven peaks corresponding to one ligand azpy. It was due to the symmetry of the molecule. It was similar to $[Ru(azpy)_2L]^{2+}$ complexes, where L= bpy and phen, but the $[Ru(azpy)_3]^{2+}$ and $[Ru(azpy)_2azpym]^{2+}$ complexes were not equivalent. The ^{13}C NMR signals of those complexes showed the aromatic region (δ 110-165 ppm) corresponding to three azpy and two azpy, one azpym.

4.5 Cyclic voltammetry

The electochemical behavior of the ruthenium complexes was studied in the acetonitrile solution by cyclic voltammetry. The electrolyte was tetrabutylammonium hexafluorophosphate (TBAH). Ferrocene were used as internal standard.

4.5.1 Reduction range

The reduction potential displayed the electron accepting ability of ligand. The more positive potential was the greater electron accepting ability. Recently, Goswami and co-worker reported that the free 2-(phenylazo)pyridine ligand displayed two quasi-reversible couples in the reduction potential region. Results from differential pulse voltammograms showed that azpy accepted two electrons in its lowest unoccupied molecular orbital (LUMO) which was primary azo in character (Goswami, *et al.*, 1983). In this work, the reduction potential of azpy and azpym ligands showed cathodic peak which became clearly couples at higher scan rate (200-1000 mV/s). It was assigned to the azo function, -N=N-.

The negative potential values of azpy and azpym were compared and showed that azpym (E_{pc} = -1.47 V) could accept the electron better than azpy (E_{pc} = -1.62 V). The precursor complex, *ctc*-Ru(azpy)$_2$Cl$_2$, gave two quasi-reversible at $E_{1/2}$ = -0.94 (ΔE_p= 64 V) and $E_{1/2}$ = -1.79 (ΔE_p= 185 V). In addition, the result from this range showed one cathodic peak. This potential may be due to reductions of azoimine function in azpy ligands.

The cyclic voltammetric data of [Ru(azpy)$_2$L]$^{2+}$ complexes (L = azpy, azpym, bpy and phen) are listed in Table 36.

Table 36 Reduction potential data of $[Ru(azpy)_2L]^{2+}$ in 0.1 M TBAH acetonitrile at
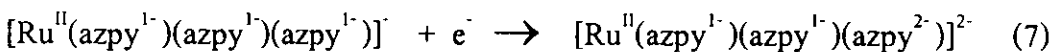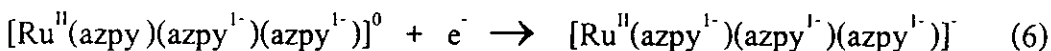
scan rate 50 mV/s (ferrocene as an internal standard)

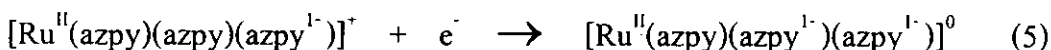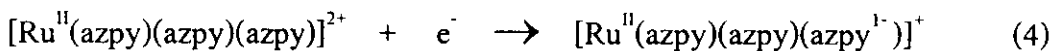| Complex	$E_{1/2}$, V (ligand reduction)				
	I	II	III	IV	V
α-Ru(azpy)$_2$Cl$_2$	-0.78	-1.04[a]	-1.79	-	-
$[Ru(azpy)_3]^{2+}$	-0.39	-0.70	-1.14	-1.78	-1.98
$[Ru(azpy)_2azpym]^{2+}$	-0.29	-0.67	-1.14	-1.71	-1.96
$[Ru(azpy)_2bpy]^{2+}$	-0.55	-1.03	-1.80	-2.17	-
$[Ru(azpy)_2phen]^{2+}$	-0.51	-1.10	-1.79	-2.15	-

[a]cathodic peak
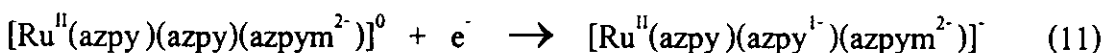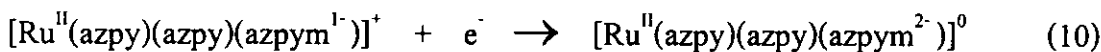
The cyclic voltammogram of $[Ru(azpy)_2L]^{2+}$ complexes displayed reductions couple at the negative side. These were assigned to the reductions of coordinate azo (-N=N-) groups. The N=N function in the azopyridine and azopyrimidine ligands were known to be a potential electron transfer center and could accept a maximun of two electrons. Polypyridyl ligands were also capable of accepting electrons. However, it was well documented in literature that the azopyridine ligands were better π-acceptor and under went easier reductions than those of the polypyridyl ligands (Krause and Krause, 1980). Then, the six successive one-electron azo reductions were expected in the $[Ru(azpy)_2L]^{2+}$ complexes.

