Chapter 4

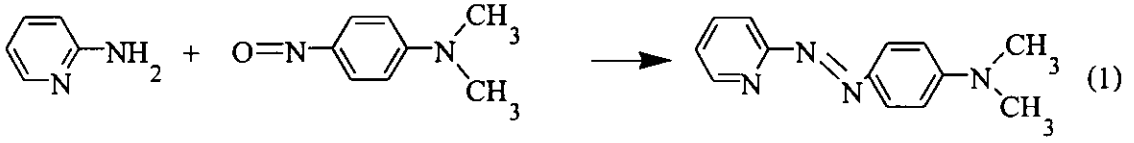
DISCUSSION

Complexes of ruthenium (II) with polypyridine ligands, such as 2,2': 6',2"-terpyridine (tpy) and bidentate ligands have been extensively studied. Thorp and co-workers have demonstrated that the oxoruthenium (IV) complex, $[Ru^{IV}(tpy)(bpy)O]^{2+}$ (bpy = 2,2'-bipyridine), is an efficient DNA cleavage reagent (Gupta, *et al.*, 1993).

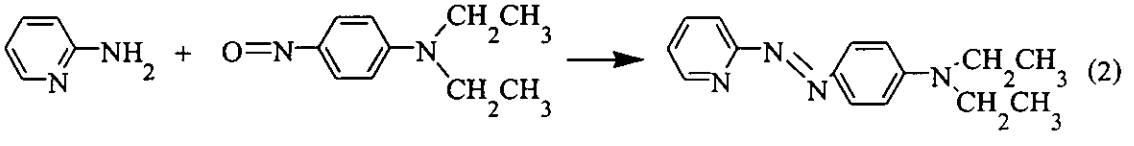
The interesting properties of the $[Ru^{IV}(tpy)(bpy)X]^{n+}$, where X are monodentate ligands, lead to synthesize ruthenium complexes with other bidentate ligands which are better π-acceptors than bpy, such as 2-(phenylazo)pyridine (azpy) (Krause and Krause, 1980). Azpy consisting of one pyridine ring with a pendent nitrogen donor atom from an azo function has been employed in the development of transition metal coordination chemistry. Due to unsymmetric N-donor sites in the azo imine function, -N=N-C=N-, isomeric complexes in ruthenium and osmium have been extensively studied (Misra, *et al.*, 1998). In the present study, 2-(4'-*N,N*-dimethylaminophenyl azo) pyridine (dmazpy) and 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy) have been chosen as bidentate ligands. Dmazpy and deazpy are the derivatives of 2-(phenylazo) pyridine (azpy). The chemistry of chloro-, nitro-, and acetonitrile- complexes of ruthenium incorporating tpy, dmazpy and deazpy ligands is reported in this work.

4.1 Preparation of ligands and complexes

The azoimine ligand, dmazpy was obtained by condensing 2-aminopyridine with *N,N*-dimethyl-4-nitrosoaniline in the presence of sodium hydroxide and toluene under refluxing conditions. In the preparation of deazpy ligand, *N,N*-diethyl-4-nitrosoaniline was used instead of *N,N*-dimethyl-4-nitrosoaniline. The reactions were followed by equation (1) and (2).



(1)



(2)

The [Ru(tpy)(L)Cl] (L = dmazpy and deazpy) complexes were synthesized by following general route shown in equation (3). It was interesting to note here that triethylamine is the probable reducing agent then ruthenium has undergone a one-electron reduction during the course of this synthetic reaction.

The role of LiCl is to prevent any possible dissociation of the coordinated chloride ion and thus to increase the yield of the desired product.

$$[Ru^{III}(tpy)Cl_3] + L + e^- \xrightarrow[EtOH,\ LiCl]{NEt_3} [Ru^{II}(tpy)(L)Cl]Cl + Cl^- \qquad (3)$$

As ligands were unsymmetrical bidentate ligands, the [Ru(tpy)(L)Cl]Cl complexes might exist in two isomeric forms, *trans* and *cis*. The *trans* and *cis* labels have been defined based on the relative position of the coordinating nitrogen on azo

group with regard to the chlorine atom. Two isomers were indeed obtained upon column chromatography of the crude products. The *trans* isomer was expected to be less polar than the *cis* isomer. Hence, the isomer that was eluted first was assigned the *trans* structure, while the isomer, which had the *cis* structure was eluted later. The *trans* isomers of [Ru(tpy)(L)Cl]Cl (L = dmazpy and deazpy) were obtained in much greater yield than the *cis* isomers (Sinha, *et al.*, 1996). Therefore, only the *trans* isomers were studied in this work.

Each ruthenium complex containing various ligands other than Cl^- was prepared by replacement of chloride with other monodentate ligands in the presence of Ag^+ as shown in equation (4), and (5) to give $[Ru(tpy)(dmazpy)NO_2]PF_6$ and $[Ru(tpy)(deazpy)NO_2]PF_6$.

$$[Ru^{II}(tpy)(L)Cl]Cl \xrightarrow[AgNO_3,\ reflux]{Acetone/H_2O} [Ru^{II}(tpy)(L)(H_2O)]^{2+} + AgCl \qquad (4)$$

$$[Ru^{II}(tpy)(L)(H_2O)]^{2+} \xrightarrow[EtOH/H_2O,\ reflux]{NaNO_2} [Ru^{II}(tpy)(L)(NO_2)]^{+} \qquad (5)$$

$$[Ru^{II}(tpy)(L)(H_2O)]^{2+} \xrightarrow[reflux]{acetonitrile} [Ru^{II}(tpy)(L)(CH_3CN)]^{2+} + [Ru^{II}(tpy)(L)(H_2O)]^{2+} \qquad (6)$$

Reaction between $[Ru(tpy)(L)(H_2O)](PF_6)_2$ (L = dmazpy and deazpy) complexes and acetonitrile under refluxing afforded a product mixture that shown in equation (6). The mixture was purified by column chromatography with acetonitrile as the eluent. The first band was $[Ru(tpy)(L)H_2O](PF_6)_2$ that did not react with acetonitrile. The second band was $[Ru(tpy)(L)CH_3CN](PF_6)_2$. The $[Ru(tpy)(L)CH_3CN](PF_6)_2$ complexes were not stable and changed to $[Ru(tpy)(L)H_2O](PF_6)_2$ when contacting

moisture. Acetonitrile might act as adduct which was replaced rapidly by water. The acetonitrile complexes were characterized by FAB mass spectrometry, UV-Visible spectroscopy, Infrared spectroscopy, and ^{1}H NMR spectroscopy.

