

Chapter 4

DISCUSSION

The new 2,6-(diphenylazo)pyridine ligand was synthesized by coupling reaction of the 2,6-diaminopyridine with nitrosobenzene in base condition. This ligand contained two N=N (azo) groups. Moreover, it acted as both bidentate and tridentate ligand. The structure of the diazpy ligand was presented previously.

In the present work, the ruthenium complexes with diazpy were obtained. When the diazpy ligand reacted with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in EtOH solution, it gave rise to five-coordinated $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex, where the diazpy acted as a tridentate ligand. Then the $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex was starting material to synthesize the mixed complexes of ruthenium(II) with other bidentate ligands. In this experiment, the azpy, bpy and phen ligands were chosen. The results of synthesis gave the six-coordinated $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ (L = azpy, bpy and phen) complexes, where diazpy acted as a bidentate ligand.

Therefore, the interesting properties of the diazpy ligand and ruthenium(II) complexes with diazpy were studied by FAB mass spectrometry, UV-Visible absorption spectroscopy, Infrared spectroscopy, and NMR spectroscopy and the structures of the diazpy ligand and $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ complex were determined by X-ray crystallography.

4.1 FAB mass spectrometry

The FAB mass spectrometry is a basic technique to determine of molecular weight of molecule.

The parent peak of the diazpy ligand gave 100% relative abundance at m/z 288, which was molecular weight of ligand with one protonation.

The $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex showed the most intense peak at m/z 423, which was assigned to $[\text{Ru}(\text{diazpy})\text{Cl}]^+$ (100%).

In the case of $[\text{Ru}(\text{diazpy})(\text{L})_2](\text{BF}_4)_2$, fragmentation characters of complexes showed different patterns. The parent peak of $[\text{Ru}(\text{diazpy})(\text{azpy})_2](\text{BF}_4)_2$ complex gave 100% relative abundance at $m/z = 755$ corresponded to $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ ion. This caused by losing of two BF_4^- ions from molecule. Whereas, the $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2](\text{BF}_4)_2$ complexes showed intense peaks at $m/z = 788$ and 836 which gave 100% relative abundance, corresponded to dissociation of one BF_4^- ion. This method could be confirmed the formula and molecular mass of ligand and complexes as expected.

4.2 UV-Visible absorption spectroscopy

The UV-Visible absorption spectra of ligands and complexes were studied within the range 200-800 nm in various solvents. The free ligands exhibited intense absorption bands in the UV region (ϵ in the 10^3 - 10^4 $\text{M}^{-1}\text{cm}^{-1}$ range), whereas in the metal complexes exhibited intense structured absorption in the ultraviolet region and moderately intense and broad absorption band in the visible range ($\epsilon \sim 10^3$ $\text{M}^{-1}\text{cm}^{-1}$).

The electronic spectra of the diazpy, azpy, bpy and phen ligands were studied as well. Only diazpy and azpy were colored. Free diazpy displayed absorption band in CH_3CN solution at ~ 321 nm ($\epsilon \sim 28200$ $\text{M}^{-1}\text{cm}^{-1}$) and at ~ 440 nm ($\epsilon \sim 1400$ $\text{M}^{-1}\text{cm}^{-1}$) these were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The absorption spectrum of the azpy ligand was very similar to diazpy. The bands occurred at ~ 314 nm ($\epsilon \sim 15000$ $\text{M}^{-1}\text{cm}^{-1}$) and ~ 442 nm ($\epsilon \sim 600$ $\text{M}^{-1}\text{cm}^{-1}$).

These were attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The bpy and phen ligands had only two $\pi \rightarrow \pi^*$ transitions in the UV region.

The absorption spectrum of the $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex showed intense bands at ~ 287 nm ($\epsilon \sim 28000 \text{ M}^{-1}\text{cm}^{-1}$) in UV region. It was assigned to $\pi \rightarrow \pi^*$ transition of coordinated ligand. Whereas, the complex presented an intense band at 426 ($\epsilon \sim 92000 \text{ M}^{-1}\text{cm}^{-1}$) and a broad bands at ~ 522 nm ($\epsilon \sim 2600 \text{ M}^{-1}\text{cm}^{-1}$) and ~ 610 nm ($\epsilon \sim 1600 \text{ M}^{-1}\text{cm}^{-1}$) in the visible region. They were assigned to a metal-to-ligand charge transfer (MLCT) process.

