Chapter 4

DISCUSSION

2-(*N,N*-dimethylphenylazo)thiazole(dmsazpy) and 2-(*N,N*-diethylphenylazo) thiazole (desazpy) were synthesized by coupling the thiazolyldiazonium ions with *N,N*-dimethylaniline and *N,N*-diethylaniline, respectively at pH 7. Purification was carried out by chromatographic technique. These ligands used N(th) and N(azo) act as donor atoms bound to metal ion. The structures of these ligands were presented previously. $Ru(dmso)_4Cl_2$ complexes and dmsazpy or desazpy ligands in a 1:2 molar ratio in chloroform solution were refluxed for 21 h. The complex solution was purified by chromatographic technique. The greenish-blue and pink-purple bands of *trans* and *cis*-$Ru(L)_2Cl_2$ (L= dmsazpy and desazpy) were isolated.

In the present work, the four isomeric complexes of *trans*- and *cis*-$Ru(L)_2Cl_2$ complexes were isolated. They were characterized by spectroscopic methods on the basis of Electrospray mass spectrometry (ES-MS), Infrared spectroscopy (IR), Proton nuclear magnetic resonance spectroscopy (^1H NMR) and UV-Visible spectroscopy (UV- Visible). However, only two isomers of $Ru(dmsazpy)_2Cl_2$ were determined by X-ray diffraction analysis. The results from X-ray data supported that both complexes were *tcc* and *ctc* in *trans*-$Ru(dmsazpy)_2Cl_2$ and *cis*-$Ru(dmsazpy)_2Cl_2$ configuration, respectively.

The structures of these ligands were similar to that of azpy by the replacement pyridine ring with thiazole ring and containing the substituent as electron-donating groups ($-NR_2 = CH_3, C_2H_5$). Thus, the objectives of this work are to study the chemical effects of dmsazpy and desazpy ligands on the complexes, compared to azpy complexes and to find the σ-donor and π-acceptor on the basis of X-ray structure, spectroscopic methods and redox properties.

4.1 Electrospray mass spectrometry

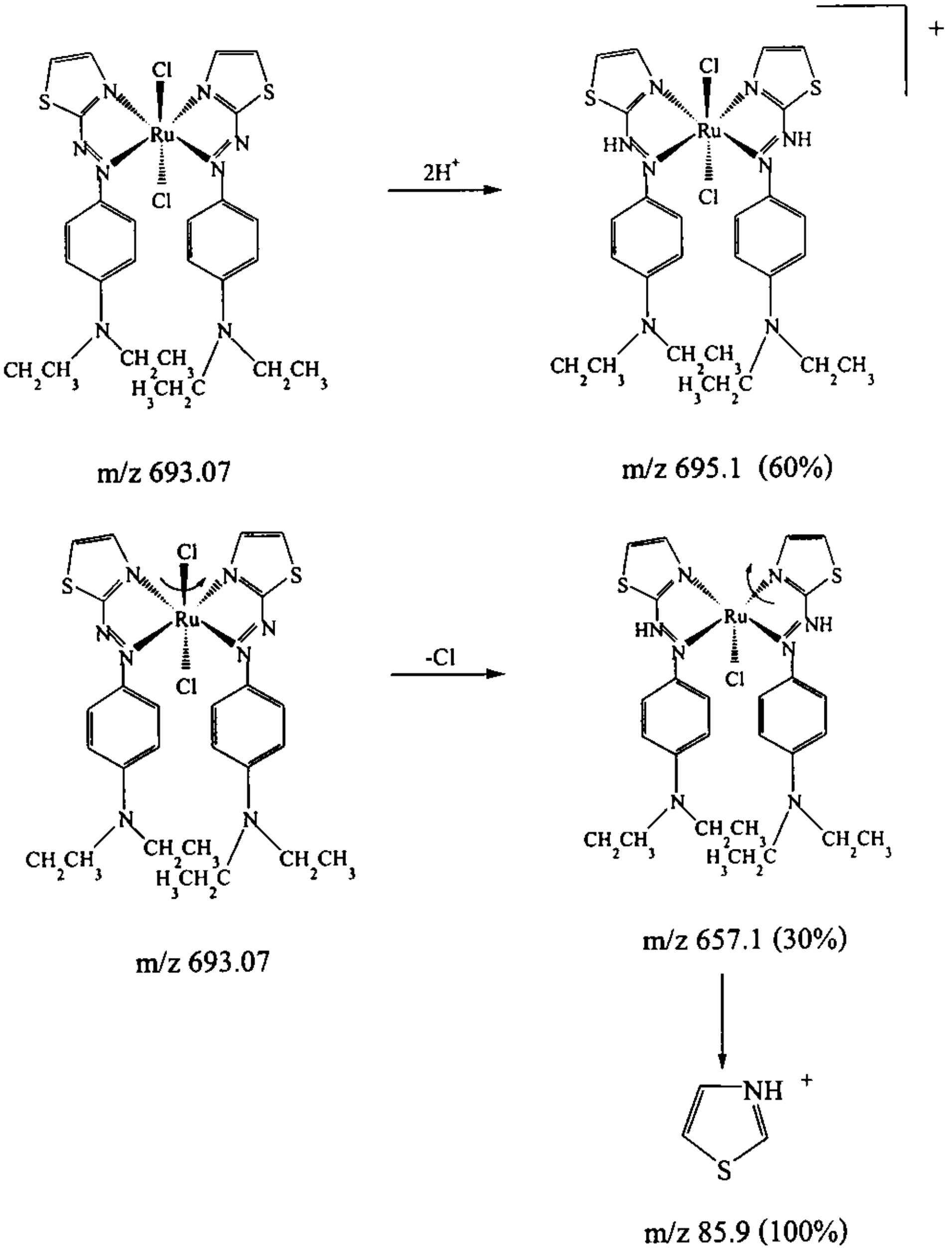
The electrospray mass spectrometry is a technique to confirm the molecular weight of complexes. This technique is useful for analyzing the different isomeric complexes, which give the different fragment pattern.