4.2. The electrospray and the the FAB mass spectrometry

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

The parent peaks of each ligand which gives 100% relative abundance, was molecular weight of ligand with one protonation.

Fragmentation characters of complexes showed different patterns. The [Ru(tpy)(dmazpy)Cl]Cl complex showed the most intense peak at m/z 596, which was assigned to $[Ru(tpy)(dmazpy)Cl]^+$ (100%). One chlorine atom was lost from the complex. Whereas, the $[Ru(tpy)(dmazpy)Cl]PF_6$ complex gave the intense peak of deprotonated $[Ru(tpy)(dmazpy)Cl\text{-}H]^+$ species. The molecular weight of $[Ru(tpy)(dmazpy)NO_2]^+$ was 607.1 g/mol and the electrospray mass spectrum showed the parent peak at m/z 607.1. It meant that the m/z 607.1 was used to confirm the molecular weight of nitro complex. FAB mass spectrum of $[Ru(tpy)(dmazpy)CH_3CN](PF_6)_2$ exhibited the parent peaks at m/z 602 (100%) for $[Ru(tpy)(dmazpy)CH_3CN]^{2+}$.

The electrospray mass spectra of [Ru(tpy)(deazpy)Cl]Cl and [Ru(tpy)(deazpy)Cl]PF_6 complexes showed the parent peaks at m/z 624 for $[Ru(tpy)(deazpy)Cl]^+$. The $[Ru(tpy)(deazpy)NO_2]PF_6$ complex showed the most intense peak at m/z 607, which was assigned to protonated $[Ru(tpy)(deazpy)NO_2]^+$ species which lost one ethyl group from deazpy ligand. The peak at m/z 775 (60%) corresponded to $[Ru(tpy)(deazpy)CH_3CN]^+$ (PF_6) (60%), but the parent peak at m/z 608 (100%) was assigned to $[Ru(tpy)(deazpy)H_2O]^+$. From this result, it indicated that the acetonitrile ligand was replaced rapidly by water.

4.3. UV-Visible Absorption Spectroscopy

Absorption spectra of dmazpy and deazpy ligands show intense bands in visible region are assigned to be $\pi \rightarrow \pi^*$ transitions. In the case of azpy ligand, the absorption bands in visible region is assigned to be $n \rightarrow \pi^*$ transition. Because the substituents, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$ at para position are electron-donating groups, these give rise to shift of absorption band in visible region, therefore they enhance π-electron density in molecules. In addition, the substituents are high polarity auxochrome which have effect to the absorption of bonded chromophores. The most effective chromophore should be phenyl part, which leads to moderate intense color of dmazpy and deazpy ligands (Shriver, *et al.*, 1994).

The π^* orbital of azpy ligand is lower than in tpy ligand (Krause and Krause, 1980). Then, the lowest energy of each complexe is attributable to the metal-to-ligand charge transfer (MLCT) transition d (Ru) $\rightarrow \pi^*$(dmazpy, deazpy). The spectrum consists of two MLCT intense bands with different molar extinction coefficients. The maximum wavelength was the most intense band. The spectra also that posses intense $\pi \rightarrow \pi^*$ transition in UV region attributed to polypyridine ligands.

Comparison with azpy complex, the MLCT band of $[Ru(tpy)(dmazpy)Cl]PF_6$ (λ_{max} = 570 nm) and $[Ru(tpy)(deazpy)Cl]PF_6$ (λ_{max} = 582 nm) are shifted to lower energy related to $[Ru(tpy)(azpy)Cl]ClO_4$ (λ_{max} = 505 nm) (Pramanik, *et al.*, 1998). This reflects from the effect of electron donating substituents, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$, which extend π conjugation of ligands then π^* levels are reduced. Furthermore, the MLCT bands in visible region have no effect from the monodentate ligands (X = Cl^-, NO_2^- and CH_3CN).

4.4 Infrared spectroscopy

It is possible to use vibrational spectroscopy as a probe. Infrared spectra of ligands and complexes show the important peaks in the range 1600-400 cm^{-1}. The objects in studying the infrared spectra are 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. In favorable cases the detailed molecular structure can be explored, such as, Krause reported that the N=N (azo) stretching modes of azpy could be used to diagnostic of the coligand (AB) π-accepting behavior in $[Ru(azpy)_2(AB)]^{n+}$ (where AB = 2,2'-bipyridine, 4,4'-bithiazole, 1,2-diaminoethane, 2,4-pentanedioneanion and X_2 (X = NO_2^-, CN^-, Br^-, N_3^- and thiourea)), which strong π-accepting coligands gave the highest N=N(azo) stretching frequencies (Krause and Krause, 1982). There fore, N=N stretching mode can be used to determine the π-acceptor properties of ligands.

From Infrared spectroscopic data can be observed that the subsitituents group of dmazpy and deazpy effect on N=N stretching mode. Infrared spectra of dmazpy and deazpy show the N=N stretching vibration at 1402 and 1399 cm^{-1}, respectively. Meanwhile, the N=N stretching mode of azpy appears at higher frequency, 1420 cm^{-1} (Grover, *et al.*, 1992). These results indicate that the N=N bond of the free azpy ligand is stronger than those in dmazpy and deazpy ligands. The decreasing of N=N bond order in dmazpy and deazpy can be due to the substituents, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$, which are electron donating group. The electrons delocalize to the π^* orbital of azo function. This leads to decrease the N=N bond order. Then the bonding of N=N (azo) is weaker than that of azpy.

The N=N(azo) stretching mode in $[Ru(tpy)(azpy)Cl](ClO_4)_2$ complex occurs at 1310 cm^{-1}. Whereas, the N=N(azo) stretching modes in $[Ru(tpy)(dmazpy)Cl]PF_6$ and $[Ru(tpy)(deazpy)Cl]PF_6$ appear at 1294 and 1293 cm^{-1}, respectively. The azpy complex

shows the N=N stretching mode at higher energy than those in the dmazpy and deazpy complexes, because dmazpy and deazpy accept electrons both from Ru (II) center and from substituent groups. Then the N=N bond order in dmazpy and deazpy complexes are reduced. From these results, it can be indicated that azpy is stronger π-acid than dmazpy and deazpy.