The spectra of all $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes in UV region were dominated by the two intense bands of the ligands. In visible region, all complexes exhibited one transition. On the basis of their high intensities this band was assigned to charge transfer nature. The spectral data in UV region are summarized in Table 31 in the case of using acetonitrile as the solvent.

Table 31 The lowest energies of MLCT absorption bands of complexes in CH_3CN solution

Complexes	λ_{max} nm, ($\epsilon^a \times 10^{-4} \text{ M}^{-1}\text{cm}^{-1}$)
$[\text{Ru}(\text{diazpy})\text{Cl}_2]$	610 (0.16)
$[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$	491 (0.8)
$[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$	502 (0.6)
$[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$	502 (0.5)

^aMolar Extinction coefficient

Results from Table 31 showed that all the complexes appeared to be charge-transfer (CT) at different absorption energies. The MLCT band for the complexes of $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ occurred at the lower energies than that of the $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex. Since, the azpy (which had N=N (azo) function) was better π -acceptor ligand than bpy and phen. Then the $d\pi$ levels of Ru (II) were stabilized and gave rise to increase the MLCT energy.

Comparison MLCT band energies between $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$, where L = azpy, bpy and phen complexes with $[\text{Ru}(\text{L})_3]^{2+}$, where L = azpy, bpy and phen complexes were shown in Table 32.

Table 32 The lowest energies of MLCT absorption bands of complexes in CH_3CN solution

Complexes	λ_{max} nm, ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)
^a $[\text{Ru}(\text{azpy})_3]^{2+}$	494 (1.3)
$[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$	491 (0.8)
^b $[\text{Ru}(\text{bpy})_3]^{2+}$	450 (1.4)
$[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$	502 (0.6)
^c $[\text{Ru}(\text{phen})_3]^{2+}$	446 (1.0)
$[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$	502 (0.5)

^a(Changsaluk, U. 2003), ^b(Tempiam, S. 2002), and ^c(Rattanawit, N. 2002)

From Table 32, the MLCT band of $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ complexes appeared at lower energies than $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$

complexes, respectively. In this case, the position of the MLCT band was related to the degree of π delocalization in ligands. As the number of ligand π system interacting with the metal center increased, the energies of $d\pi \rightarrow \pi^*$ transition changed to red shifts. The diazpy ligand, not only had more π system than bpy and phen, but also contained two N=N (azo) groups. Therefore the π^* (LUMO, lowest unoccupied molecular orbital) level of diazpy was decreased. However, the MLCT absorption wavelength of the $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex was very close to that of the $[\text{Ru}(\text{azpy})_3]^{2+}$ complex. This is may be due to both azpy and diazpy contained similar azoimine character.

4.3 Infrared spectroscopy

It is possible to use vibration spectroscopy as a probe. Infrared spectra of ligands and complexes showed the important peaks in the range $1600\text{-}400\text{ cm}^{-1}$. An aim in studying the infrared spectra were located the important functional groups such as C=N stretching, N=N stretching, C=C stretching modes.

The observed vibration frequencies of N=N stretching mode can be suggested π -accepting behavior of ligands.

The one N=N stretching mode of the azpy ligand appeared at 1421 cm^{-1} . Meanwhile, both N=N bond stretching of the diazpy ligand occurred at 1447 cm^{-1} and 1420 cm^{-1} . Different frequencies of both N=N azo modes may be due to nonplanarity of diazpy molecule. From results of X-ray structure showed different dihedral angles between the N=N (azo) with phenyl ring (1.772° and 7.748°). The stretching vibration frequency values of ligands and complexes are listed in Table 33. The broad band was observed at 1084 cm^{-1} . It was due to the present of BF_4^- salt.