In this work, the four isomeric complexes give the different pattern of fragmentation and can be divided into two groups. In addition, X-ray and ^{1}H NMR method can confirm the different of these complexes which are *trans*- and *cis*-isomers.

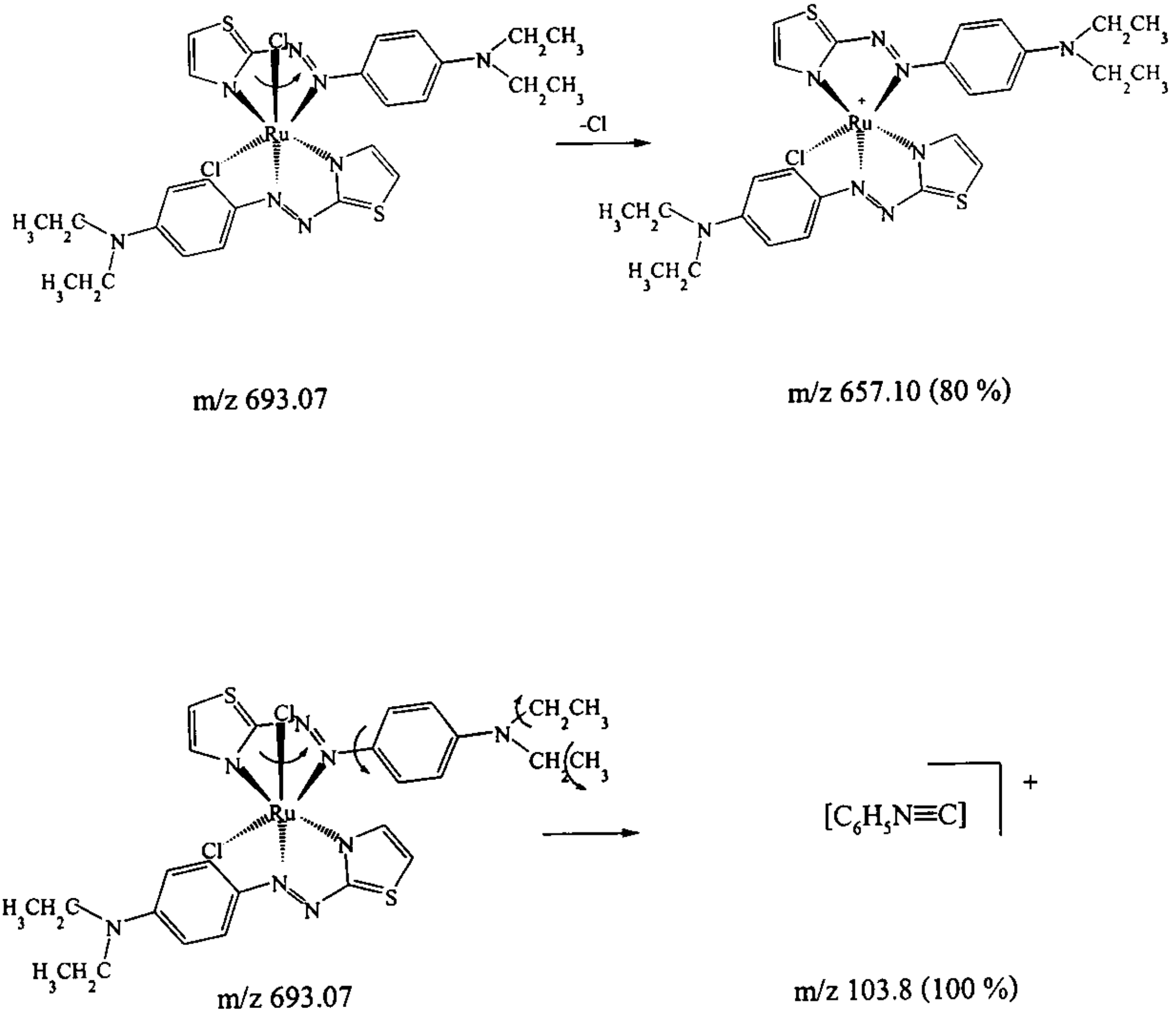
The *trans*-Ru(dmsazpy)$_2$Cl$_2$ complex shows the major stable fragment ion at m/z 624.2 which is assigned to [Ru(dmsazpy)$_2$2HCl$_2$-CH$_3$]$^+$ (100%). This complex is preferred to have protonation in its structure. However, the *trans*-Ru(dmsazpy)$_2$Cl$_2$ loses methyl group immediately after two protonation. It may result from steric structure of complex.