Since three of such kind of -N=N- groups were presented in the $[Ru(azpy)_3]^{2+}$ complex and LUMO was primarity dominated by the -N=N- function, six successive

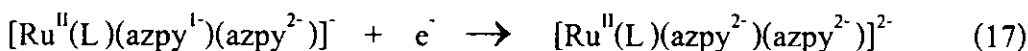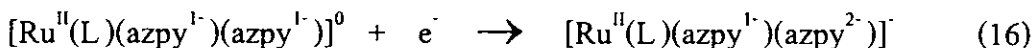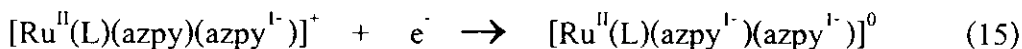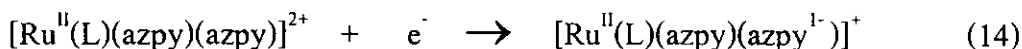one-electron azo reductions were expected. However, in this work five -N=N- reductions (near –0.39, -0.70, -1.14, -1.78 and –1.98, respectively) have been detected within the specified potential range. The reductions were actually observed in careful cyclic voltammetric experiments, equations (4) – (8).

$$[Ru^{II}(azpy)(azpy)(azpy)]^{2+} \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy)(azpy)(azpy^{1-})]^+ \qquad (4)$$

$$[Ru^{II}(azpy)(azpy)(azpy^{1-})]^+ \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy)(azpy^{1-})(azpy^{1-})]^0 \qquad (5)$$

$$[Ru^{II}(azpy)(azpy^{1-})(azpy^{1-})]^0 \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy^{1-})(azpy^{1-})(azpy^{1-})]^- \qquad (6)$$

$$[Ru^{II}(azpy^{1-})(azpy^{1-})(azpy^{1-})]^- \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy^{1-})(azpy^{1-})(azpy^{2-})]^{2-} \qquad (7)$$

$$[Ru^{II}(azpy^{1-})(azpy^{1-})(azpy^{2-})]^{2-} \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy^{1-})(azpy^{2-})(azpy^{2-})]^{3-} \qquad (8)$$

Another one expected reduction was not observed, presumably due to solvent cut off. Similar -N=N- reduction for $[Ru(azpy)_2azpym]^{2+}$ have been observed. The reductions were actually observed in experiments, equations (9) – (13).

$$[Ru^{II}(azpy)(azpy)(azpym)]^{2+} \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy)(azpy)(azpym^{1-})]^+ \qquad (9)$$

$$[Ru^{II}(azpy)(azpy)(azpym^{1-})]^+ \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy)(azpy)(azpym^{2-})]^0 \qquad (10)$$

$$[Ru^{II}(azpy)(azpy)(azpym^{2-})]^0 \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy)(azpy^{1-})(azpym^{2-})]^- \qquad (11)$$

$$[Ru^{II}(azpy)(azpy^{1-})(azpym^{2-})]^- \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy^{1-})(azpy^{1-})(azpym^{2-})]^{2-} \qquad (12)$$

$$[Ru^{II}(azpy^{1-})(azpy^{1-})(azpym^{2-})]^{2-} \;+\; e^- \;\longrightarrow\; [Ru^{II}(azpy^{1-})(azpy^{2-})(azpym^{2-})]^{3-} \qquad (13)$$
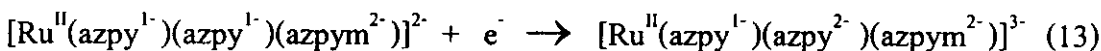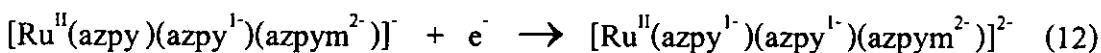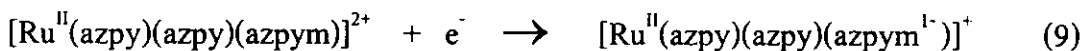
From cyclic voltammetric data, in the case of the bpy and phen (L) complexes only four reductions were observed with one electron transfer in each equation (14)-(17).