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

Compound	$\nu_{\text{N=N}}, \text{cm}^{-1}$
diazpy	1447, 1420
azpy	1421
[Ru(diazpy)Cl ₂]	1246, 1229
[Ru(diazpy)(azpy) ₂](BF ₄) ₂	1432, 1365
[Ru(diazpy)(bpy) ₂](BF ₄) ₂	1410, 1341
[Ru(diazpy)(phen) ₂](BF ₄) ₂	1409, 1340

The N=N stretching mode in complexes occurred at lower frequency than that in free ligand, ca. 55-190 cm⁻¹, due to $t_{2g} \rightarrow \pi^*$ (azo) donation (π -back bonding). The bond order of N=N (azo) decreased, then vibration energies decreased.

In the precursor complex, [Ru(diazpy)(Cl)₂], the N=N stretching frequencies appeared at lower energies (1246 cm⁻¹ and 1229 cm⁻¹) than [Ru(diazpy)(L)₂](BF₄)₂ complexes. Both N=N stretching frequencies corresponded to two N=N azo of diazpy which coordinated with ruthenium metal center.

Since, diazpy acted as a bidentate ligand in the [Ru(diazpy)(L)₂](BF₄)₂ complexes by using N-pyridine and N-azo bonded with ruthenium center. Therefore, another N=N azo was free. In the case of the [Ru(diazpy)(bpy)₂](BF₄)₂ and [Ru(diazpy)(phen)₂](BF₄)₂ complexes showed the N=N stretching frequencies of coordinated N=N azo at 1341 and 1340, respectively. Whereas, the N=N stretching frequencies of free N=N azo occurred at 1410 and 1409, respectively. The coordinated N=N frequencies was shifted to lower energies than free N=N because of the strong $d\pi(\text{Ru}) \rightarrow \pi^*(\text{L})$ back bonding.

For the $[\text{Ru}(\text{diazpy})(\text{azpy})_2](\text{BF}_4)_2$ complex, the N=N stretching frequencies at 1432 cm^{-1} and 1365 cm^{-1} corresponded to these of free N=N azo and coordinated N=N azo, respectively. Moreover, the N=N stretching frequencies of $[\text{Ru}(\text{diazpy})(\text{azpy})_2](\text{BF}_4)_2$ appeared at higher energies than $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2](\text{BF}_4)_2$ complexes because of good π -acceptor ability of azpy. It resulted in less π -back donation to the azo group.

4.4 Nuclear Magnetic Resonance spectroscopy

^1H NMR spectroscopy

The ^1H NMR spectroscopic data of the diazpy and azpy ligands showed different data because diazpy was a symmetric molecule but azpy was an asymmetric molecule.

The signal of proton H6 in azpy occurred at the lowest field, because proton H6 located next to nitrogen atom on pyridine. Meanwhile, proton H4 on pyridine ring of diazpy occurred at the most downfield, this may be due to resonance effects in diazpy molecule. Moreover, the diazpy ligand showed only 5 signals (H3, H4, H7, H8 and H9) for 13 protons. This result indicated that the diazpy ligand was symmetric molecule. The molecular structures of ligands are shown in Figure 67.

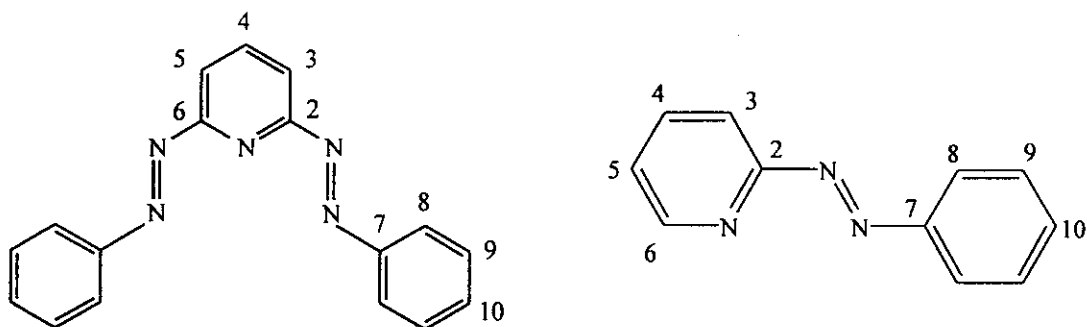


Figure 67 The molecular structures of the diazpy and azpy ligands.