The infrared spectra of ruthenium (II) complexes, [Ru(tpy)(dmazpy)X] PF_6 and [Ru(tpy)(deazpy)X]PF_6, where X = Cl^-, NO_2^-, and CH_3CN, are recorded. The N=N(azo) stretching modes in complexes occur in a spectral region ca. 1355-1294 cm^{-1}. The N=N (azo) stretching vibrations were varied with the π-acceptor ability of the X ligands, this indicates that the N=N(azo) stretching frequencies acts as a π-bonding probe.

4.4.1. Infrared Spectroscopy of [Ru(tpy)(dmazpy)Cl]PF_6

The infrared spectrum of [Ru(tpy)(dmazpy)Cl]PF_6 showed the N=N (azo) vibrational frequency at 1294 cm^{-1}, shifted from the free dmazpy ligand, because of the π-backbonding between dmazpy and ruthenium(II) center. It decreased the vibrational energy of the N=N (azo) stretching mode. Intense vibrational frequency was observed at 847 cm^{-1} due to the presence of PF_6^- salt. Then, another vibrational frequencies in this region were too complicated to be assigned.

4.4.2. Infrared Spectroscopy of [Ru(tpy)(dmazpy)NO_2]PF_6

The strong vibration observed at 1355 cm^{-1} in nitro complex was assigned to the N=N (azo) stretching frequency, shifted from the free ligand about 61 cm^{-1}. The bonding mode of the nitro ligand had two vibrational modes, NO_2 asymmetric

stretching vibrational (ν_{as} N-O) which appeared at 1380 cm^{-1} and NO_2 symmetric stretching vibrational (ν_s N-O) appeared at 1245 cm^{-1} (Dovletoglou, *et al.*, 1996). However, the nitro ligand vibrational modes were not observed clearly in this complex because they were concealed by the N=N (azo) stretching vibration.

4.4.3. Infrared Spectroscopy of $[Ru(tpy)(dmazpy)CH_3CN](PF_6)_2$

The N=N (azo) stretching vibrational frequency of acetonitrile complex was observed at 1294 cm^{-1}. The bonding mode of acetonitrile ligand is the C-N stretching ($\nu_{C\equiv N}$), at ca. 2100 cm^{-1}. It could not be detected in this complex. The broad band was observed at 3450 cm^{-1} which was assigned to O-H stretching mode. It could indicate that the acetonitrile ligand was replaced by water when the complex contacted the moisture.

4.4.4. Infrared Spectroscopy of $[Ru(tpy)(deazpy)Cl]PF_6$

Infrared spectrum $[Ru(tpy)(deazpy)Cl]PF_6$ showed the N=N (azo) vibrational frequency at 1293 cm^{-1}, shifted from free deazpy ligand, because of the π-back bonding between deazpy and ruthenium(II). It decreased the vibrational energy of the N=N (azo) stretching mode.

4.4.5. Infrared Spectroscopy of $[Ru(tpy)(deazpy)NO_2]PF_6$

The strong vibration observed at 1355 cm^{-1} in nitro complex was assigned to the N=N (azo) stretching frequency, shifted from the free ligand about 66 cm^{-1}. The bonding mode of the nitro ligand had two vibrational modes, NO_2 asymmetric

stretching vibrational (ν_{as} N-O) which appeared at 1384 cm^{-1} and NO_2 symmetric stretching vibrational (ν_s N-O) appeared at 1272 cm^{-1}(Dovletoglou, *et al.*, 1996).

4.4.6. Infrared Spectroscopy of $[Ru(tpy)(deazpy)CH_3CN](PF_6)_2$

The N=N (azo) stretching vibrational frequency of acetonitrile complex was observed at 1300 cm^{-1}. The bonding mode of acetonitrile ligand is the C-N stretching ($\nu_{C\equiv N}$), at ca. 2100 cm^{-1} which could not be detected in this complex. The broad band was observed at 3450 cm^{-1} that was assigned to O-H stretching mode. The infrared data was similar to those of $[Ru(tpy)(dmazpy)CH_3CN](PF_6)_2$.

The N=N (azo) stretching vibrational frequencies of dmazpy, deazpy ligands and complexes are summarized in Table 35.

Table 35 The N=N (azo) stretching vibrational frequencies of ligands and complexes.

Compounds	$\nu_{N=N}$, cm^{-1}
dmazpy	1402
$[Ru(tpy)(dmazpy)Cl]PF_6$	1294
$[Ru(tpy)(dmazpy)NO_2]PF_6$	1355
$[Ru(tpy)(dmazpy)CH_3CN](PF_6)_2$	1294
deazpy	1399
$[Ru(tpy)(deazpy)Cl]PF_6$	1293
$[Ru(tpy)(deazpy)NO_2]PF_6$	1359
$[Ru(tpy)(deazpy)CH_3CN](PF_6)_2$	1300

As expected the N=N (azo) vibrational frequencies are varied with π-accepting behavior of X ligands. The N=N (azo) vibrational frequencies of the compounds are shifted from free ligand, ca. 60-100 cm^{-1}. As the monodentate ligand, NO_2^- has π-acceptor ability. In $[Ru(tpy)(dmazpy)NO_2]PF_6$ and $[Ru(tpy)(deazpy)NO_2]PF_6$, there are competition between nitro group and bidentate ligand for the ruthenium t_{2g} electron then the π- back donation of dmazpy and deazpy ligand become less. This gives rise to increase the azo bond order. Thus, when the X ligand becomes a strong π-acid, the azo stretching mode occurred at higher energy, close to the free ligand value.

4.5. ^{1}H NMR Spectroscopy

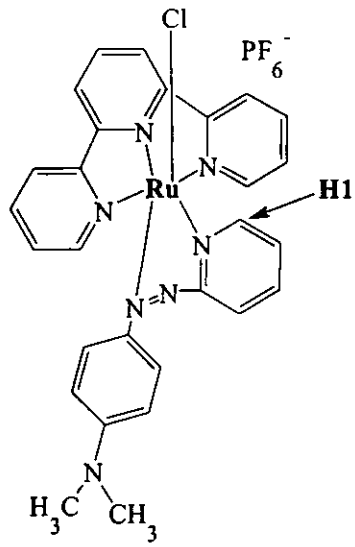
From the ^{1}H NMR spectroscopic data, the proton H1 of pyridine ring in all complexes show a sole downfield chemical shift as a doublet. The proton H1 of dmazpy and deazpy ligand lie in the outer ring currents of tpy ligand from the molecular models and X-ray structure data. In addition, the proton H1 locates closed to the nitrogen atom and monodentate ligand. The resonance is shifted downfield accordingly.