The *cis*-Ru(dmsazpy)$_2$Cl$_2$ complex shows the major stable fragment ion at m/z 637.2, which is assigned to [Ru(dmsazpy)$_2$Cl]$^+$ (100%). This complex is preferred to lose chloride atom from its complex. This may result from electron repulsion between two Cl atoms in *cis* position which are orthogonal (92.71 (2)$^{\circ}$) The average Ru-Cl bond distance of *cis*-Ru(dmsazpy)$_2$Cl$_2$, 2.410(2) Å, is longer than Ru-Cl bonds observed in Ru(azpy)$_2$Cl$_2$ (2.399 Å) complexes. These data are results from chlorine atoms which are trans to N(azo) (Ru-N(azo) 2.026 Å). Therefore, the average Ru-Cl bond distances are increased. Furthermore, the Ru-Cl bond distance of *cis*-Ru(dmsazpy)$_2$Cl$_2$ are longer than *trans*-Ru(dmsazpy)$_2$Cl$_2$. Thus, the Cl atom in *cis*-Ru(dmsazpy)$_2$Cl$_2$ is usually lost first.

Although, *trans*- ans *cis*-Ru(desazpy)$_2$Cl$_2$ have not been determined by X-ray analyses but the fragmentation patterns of these complexes are similar to *trans*- and *cis*-Ru(dmsazpy)$_2$Cl$_2$ complexes. The *trans*-Ru(desazpy)$_2$Cl$_2$ receives two protons and display at m/z 695.1 (60%). It is unstable, thus the other fragmentations are also obtained. The complex of *cis*-Ru(desazpy)$_2$Cl$_2$ is similar to *cis*-Ru(dmsazpy)$_2$Cl$_2$ that chlorine atom is lost from its complex. The fragmentation mechanism of some peaks in *trans*- and *cis*-Ru(desazpy)$_2$Cl$_2$ complexes can be proposed in the Scheme I and II, respectively.



Scheme I.



Scheme II.

4.2 Infrared spectroscopy

All of complexes display many characteristic frequencies in the range 4000-200 nm. Especially, in the range 430-200 nm gives the information of ligand bound to metal such as Ru-Cl, Ru-N(th) and Ru-N(azo) stretching modes. Furthermore, in the range 1600-600 cm^{-1} is assigned to some characteristic peaks of free ligands. Therefore, the objective in studying the IR spectra are to find the N=N mode, identify of the Ru-L stretching modes, and symmetry were possible. Besides, the IR results can be used to determine the π-acceptor properties of ligands.

In general, the N=N stretching appears near 1424 cm^{-1} in azpy ligand. (Krause and Krause, 1980). In dmsazpy and desazpy ligands, these peaks have been observed at 1367 and 1358 cm^{-1}, respectively. These peaks appear at lower energy than that of azpy. This may result from the substituents, $-NR_2$ (R = CH_3 and C_2H_5) of dmsazpy and desazpy which donate electrons to phenyl ring. It leads to increase delocalized electrons into π^* orbital of azo function, thus the N=N bond orders are decreased. In comparison to the azo mode in dmsazpy appears at higher energy than that of desazpy. It means that the electron donating ability of ethyl group are greater than the methyl group.