The $[\text{Ru}(\text{diazpy})(\text{Cl})_2]$ showed only 5 signals for 13 protons of diazpy, where diazpy as tridentate chelating ligand (Figure 68), similar to data in the free diazpy ligand. This remarkable results indicated that the coordinated diazpy ligand remain symmetric in this complex. But, at the lowest field appeared doublet of doublet peak of proton H3 (or H5) caused by the influence of coordinated nitrogen atom on pyridine ring.

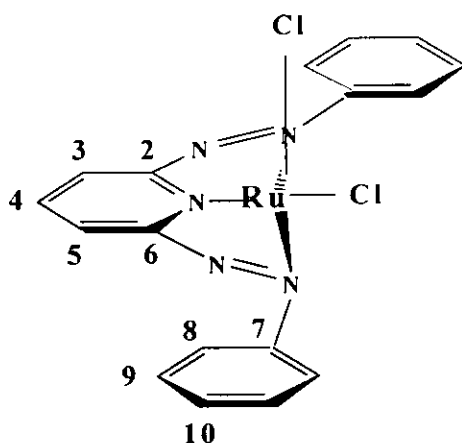


Figure 68 The molecular structure of $[\text{Ru}(\text{diazpy})(\text{Cl})_2]$.

The ^1H NMR spectra of the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes (L = azpy, bpy and phen) were measured in acetone- d_6 . Figure 69 showed bidentate acting of diazpy, which used N-pyridine and one N-azo coordinated with ruthenium center. Therefore, the ^1H signals of diazpy showed no equivalent signals. The chemical shift of diazpy in the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes are listed in Table 34.

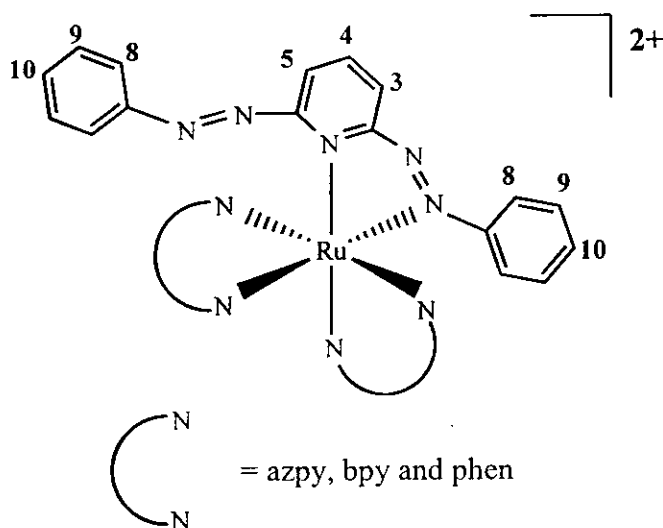


Figure 69 The molecular structures of the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes.

Table 34 ^1H NMR chemical shift diazpy in $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ in acetone- d_6

Compound	δ (ppm) of diazpy in $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$					
	Pyridine ring			Phenyl ring		
	H3	H4	H5	H8	H9	H10
Free diazpy	7.92	8.27	7.92	8.27	7.65	7.65
$[\text{Ru}(\text{diazpy})\text{Cl}_2]$	8.53	8.08	8.53	8.29	8.05	8.06
$[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$	8.87	7.95	7.38	7.68 7.57	7.57 7.48	7.34
$[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$	9.08	8.62	7.74	7.49 7.38 7.22	7.62 7.23 7.19	7.06
$[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$	9.13	8.62	7.67	6.95 6.79	7.38 6.95	7.58 7.11

In the case of the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ ($\text{L} = \text{bpy}$ and phen) complexes, signals of both L ligands in each complex showed no equivalent. This result could indicate that both complexes were not symmetric molecules. The ^1H signals of the bpy or phen ligands which was trans to coordinated $\text{N}=\text{N}$ azo of diazpy occurred at lower field than another that was trans to N -pyridine of diazpy. This is due to a strong withdrawing group of azo ($\text{N}=\text{N}$). In addition, the ^1H signals of phenyl ring (that bonded with free $\text{N}=\text{N}$) appeared at higher field than the free diazpy ligand. This may be due to difficult electron delocalization in asymmetric diazpy molecule.