In addition, the peak of proton H1 gives a valuable method for detecting changes in X at Ru-X coordination site. Previous studies on the ^{1}H NMR spectra for $[Ru(bpy)_2(py)X]^{+/2+}$ complexes (X = Cl^-, Br^-, NO^-, NO_2^-, OH_2, etc.) showed that the chemical shift of 6 or 6' proton of the bipyridine appeared as an isolated doublet of doublet in the downfield, because it was out of ring current of both bpy and py ligands (Dobson, *et al.*, 1989).

The chemical shifts of the proton H1 for $[Ru(tpy)(dmazpy)Cl]PF_6$ and $[Ru(tpy)(deazpy)Cl]PF_6$ complexes move further downfield than those in $[Ru(tpy)(dmazpy)X](PF_6)_n$ and $[Ru(tpy)(deazpy)X](PF_6)_n$ complexes (X = NO_2^- and CH_3CN), because the protons of the dmazpy and deazpy have short intramolecular contact with the adjacent electronegative Cl atom as shown in X-ray structure. This downfield shift is due to more

effective shielding by electron density d_{xy} orbital (taking the z axis to lie along the Ru-X (X = NO_2^- and CH_3CN). The chemical shifts of the proton H1 are summarized in Table 36.

Table 36 Summary of the chemical shift of H1 for $[Ru(tpy)(dmazpy)X](PF_6)_n$ and $[Ru(tpy)(deazpy)X](PF_6)_n$ complexes (X = Cl^-, NO_2^- and CH_3CN) in d_6-DMSO.



X	Chemical shift, ppm	
	H1 in dmazpy complexes	H1 in deazpy complexes
Cl^-	9.80	9.80
NO_2^-	9.48	9.46
CH_3CN	9.64	9.63

In $[Ru(tpy)(L)CH_3CN](PF_6)_2$ complexes (L = dmazpy and deazpy), the singlet peak of proton of acetonitrile ligand is observed at 2.37 ppm. Whereas, $[Ru(tpy)(L)OH_2](PF_6)_2$ complexes (L = dmazpy and deazpy) do not have signals. From this difference, one can confirm the existing of acetonitrile complexes.

4.6. Cyclic voltammetry

4.6.1. Dmazpy and deazpy ligands

Reduction range

The reduction peaks of dmazpy and deazpy ligands were less stable. At the low scan rate (50 mV/s), the forward scan showed only one cathodic peak at –1.76 V for dmazpy and –1.71 V for deazpy. Even at the higher scan rate (100 to 2000 mV/s), the reduction species could not give reversible oxidation. Then, the species in reduction range displayed irreversible peaks, which were defined to the dmazpy, deazpy anion as shown in equation (7). It was believed that the azo function, -N=N-, was electron acceptor

$$\text{dmazpy} + 2e^- \longrightarrow \text{dmazpy}^{2-} \qquad (7)$$

$$\text{deazpy} + 2e^- \longrightarrow \text{deazpy}^{2-} \qquad (8)$$

There were different characters from the free azpy ligand. In azpy, it displayed the quasi-reversible couple in the negative potential region at $E_{1/2}$ = -1.58 V (ΔE_p = 171 mV). It was demonstrated that azpy accepted two electrons into its lowest unoccupied molecular orbital (LUMO) which was primary azo in character (Goswami, *et al.*, 1983). The mechanism of the azpy reduction exhibits in equation (9) (Sadler and Bard, 1968).

$$\text{azpy} + 2e^- \rightleftharpoons \text{azpy}^{2-} \qquad (9)$$

The reduction potential exhibits the electron accepting ability of the ligand. The more positive potential is the greater electron accepting ability. The negative potential values of azpy, dmazpy and deazpy are compared and show that azpy can

accept the electron better than dmazpy and deazpy. This corresponds to infrared spectroscopic data.

Oxidation range

Both ligands showed two quasi-reversible couples. Cyclic voltammogram of azpy ligand displayed no peak in oxidation range. The difference might be due to substituent effect in dmazpy and deazpy molecules. The starting material, *N,N*-dimethyl-4-nitrosoaniline and *N,N*-diethyl-4-nitrosoaniline, were studied by cyclic voltammetry. The cyclic voltammograms of both compounds showed quasi-reversible couples in oxidation range (Figure 52, Appendix A).

The couple I was studied in the range 400-700 mV. The cyclic voltammograms showed the anodic peak at low scan rate (50, 100 mV/s). However, this group became clearly quasi-reversible couple at higher scan rate (200 to 4000 mV/s). The currents of the cathodic peak increased when high potentials were supplied. The electron transfer process is followed by equation (10), which the redox reaction occurred at phenyl ring. The electron donating groups, R referred to $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$ provide the ease of redox reaction on the phenyl ring. The cyclic voltammograms of this couple of both ligands are shown in Figure 50, Appendix A.

$$NC_5H_4N{=}NC_6H_5\text{-}N(R)_2 \rightleftharpoons NC_5H_4N{=}NC_6^{+}H_5\text{-}N(R)_2 + e^- \quad (10)$$

The couple II was studied in the range 400-1400 mV. The cyclic voltammograms of couple II of both ligands are shown in Figure 51, Appendix A. The couple II was occurred from the couple I, $NC_5H_4N{=}NC_6^{+}H_5\text{-}N(R)_2$ species, at +0.74 V (ΔE_p = 84 mV) for dmazpy and +0.81 V (ΔE_p = 84 mV) for deazpy followed the equation (11).

$$NC_5H_4N{=}NC_6^{+}H_5\text{-}N(R)_2 \rightleftharpoons NC_5H_4N{=}NC_6^{2+}H_5\text{-}N(R)_2 + e^- \quad (11)$$

4.6.2. $[Ru(tpy)(L)Cl]PF_6$ and $[Ru(tpy)(L)NO_2]PF_6$ complexes (L = dmazpy and deazpy).