$$[Ru^{II}(L)(azpy)(azpy)]^{2+} \ + \ e^{-} \ \longrightarrow \ [Ru^{II}(L)(azpy)(azpy^{I-})]^{+} \qquad (14)$$

$$[Ru^{II}(L)(azpy)(azpy^{I-})]^{+} \ + \ e^{-} \ \longrightarrow \ [Ru^{II}(L)(azpy^{I-})(azpy^{I-})]^{0} \qquad (15)$$

$$[Ru^{II}(L)(azpy^{I-})(azpy^{I-})]^{0} \ + \ e^{-} \ \longrightarrow \ [Ru^{II}(L)(azpy^{I-})(azpy^{2-})]^{-} \qquad (16)$$

$$[Ru^{II}(L)(azpy^{I-})(azpy^{2-})]^{-} \ + \ e^{-} \ \longrightarrow \ [Ru^{II}(L)(azpy^{2-})(azpy^{2-})]^{2-} \qquad (17)$$

For bpy and phen complexes, five and six reduction couples were not observed in the window. These couples were attributed to the bpy and phen ligands, respectively. The reduction potential values of $[Ru(azpy)_2L]^{2+}$ complexes were compared and azpym ligand was the best π-acceptor among these ligands. Therefore, the $[Ru(azpy)_2azpym]^{2+}$ complex could accept electron better than $[Ru(azpy)_3]^{2+}$ and $[Ru(azpy)_2bpy]^{2+} \approx [Ru(azpy)_2phen]^{2+}$, respectively. This was in accorded with the π-acidity order of the ligands: bipyridine < azopyridine < azopyrimidine (Santra, *et al.*, 1999)

4.5.2 Oxidation range

The cyclic voltammogram of complexes displayed metal oxidation in oxidation range. The $[Ru(azpy)_2L]^{2+}$ complexes and precursor complex, $Ru(azpy)_2Cl_2$, were studied in the range of 0.0-1.0 V. The $Ru(azpy)_2Cl_2$ complex was found to be quasi-reversible. The $E_{1/2}$ potential of $Ru(azpy)_2Cl_2$ was +0.73(88) V.

In the $[Ru(azpy)_2L]^{2+}$ complexes the couple of Ru(II/III) in this range were not observed because the redox of Ru(II/III) was too positive to be observed within solvent window.

4.6 X-ray diffractometer

There were three complexes, [Ru(azpy)$_3$](PF$_6$)$_2$, [Ru(azpy)$_2$phen](BF$_4$)$_2$ and [Ru(azpy)$_2$bpy](PF$_6$)$_2$, which their single crystals were suitable for X-ray diffraction studied. Table 27, 29 and 31 show importance distances of those complexes.

4.6.1 [Ru(azpy)$_3$](PF$_6$)$_2$

A view of the cationic part of [Ru(azpy)$_3$](PF$_6$)$_2$ complexes was shown in Figure 78. The complex of [Ru(azpy)$_3$](PF$_6$)$_2$ was crystallized from methanol. The ruthenium of this complex was six-coordinated. The crystal of this complex showed two isomers, Δ-[Ru(azpy)$_3$](PF$_6$)$_2$ and Λ-[Ru(azpy)$_3$](PF$_6$)$_2$. The coordination sphere around ruthenium of both isomers were approximately octahedral involving the three azpy ligands in meridional geometry.

In Figure 78, the Ru(1) and Ru(2) metal centers were Δ-[Ru(azpy)$_3$](PF$_6$)$_2$ and Λ-[Ru(azpy)$_3$](PF$_6$)$_2$, respectively. Results from table 27 indicated that in the Δ-[Ru (azpy)$_3$](PF$_6$)$_2$, the three atomic groups Ru(1), N(7), C(27), N(8), N(9); Ru(1), N(6), N(5), C(16), N(4) and Ru(1), N(1) C(5), N(2), N(3) separately constitute three chelate planes. The structure consisting of three chelate rings of azoimine group had experienced heavy perturbation and was responsible for deviation from octahedral geometry. The planes were mutually orthogonal (dihedral angle 73-76°). The N(9)-Ru (1)-N(4), N(7)-Ru(1)-N(1) and N(6)-Ru(1)-N(3) angle were 169.6(3), 170.7(3) and 169.8(3) $^\circ$, respectively. The angles were deviated from trans-angular value (180°). The Ru(1)-N(azo) bond length (average, 2.050(8) Å) was shorter than the Ru-N (pyridine) (average, 2.081(8) Å) bond distance by 0.031 Å.