The $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex also showed different signals of diazpy. From Figure 70, pyridine rings of both azpy were trans and they had similarly environment. Therefore, their ^1H signals occurred at the same position. The ^1H signals of phenyl rings C and B appeared at lower field than other phenyl rings because they were trans to $\text{N}=\text{N}$ withdrawing group. In addition, the ^1H signals of phenyl ring A appeared at higher field than that of the free diazpy ligand, because of symmetry of molecule was decreased.

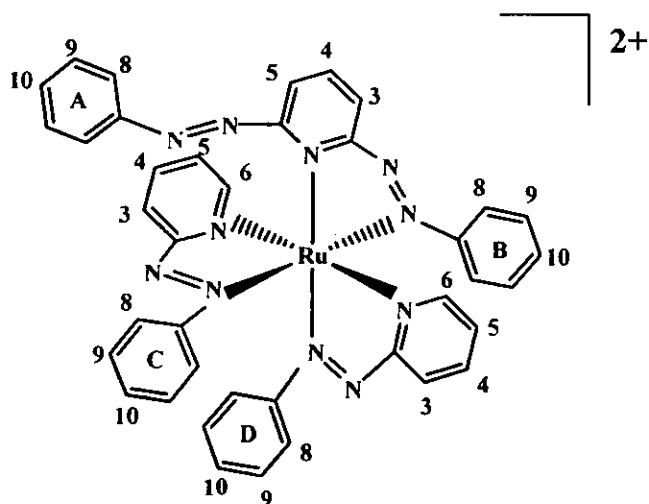


Figure 70 The molecular structure of $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex.

The proton H3 on pyridine ring of all $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes appeared at the lowest field. This owing to results of coordinated nitrogen atoms. In addition, the ^1H NMR results were supported by ^1H - ^1H COSY NMR data, which exhibited correlation of proton-proton coupling.

^{13}C NMR spectroscopy

The ^{13}C NMR data of the compounds were summarized in chapter 3. The number of carbon atoms in each ligand and complex corresponded to the formula structure, which assigned from ^1H - ^{13}C HMQC spectra. The free diazpy ligand had 17 carbon atoms in molecule but it was symmetric molecule. Therefore, signals of carbons appeared only 7 signals (2 weak signals of quaternary carbon and 5 signals of methine carbon). The ^{13}C NMR data result of the $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex displayed 7 signals similar to free diazpy ligand but each ^{13}C signal was slightly shifted to lower field than free ligand.

The ^{13}C NMR data of $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ ($\text{L} = \text{azpy}$, bpy and phen) complexes showed no equivalent ^{13}C NMR signals of the diazpy and both L ligands. Besides, also the DEPT spectral data showed only signal of methine carbon and supported ^{13}C NMR result.

4.5 Cyclic Voltammetry

The electrochemical behaviors of the free ligands and the complexes have been studied by using cyclic voltammetry (CV) in acetonitrile (0.1 M TBAH). The potential range -2.5 to $+2.0$ V was applied by using a platinum electrode. Ferrocene were used as an internal standard.

Reduction range

The electron accepting capability of ligands were considered in the reduction range. The more positive potential was the greater electron accepting ability. Research of Goswami and co-worker (1983) indicated that the free 2-(phenylazo)pyridine (azpy) ligand, displayed two quasi-reversible couples in negative potential region. It showed that the azpy ligand accepted two electrons in its lowest unoccupied molecular orbital (LUMO) which was primary azo in character.

In this work, the reduction potential of diazpy, which had two azo groups showed two irreversible cathodic peaks at scan rate 50 mV/s. Even at the higher scan rate (100-1000 mV/s), the reduction species could not give reversible oxidation. Then, the species in reduction range displayed irreversible peaks. The first cathodic peak appeared at -1.43 V more positive potential than azpy (-1.61 V). The negative potential values of diazpy and azpy were compared and showed that diazpy could be accepted electron better than azpy. This may be due to more π system of diazpy molecule.