Reduction range

The reduction range of $[Ru(tpy)(dmazpy)Cl]PF_6$ gave two quasi-reversible couple. The quasi-reversible couple at -1.21 V (ΔE_p = 103 mV) in $[Ru(tpy)(dmazpy)Cl]PF_6$ complex exhibited the one electron transfer process as described by equation (12). Next couple at -1.79 V (ΔE_p = 105 mV) was occurred at higher potential with one electron transfers process. The couple II was occurred from the couple I that followed the equation (13). The $[Ru(tpy)(deazpy)Cl]PF_6$ complex also had similar redox properties to the $[Ru(tpy)(dmazpy)Cl]PF_6$ complex. Two quasi-reversible couple of $[Ru(tpy)(deazpy)Cl]PF_6$ complex occurred at -1.17 V (ΔE_p = 64 mV) and -1.89 V (ΔE_p = 103 mV) (Figure 55, Appendix A). The reduction potentials of tpy ligand were too negative to be observed within solvent window.

$$[Ru^{II}(tpy)(dmazpy)Cl]^+ + e^- \rightleftharpoons [Ru^{II}(tpy)(dmazpy^-)Cl]^0 + e^- \quad (12)$$

$$[Ru^{II}(tpy)(dmazpy^-)Cl]^0 + e^- \rightleftharpoons [Ru^{II}(tpy)(dmazpy^{2-})Cl]^- + e^- \quad (13)$$

Besides, comparison with $[Ru(tpy)(azpy)Cl]BF_4$ (Saeteaw, 2000), it showed two reversible reduction couple at –1.09 V (ΔE_p = 64 mV) and –1.75 V (ΔE_p = 77 mV). From the reduction potential, it could be arranged the π-accepting ability as order, azpy > dmazpy ~ deazpy. It corresponded to infrared spectroscopic data. Table 37 exhibits reduction potentials data of $[Ru(tpy)(azpy)Cl]BF_4$ and $[Ru(tpy)(L)Cl]PF_6$ (L = dmazpy and deazpy).

Table 37 Reduction potentials data of $[Ru(tpy)(azpy)Cl]BF_4$ and $[Ru(tpy)(L)Cl]PF_6$ (L = dmazpy and deazpy) (ferrocene as an internal standard).

Assigned	$E_{1/2}$, V		
	$[Ru(tpy)(azpy)Cl]BF_4$	RudmCl	RudeCl
1st reduction (I)	-1.09	-1.21	-1.22
2nd reduction (II)	-1.75	-1.79	-1.79

RudmCl = $[Ru(tpy)(dmazpy)Cl]PF_6$

RudeCl = $[Ru(tpy)(deazpy)Cl]PF_6$

In the case of $[Ru(tpy)(L)NO_2]PF_6$ (L = dmazpy and deazpy) complexes, there have complete reversible couple and quasi-reversible couple in reduction range. The complete reversible couples occurred at –1.15 V (ΔE_p = 68 mV) for dmazpy complex and –1.17 V (ΔE_p = 64 mV) for deazpy complex at low scan rate (50 mV/s). It noticed that the first reduction couple in nitro complexes is complete reversible couple, whereas in chlro complex is quasi-reversible couple. It indicated that the nitro ligand could support the electron transfer of ligand (Figure 56, Appendix A). The quasi-reversible couple (II) exhibited at –1.88 V (ΔE_p = 76 mV) for dmazpy complex and -1.89 V (ΔE_p = 62 mV) for deazpy complex (Figure 57 and 58, Appendix A).

The reduction potentials of $[Ru(tpy)(L)X]PF_6$ (where L = dmazpy and deazpy, X = Cl and NO_2^-) were summarized in Table 38.

Table 38 Summary of reduction potential data of complexes (ferrocene as internal standard).

Assigned	$E_{1/2}$, V			
	RudmCl	$RudmNO_2$	RudeCl	$RudeNO_2$
1st reduction (I)	-1.21	-1.15	-1.22	-1.17
2nd reduction (II)	-1.79	-1.88	-1.79	-1.89

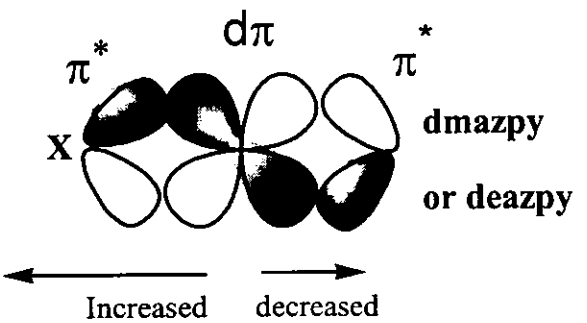
RudmCl = $[Ru(tpy)(dmazpy)Cl]PF_6$

$RudmNO_2$ = $[Ru(tpy)(dmazpy)NO_2]PF_6$

RudeCl = $[Ru(tpy)(deazpy)Cl]PF_6$

$RudeNO_2$ = $[Ru(tpy)(deazpy)NO_2]PF_6$

One can see that the couples in reduction potential of these complexes were observed to be slightly sensitive to the nature of X ligands when monodentate ligands (X) are *trans* to N (azo) of the dmazpy and deazpy. As the π-electron accepting nature of the monodentate increased (NO_2^-), the first couple was observed to occur at more positive potential. The extent of π-back donation to the other was reduced, this also decreased their π^* orbital of the ligands as shown in scheme 1.



Backdonation

Scheme 1

Oxidation range

In the oxidation range, in this case all complexes showed the redox of property of both the metal center and ligand center.

The ligand couple III was occurred at less positive at +0.59 V (ΔE_p = 76 mV) for [Ru(tpy)(dmazpy)Cl]PF_6, +0.65 V (ΔE_p = 60 mV) for [Ru(tpy)(dmazpy)NO_2] PF_6, +0.58 V (ΔE_p = 67 mV) for [Ru(tpy)(deazpy)Cl]PF_6, and +0.64 V (ΔE_p = 68 mV) for [Ru(tpy)(deazpy)NO_2]PF_6 (Figure 53 and 54, Appendix A). The shift of the ligand couple III was 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 redox potentials of Ru (II/III) in chloro complex were found to be quasi-reversible couples (Figure 46). The Ru (II/III) couples were occurred at +0.96 V (ΔE_p = 107 mV) for dmazpy complex and +0.98 V (ΔE_p = 80 mV) for deazpy complex. The Ru (II/III) redox potentials of [Ru(tpy)(dmazpy)Cl]PF_6 and [Ru(tpy) (deazpy)Cl]PF_6 were compared with those of related complexes [Ru(tpy)(N-N)Cl]$^+$ where N-N = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 2-(phenylazo) pyridine (azpy) listed in Table 39.