The average N-N distances of azoimine function were longer than free azpy ligand (N=N 1.248(2) Å, Panneerselvam *et al.*, 2000). In the same way, the Ru(1)-N (azo) distaances N(9)-Ru(1)-N(4), (2.025(8), 2.051(8) and 2.050 Å) of the Λ-isomer were slightly shorter than the Ru-N(py) distances (2.039(8), 2.056(8), 2.063(8) Å). The N-N distances of 1.301(11), 1.308(12), 1.249(11) Å were shorter than free azpy ligand. The shortness of Ru-N bond and longness of N-N in this complex was attributed to strong $d\pi$-$p\pi$ interactions between ruthenium (t_2) and the low-lying π^*(azo) orbitals of azpy.

4.6.2 [Ru(azpy)$_2$bpy](PF$_6$)$_2$

A view of single cryatal of [Ru(azpy)$_2$bpy](PF$_6$)$_2$ complexes was shown in Figure 79. The complex of [Ru(azpy)$_2$bpy](PF$_6$)$_2$ was crystallized from methanol. The ruthenium ion of this complex was six-coordinated. The coordination geometry of ruthenium(II) was distorted octahedral with coordinating from two N-donor centres of bpy and four N-donor centres of two azpy unit. The pyridine rings of azpy were trans position and the two pyridine rings of bpy ligand were trans to azo of azpy ligand. From table 29, the trans-angles around the ruthenium center in the plane ranged from 171.3(2) to 175.9(2)° indicating distortions from the rectilinear geometry. The chelate angles extended by two azpy and one bpy were 76.1(2), 75.9(2) and 77.9(2)°, respectively. Two chelate plane of azpy were deviated from orthogonality (dihedral angles was 101.32 (0.19) °) possibly due to steric interaction.

The Ru-N(azo) (2.003(5), 2.036(5) Å) distances were shorter than Ru-N (pyridine) of azpy (2.039(6), 2.047(5) Å). The shortening may be due to greater π-backbonding, $d\pi$(Ru)$\longrightarrow$$\pi^*$(azo). In this complex the N-N distances of azpy were 1.272(7) and 1.269(8) Å which were slightly longer than those of free azpy (N=N

1.248(2) Å, Panneerselvam *et al.*, 2000). The coordination could lead to a decrease in the N-N bond order due to σ-donor and π-acceptor character of the ligands. The Ru-N (pyridine) of bpy was 2.082(5) and 2.090(5) Å which longer than Ru-N(pyridine) distances in azpy. Owing to pyridine rings of bpy was trans to azo function of azpy.

4.6.3 [Ru(azpy)$_2$phen](BF$_4$)$_2$

The crystal structure of [Ru(azpy)$_2$phen](BF$_4$)$_2$ complex was shown in Figure 80. The ruthenium center was surrounded by a distorted octahedral coordination environment of two azpy and one phen ligands. Therefore chelate planes were constituted by two azpy and one phen ligand. From table 32, the two azpy ligand were coordinated to ruthenium with a bite angle of 76.3(2) and 76.1(2)°, respectively. The angle N(1)-R(1)-N(2) was also small well values of 78.7(2)°.The two azo nitrogen atoms of the azpy approach the metal center more colsely (Ru-N(5)/(8), 2.014(60) and 2.021(5) respectively) than four Ru-N bonds.

The Ru-N(azo) (2.014(6), 2.021(5) Å) distances were slightly shorter than Ru-N(pyridine) of azpy (2.050(6), 2.054(6) Å). The shortening may be due to π-back bonding in dπ(Ru)→π*(azo). The N-N distances of both azpy were 1.284(8), 1.279 (8)°. It was similar to the N-N distances in [Ru(azpy)$_2$bpy](PF$_6$)$_2$ (1.272(7), 1.269 (8)°).