The cyclic voltammetric data of the precursor complex, $[\text{Ru}(\text{diazpy})(\text{Cl})_2]$, gave two quasi-reversible at $E_{1/2} -0.79$ V ($\Delta E = 85$ mV) and $E_{1/2} = -1.68$ V ($\Delta E = 120$ mv). In addition, the result from this range showed one cathodic peak at -1.12 V. This potential may be due to reduction of both azo functions of the tridentate diazpy ligand.

The negative potential values of $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes (L = azpy, bpy and phen) are listed in Table 35.

Table 35 Reduction potential data of $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ 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	VI
$[\text{Ru}(\text{diazpy})\text{Cl}_2]$	-0.79	-1.12 ^a	-1.68	-	-	-
^b <i>ctc</i> - $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$	-0.94	-1.04 ^a	-1.79	-	-	-
$[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$	-0.38	-0.78	-1.22	-1.72	-1.81	-2.13
^b $[\text{Ru}(\text{azpy})_3]^{2+}$	-0.39	-0.70	-1.14	-1.78	-1.98	-
$[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$	-0.83	-0.98	-1.45	-1.62	-1.97	-2.21
^c $[\text{Ru}(\text{bpy})_3]^{2+}$	-1.74	-1.93	-2.17	-	-	-
$[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$	-0.82	-0.95 ^a	-1.42	-1.62	-1.93	-2.22
^d $[\text{Ru}(\text{phen})_3]^{2+}$	-1.72	-1.89 ^a	-	-	-	-

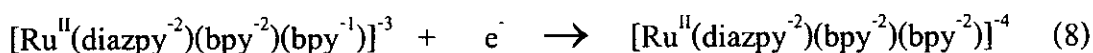
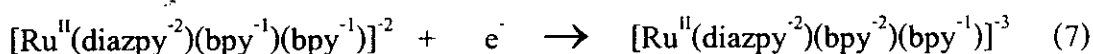
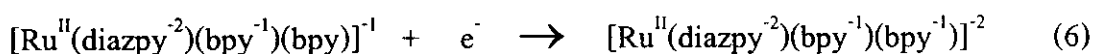
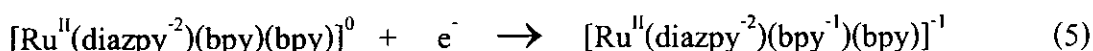
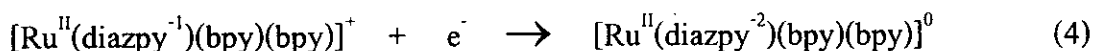
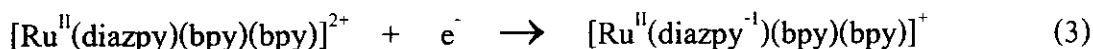
^acathodic peak, ^bChangsaluk, U. 2003., ^cTempiam, S. 2002.

^dTokel-Takvoryan, *et al.*, 1973.

The cyclic voltammogram in negative range of $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes showed reductions of all coordinate ligands within this solvent window. 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).

The cyclic voltammogram of the $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ complex displayed six electron reductions. The data from Table 35, the first and the second of these reductions occurred at more positive potentials relative to the reduction of azo function of diazpy.

While, four reversible couples were related to the reduction of both bpy with one electron transfer in each couple (Sullivan, *et al.*, 1979). The cathodic peak I was occurred from the cathodic peak II that followed the equation (3-4). The expected reduction processes are displayed in equations (3-8).