Table 39 Summary of Ru (II/III) oxidation potential data of $[Ru(tpy)(N\text{-}N)Cl]^+$ complexes, where N-N = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 2-(phenylazo)pyridine (azpy).

compounds	Ru (II/III) oxidation potential, V
$[Ru(tpy)(phen)Cl]^{+}$ [c]	+0.71
$[Ru(tpy)(bpy)Cl]PF_6$ [b]	+0.74
$[Ru(tpy)(azpy)Cl]BF_4$ [a]	+0.85
$[Ru(tpy)(dmazpy)Cl]PF_6$	+0.96
$[Ru(tpy)(deazpy)Cl]PF_6$	+0.98

[a] Vs Ag/Ag^+ (ferrocene = 0 V). All measurements were made in a 0.1 M $TBAPF_6$ acetonitrile solution (Seateaw U., 2000)

[b] Vs Ag/Ag^+ (ferrocene = 0 V). All measurements were made in a 0.1 M $TBAPF_6$ acetonitrile solution (Gerli, *et al.*, 1995)

[c] Vs Ag/Ag^+ (ferrocene = 0 V). All measurements were made in a 0.1 M $TBAPF_6$ acetonitrile solution (Thorp, *et al.*, 1993)

The following data gave the Ru (II/III) oxidation potential in order deazpy ~ dmazpy > azpy > bpy > phen. The dmazpy and deazpy ligands could stabilize the Ru(II) in the complexes better than other bidentate ligands. The substituents, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$, could donate electrons to the molecule and increased the strength of σ bonding at pyridine toward Ru(II). The redox reaction was described in equation (14).

$$[Ru^{II}(tpy)(L)Cl]^{+} + e^{-} \rightleftharpoons [Ru^{III}(tpy)(L)Cl]^{2+} \qquad (14)$$

The redox of Ru (II/III) in nitro complexes occurred at higher potential, +1.15 V for $[Ru(tpy)(dmazpy)NO_2]PF_6$ and +1.18 V for $[Ru(tpy)(deazpy)NO_2]PF_6$. Only oxidation peak was observed in nitro complexes, this could be resulted from the chemical reduction of Ru (III) → Ru (II) by other species. This occurred faster than the usual electrochemical reductions (Figure 47).

The Ru (II/III) oxidation potential in these complexes was observed to be sensitive to the nature of X ligands. As the π-electron accepting nature of the monodentate increased, there was an increased stabilization of Ru (II) and an increased effective nuclear charge. NO_2^- ligand has π-acceptor property that can stabilize Ru (II) center. Therefore, the ruthenium oxidation couples of nitro complexes are shifted to the more positive potentials as shown in Table 40.

Table 40 Summary of Ru (II/III) oxidation potential data of $[Ru(tpy)(dmazpy)X]PF_6$ and $[Ru(tpy)(deazpy)X]PF_6$ where $X = Cl^-, NO_2^-$.

Assigned	$E_{1/2}$, V			
	RudmCl	*RudmNO$_2$*	*RudeCl*	*RudeNO$_2$*
Ru (II/III)	+0.96	-	+0.98	-
E_{pa}	+1.00	+1.15	+1.01	+1.18

RudmCl = $[Ru(tpy)(dmazpy)Cl]PF_6$

RudmNO$_2$ = $[Ru(tpy)(dmazpy)NO_2]PF_6$

RudeCl = $[Ru(tpy)(deazpy)Cl]PF_6$

RudeNO$_2$ = $[Ru(tpy)(deazpy)NO_2]PF_6$

4.7 X-ray Diffractometer

X-ray crystallography is the most precise and comfortable technique for determination of the actual structures. There were two ligands and two complexes which their single crystals are suitable for X-ray diffraction studies.

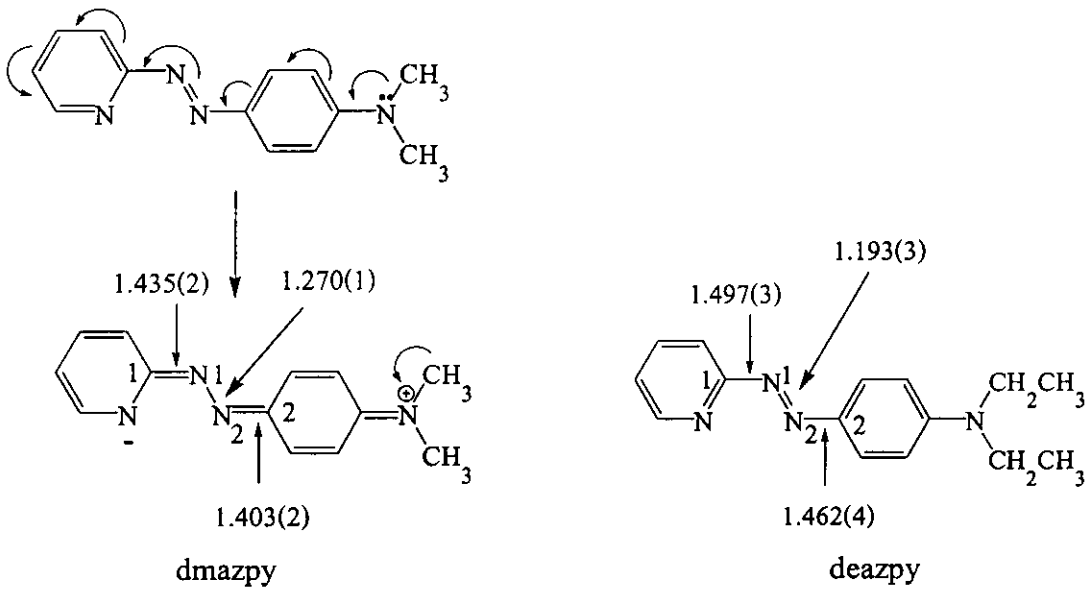
The crystal structure of 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy), 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy), [Ru(tpy)(dmazpy)Cl] BF_4 and [Ru(tpy)(dmazpy)NO_2]BF_4 were reported in this work.