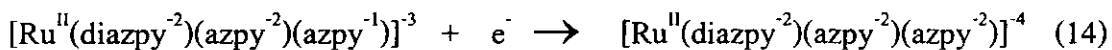
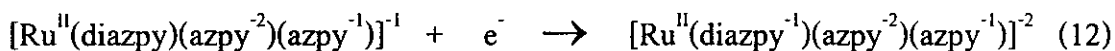
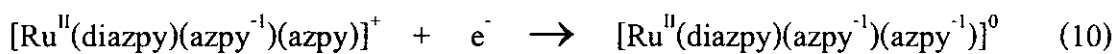
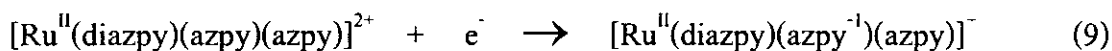


The $[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ complex also had similar reduction behavior and reduction potential values to the $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ complex (Table 33). The reduction potentials of diazpy and phen were too negative to be observed within solvent window. Moreover, the expected six electron reductions was similar to those of the $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ complex.

In comparison of the $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ complexes with the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ complexes, respectively, the first and the second reductions of the $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ complexes occurred easier than the first reduction step of the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ complexes (Table 35).

In the case of the $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex, showed four reversible couples and two cathodic peaks of diazpy (at scan rate 50 mV/s) similar to bpy and phen complexes. But the first, the second, the third and the last reversible couples at -0.38, -0.78, -1.22 and -1.72 V were related to redox processes of both azpy.

Meanwhile, the fourth and the fifth cathodic peaks were reduction potentials at -1.72 and -1.81 V of diazpy. This data indicated that azpy could accept electron better than bidentate diazpy in this complex which different from data of both free ligands. These may be due to asymmetric molecule of coordinated bidentate diazpy. Since, the azpy ligand could accept a maximum of two electrons. Therefore, the reduction process of this complex could be displayed followed equations (9-14).



In comparison with the bpy and phen complexes, the $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex showed more positive reduction potentials than those of the bpy and phen complexes. This due to azpy was better π -acceptor than bpy and phen.

Besides, comparison with $[\text{Ru}(\text{azpy})_3]^{2+}$ (Changsaluk, 2003), it was founded that both complexes, $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ and $[\text{Ru}(\text{azpy})_3]^{2+}$ had similar reduction potentials.

The negative potential values of the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes were compared and it showed that the $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ complex accepted electron better than $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+} \approx [\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ complexes. In addition, it could be concluded that the diazpy ligand was better π -acceptor than bpy and phen but less than azpy, where diazpy acting as bidentate ligand.

Oxidation range

The cyclic voltammogram of complexes displayed metal oxidation in oxidation range. The oxidation process of the $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex and $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ were studied in range of 0.0 to +2.0 V. The oxidation potentials data of all complexes were presented in Table 36.

Table 36 The oxidation potentials data of complexes in 0.1 M TBAH acetonitrile at scan rate 50 mV/s (ferrocene as an internal standard)

Complex	$E_{1/2}$, V, Ru (II/III) couple
$[\text{Ru}(\text{diazpy})\text{Cl}_2]$	+0.76
^a <i>ctc</i> - $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$	+0.73
$[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$	-
^a $[\text{Ru}(\text{azpy})_3]^{2+}$	-
$[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$	+1.31
^b $[\text{Ru}(\text{bpy})_3]^{2+}$	+0.91
$[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$	+1.28
^c $[\text{Ru}(\text{phen})_3]^{2+}$	+0.89

^aChangsaluk, U. 2003., ^bTempiam, S. 2002., and ^cRattanawit, N., 2002.

The $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ complex was found to be quasi-reversible. $E_{1/2}$ potential of $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ was +0.76 V which closed to Ru(II/III) potential of *ctc*- $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$.

In the $[\text{Ru}(\text{diazpy})(\text{bpy})_2]^{2+}$ and $[\text{Ru}(\text{diazpy})(\text{phen})_2]^{2+}$ complexes, the couple of Ru(II/III) occurred at +1.31 and +1.28 V, respectively which more positive potentials than $[\text{Ru}(\text{bpy})_3]^{2+}$ (Tempiam, 2002) and $[\text{Ru}(\text{phen})_3]^{2+}$ (Rattanawit, 2002). These results showed that diazpy could be stabilized Ru center in complexes better than bpy and phen. Whereas, $[\text{Ru}(\text{diazpy})(\text{azpy})_2]^{2+}$ were not observed because the redox of Ru(II/III) was too positive to be observed within solvent window similar to $[\text{Ru}(\text{azpy})_3]^{2+}$.