4.7.1. Dmazpy and deazpy ligands

In general, it was known that the azo compounds can have two geometrical isomers, i.e. *cis* and *trans*. Mostly the *trans* form was more stable than the other, such as crystal structure of the *trans*-azobenzene and *trans*-azpy were prepared and studied. Then, 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy) and 2-(4'-*N,N*-diethyl- aminophenylazo)pyridine (deazpy) were also crystallized in the *trans* rather than the *cis* forms.

The dmazpy molecule has one nitrogen on pyridine ring and one azo moiety similar to azpy. These nitrogen atoms are acting as the donor atoms to metal ions. The N=N(azo) bond distances of dmazpy is 1.270 Å which is longer than that of the azpy (1.248(4) Å) (Penneerselvam, *et al.*, 2000) and azobenzene (1.243 Å) (Brown,1966), because the substituent, -$N(CH_3)_2$, of dmazpy donates electrons into the π^* orbital of azo function. This leads to decrease in the N=N bond order. The planarity between substituent plane and phenyl ring is observed with dihedral angle less than 7 ° then the electrons from substituent can delocalize into the azo function as shown in Scheme 2.

Deazpy has more steric effect than dmazpy. The deazpy molecule shows the phenyl and pyridine ring are found to be *trans* and essentially coplanar with the azo linkage, the C5-N2-N3-N6 torsion angle is 179.2(2) °. The planarity between substituent plane and phenyl ring is observed with dihedral angle = 33.985(5) ° which is greater than that of dmazpy. Therefore, less electrons of substituent can delocalize into the π^* orbital of azo moiety. The N=N (azo) bond distances of deazpy is 1.193(3) Å, shorter than that of dmazpy.



Scheme 2

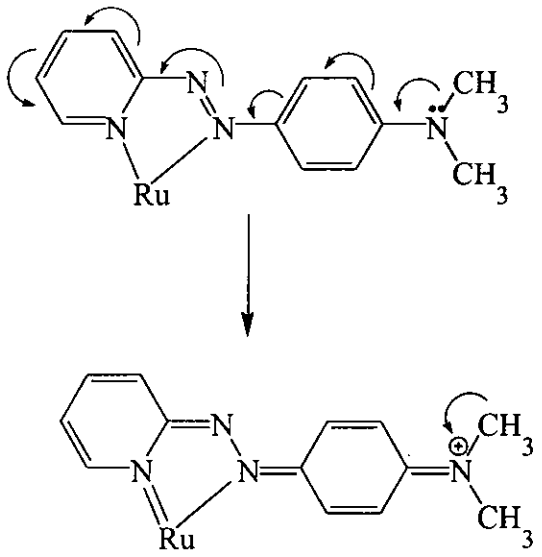
Some selected bond distances of dmazpy and deazpy ligand are shown in Scheme 2. Bond distances of C1-N1 and C2-N2 in dmazpy are shorter than that of deazpy. In dmazpy ligand, the C1-N1 bond (1.435(2) Å) and C2-N2 bond (1.403(2) Å) show more double bond character. It can confirm that the delocalization of electrons into the N=N (azo) moiety and pyridine as shown in scheme 3. This give rise to decrease N=N (azo) bond order in dmazpy. From this results it indicates that $-N(CH_3)_2$ in dmazpy ligand can delocalize more electrons into the molecule than the $-N(CH_2CH_3)_2$ in deazpy ligand.

4.7.2. [Ru(tpy)(dmazpy)Cl]BF_4

Asymmetric unit of complex consists of the cation and a disordered BF_4^- anion. The structure of [Ru(tpy)(dmazpy)Cl]BF_4 is distorted octahedral. The dmazpy ligand is bound to ruthenium with the azo *trans* to the coordinated chlorine atom. The N(5)-Ru (1)-N(7) angle is approximately 159°. Shortening of the Ru(1)-N(6) distance to the central pyridyl, approximately 0.1 Å with respect to Ru-N distance to the two outer pyridyl rings, are typical features observed in other Ru(II)tpy structure. The Ru-Cl distance of 2.410(6) Å is observed in this structure which is slightly longer than that observed in [Ru(tpy)(bpz)Cl]PF_6 (2.405(5) Å) (Gerli, *et al.*, 1995), but it is similar to those found in other Ru(II) structure.

The substituent group of $-N(CH_3)_2$ shows the extensive effects upon bond distances of Ru-N(azo), N=N(azo) and Ru-N(py) in [Ru(tpy)(dmazpy)Cl]BF_4 and [Ru (tpy)(dmazpy)NO_2]BF_4 complexes.

The planarity between substituent plane and phenyl plane is observed with dihedral angle less than 4.2° (average dihedral angle 3.190 ° for [Ru(tpy)(dmazpy) Cl] BF_4 and 5.171° for [Ru(tpy)(dmazpy)NO_2]BF_4). The lone pair electron at N-atom can delocalize into the phenyl ring. The conjugated structure is suggested in Scheme 3. The $-N(CH_3)_2$ is stabilized by electrons from the methyl group.



Scheme 3

From the conjugated structure, the Ru-N(azo) distances should be longer. whereas, the Ru-N(py) bond should be shorter related to the azpy complex. The donated electrons are delocalized in the ligand structure which extends conjugated system than that of azpy complexes. These results are shown in Table 41.

Table 41 Selected bond distance of complexes

Complexes	Bond distances (Å)			
	N=N	Ru-Cl	Ru-N (pyridine)	Ru-N (azo)
$[Ru(tpy)(dmazpy)Cl]BF_4$	1.306(2)	2.410(6)	2.055(1)	1.976(1)
$[Ru(tpy)(azpy)Cl/I]BF_4$ [a]	1.298(3)	2.428(4)	2.057(3)	1.959(3)
$[Ru(tpy)(azpy)CNCH_3](ClO_4)_2$ [b]	1.281(13)	2.057(7)	2.062(7)	1.971(7)

[a] (Saeteaw, 2000)

[b](Pramanik, *et al.*, 1998)

The bond distances of Ru-N(azo) and Ru-N(pyridine) are effected from the substituent group of $-N(CH_3)_2$. Ru-N(azo) bond distance of $[Ru(tpy)(dmazpy)Cl]BF_4$ complex is shorter than Ru-N(pyridine) bond distance due to the most π backbonding from Ru(II) to azo function. The electron-donating group shows the slightly effect on the Ru-N(pyridine) bond distances. The Ru-N(pyridine) bond distance in $[Ru(tpy)(dmazpy)Cl]BF_4$ complex is shorter than that in $[Ru(tpy)(azpy)Cl/I]BF_4$ and $[Ru(tpy)(azpy)CNCH_3](ClO_4)_2$. Results from the X-ray data show that the dihedral angle between the substituent and phenyl ring is less than 3.5 °. They are planarity, therefore the electrons can delocalize through nitrogen atom into conjugated π system. The pyridine ring donates more σ-electron to Ru (II) center. Ruthenium (II) center is rich of electrons therefore, it can give electrons back to the π^* orbital of azo function and pyridine. Then, the Ru–N (pyridine) bond in $[Ru(tpy)(dmazpy)Cl]BF_4$ is stronger than that in $[Ru(tpy)(azpy)Cl/I]BF_4$ and $[Ru(tpy)(azpy)CNCH_3](ClO_4)$. Furthermore, Ru-N (azo) bond distance in this complex is longer than that in $[Ru(tpy)(azpy)Cl/I]BF_4$. The substituent donates electron into the π^* orbital of azo character. Thus, dmazpy is better σ-donor than azpy ligand.

The azo function is known as the acceptor of π electrons from Ru(II) center. Therefore, the N=N bond distances are decreased in complexes due to the π-backbonding of $t_{2g} \rightarrow \pi^*$ orbital. The N=N distance in coordinated dmazpy is longer (1.306 Å) than that in free dmazpy (1.270 Å). It corresponds to IR data, the N=N stretching mode of dmazpy complex (1294 cm^{-1}) appeared at lower frequency than free dmazpy (1402 cm^{-1}).

$[Ru(tpy)(dmazpy)Cl]BF_4$ complex shows Ru-Cl bond distances (2.410(6) Å) which is longer than of $[Ru(tpy)(biq)Cl]PF_6$ (biq = 2,2'-biquinoline) (2.378(2) Å) (Gerli, *et al.*, 1995) and $[Ru(azpy)Cl_2]$ (2.397(1) Å) (Seal and Ray, 1984). It should be due to decreasing the strain of structure by lengthening the Ru-Cl bond.

4.7.3. $[Ru(tpy)(dmazpy)NO_2]BF_4$

The ruthenium is coordinated to dmazpy ligand with the azo nitrogen (N3) *trans* to the coordinated NO_2^- ligand. The bond distances of Ru-N3 (azo), 2.025(2) Å is shorter than that of Ru-N1 (py), 2.059(1) Å, which is attributed to the better π back-bonding $d\pi(Ru) \rightarrow \pi^*(azo)$ power of the azo function. The azo N2-N3 distance, 1.299 (2) Å is longer than that in uncoordinated ligand.

Table 42 Selected bond distance of complexes

Complexes	Bond distances (Å)			
	N=N	Ru-NO_2	Ru-N(pyridine)	Ru-N (azo)
$[Ru(tpy)(dmazpy)NO_2]BF_4$	1.299(2)	2.059(2)	2.059(2)	2.025(2)
$[Ru(tpy)(azpy)NO_2]BF_4$[a]	1.265(5)	2.066(3)	2.063(4)	2.036(4)

[a] (Hansongnern, *et al.*,2001)

The structure of $[Ru(tpy)(dmazpy)NO_2]BF_4$ is similar to that of [Ru(tpy) (dmazpy)Cl]BF_4 with X ligand *trans* to N(azo). The dihedral angle between the substituent and phenyl ring is less than 5.1°. They are planarity; therefore the electrons can delocalize into the pyridine ring. The N(py) can donate more σ-electron to ruthenium (II) center. Then, the Ru-N(py) bond distance of dmazpy complex (2.059(2) Å) is shorter than that of azpy complex (2.063(4) Å). Ru-N (azo) bond distance of complex is shorter than Ru-N(pyridine) bonds due to the most π back-bonding from Ru (II) to azo function. The Ru1-N8 (nitro) bond distance of 2.059(2) Å found in [Ru(tpy) (dmazpy)NO_2]BF_4 is significantly shorter than that in [Ru(tpy)(azpy)NO_2]BF_4. This can be due to greater Ru-N (nitro) multiple bonding in [Ru(tpy)(dmazpy)NO_2]BF_4.

The Ru-N(azo) bond distance in $[Ru(tpy)(dmazpy)NO_2]BF_4$ complex (2.025(2) Å) is longer than the values found in $[Ru(tpy)(dmazpy)Cl]BF_4$ complex (1.976(1) Å). The lengthening of the Ru-N(azo) distances suggests less Ru-N(azo) π-interaction at Ru center, possibly due to a greater Ru-NO_2 π-interaction. In addition, the observed variation of the N=N bond lengths is indication of π-backbonding between Ru(II) and the N(azo) atom. The N=N bond distance of $[Ru(tpy)(dmazpy)NO_2]BF_4$ complex (1.299 (2) Å) is shorter than that in $[Ru(tpy)(dmazpy)Cl]BF_4$ (1.306(2) Å). The N=N bond distances of $[Ru(tpy)(dmazpy)NO_2]BF_4$ complex is close to the value found in the uncoordinated dmazpy ligand (1.270(1) Å). Therefore, the N=N bond length can be a useful probe for the relative strength of the Ru-N(azo) bond. This confirms that the nitro group has π-interaction with the ruthenium center.

Comparison with azpy complex, Both Ru-N(pyridine) and Ru-N(azo) bond distances of $[Ru(tpy)(dmazpy)NO_2]BF_4$ complex are shorter than that of $[Ru(tpy)(azpy)NO_2]BF_4$ complex It can observed that dmazpy donate more electrons to the Ru(II) center because the electron density at Ru(II) center is reduced when X = NO_2. From this result, it can confirm that dmazpy is better σ-donor than azpy ligand.