4.6 X-ray Diffractometer

X-ray crystallography is the most precise and comfortable technique for determination of actual structures. There were the diazpy ligand and the $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ complex. Their single crystals are suitable for X-ray diffraction studies.

4.6.1 2,6-(diphenylazo)pyridine (diazpy) ligand

The diazpy molecule had one nitrogen on pyridine ring and two azo moiety. The nitrogen atoms were acted as the donor atoms to metal ions. The one N=N azo bond distance was 1.246 Å which was longer than another N=N, 1.240 Å. This indicated that they had different N=N bond order which correspond to difference of both N=N stretching frequencies. These results were due to delocalization of electrons in planarity diazpy molecule. It was confirmed by considering dihedral angle. The regulation planes in diazpy molecule are shown in Figure 71.

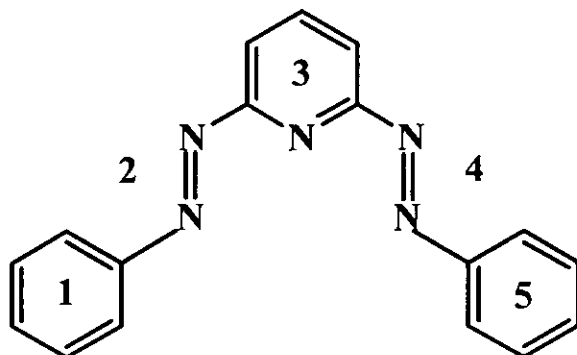


Figure 71 The regulation planes in diazpy molecule.

The dihedral angle between plane1 - plane2 = 1.772° , plane2 - plane3 = 5.325° , plane3 - plane4 = 6.576° , plane4 - plane5 = 7.748° , then the diazpy ligand had nearly complete planarity molecule.

In addition, the diazpy molecule showed the both phenyl rings were *trans* with pyridine ring, the C1A-N1A-N2A-C7A torsion angle was 178.14° and the C11A-N4A-N5A-C12A torsion angle was 179.62° (Figure 29).

4.6.2 [Ru(diazpy)(bpy)₂](BF₄)₂

The asymmetric structure of the [Ru(diazpy)(bpy)₂](BF₄)₂ complex was six-coordinated. The coordination geometry of ruthenium(II) was distorted octahedral with coordinating from four N-donor centers of two bpy units and two N-donor of diazpy. It showed that diazpy acted as a bidentate chelating ligand. The pyridine ring of diazpy trans to two pyridine ring of bpy and N=N azo of diazpy trans to two pyridine ring of another bpy. The chelate angle extended by two bpy and one diazpy were $79.7(4)^\circ$, $77.6(4)^\circ$ and $79.4(4)^\circ$, respectively. The N(1A)-Ru(1A)-N(7A), N(2A)-Ru(1A)-N(4A) and N(3A)-Ru(1A)-N(5A) angle were $169.6(4)^\circ$, $167.0(3)^\circ$ and $174.4(4)^\circ$, respectively. The angles were deviated from trans-angular value (180°).

The Ru-N(azo) (1.910(11) Å) distance was shorter than Ru-N(pyridine) of diazpy (2.060(10) Å). The shortening may be due to greater π -back bonding, $d\pi(\text{Ru}) \rightarrow \pi^*(\text{azo})$. The N=N distance in coordinated diazpy was longer (1.362(11) Å) than free N=N (1.287(13) Å) and also both N=N of free diazpy (1.246(2) Å and 1.240(2) Å). It corresponded to the IR data, the N=N stretching mode of diazpy complex (1341 cm^{-1}) appeared at lower frequencies than free N=N (1410 cm^{-1}) and free diazpy (1447 and 1420 cm^{-1}).

The Ru(1A)-N(3A) (pyridine) distances (1.422(3) Å) of bpy which trans to N=N azo of diazpy was shorter than other Ru-N pyridine (2.109(9) Å, 2.081(8) Å and (2.092(9) Å) because strong electron withdrawing of N=N azo function.