The N=N stretching modes in complexes are shifted to lower frequencies than that in free ligands about 120 cm^{-1}. This shifting is indicated that ligands are bound to metal and may be attributed to $Ru(d\pi) \rightarrow \pi^*(azo)$. As the Ru-N bond order increases, the N-N bond order must decrease. In addition, the results of the N=N stretching mode of $Ru(azpy)_2Cl_2$ complexes display similarly to dmsazpy and desazpy complexes but it appear at the higher energy. Because dmsazpy and desazpy ligands can accept electrons from both Ru(II) and substituent groups, it leads to decreasing of N=N bond order. The results from these data suggested that the azpy is stronger π-acid than dmsazpy and desazpy ligands.

The stretching vibration modes at metal-ligand appeared in the range 430-200 cm^{-1} which is the characteristic peaks of Ru-Cl, Ru-N(th) and Ru-N(azo) stretching modes. The *trans*- and *cis*-$Ru(azpy)_2Cl_2$ complexes is symmetrically C_{2v} and C_2 respectively (Kraus and Kraus, 1980). These data is also observed in *trans*- and *cis*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) complexes.

The Ru-Cl stretching modes in *trans*-$Ru(L)_2Cl_2$ are easily to assign because they show a sharp single band. However, it is hard to assign this peak in *cis*-$Ru(L)_2Cl_2$ because it appear as weak signal which two similar stretching modes. Furthermore, both of Ru-N(th) and Ru-N(azo) stretching modes appear as weak signal. Thus, it is hard to assign those peaks.

On the basis of data, it is indicated that the N=N stretching mode in complexes are relatively low compared to free ligand values due to $t_{2g} \rightarrow \pi^*$(azo) donation. The extent of this donation would increase and the N=N frequency would decrease as the t_{2g} level gets destabilized (Goswami, *et al.*, 1983). This explaination is observed in N=N stretching mode of these complexes in the order of *cis*-$Ru(desazpy)_2Cl_2$ > *cis*-$Ru(dmsazpy)_2Cl_2$ > *trans*-$Ru(dmsazpy)_2Cl_2$ > *trans*-$Ru(desazpy)_2Cl_2$. The trends in N=N frequencies and MLCT band energies are mutually consistent and are shown in Table 37.

Table 37 The selected mode of vibration and absorption spectral data of $Ru(L)_2Cl_2$ (L= dmsazpy and desazpy) complexes

Complexes	*cis* $Ru(desazpy)_2Cl_2$	*cis* $Ru(dmsazpy)_2Cl_2$	*trans* $Ru(dmsazpy)_2Cl_2$	*trans* $Ru(desazpy)_2Cl_2$
N=N (cm^{-1})	1249	1247	1244	1239
MLCT (λ_{max}, nm) in $CHCl_3$	510 (5.42) 674 (2.50)	506 (4.98) 662 (2.11)	490 (2.67) 682 (2.87)	504 (3.74) 688 (3.14)

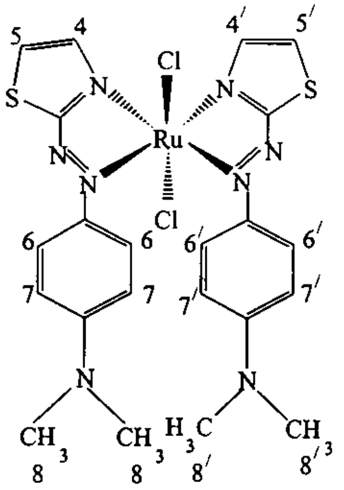
4.3 Proton nuclear magnetic resonance spectroscopy

The ^{1}H NMR data of dmsazpy and desazpy are similar patterns. The data show the proton 6,6′ are the most downfield and proton 8,8′ are the most upfield. The results of those ligands have different patterns from the *trans*- and *cis*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) complexes. In addition, the ^{1}H NMR patterns of *trans*- and *cis*-isomers are also different. Therefore, this is useful to determine the type of isomers. When L coordinated with the metal, the proton on L can be divided into two groups. One group gave downfield signals which referred to proton 4,4′ and 5,5′ on thiazole ring. The other group gave upfield signals that are referred to proton 6,6′ and 7,7′ on phenyl ring and alkyl groups on substituents. The results from these data are shown in Table 36.

Table 38 ^{1}H NMR data for dmsazpy, desazpy, *trans*- and *cis*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) complexes

H-position	δ(ppm)					
	dmsazpy	desazpy	*trans* $Ru(dmsazpy)_2Cl_2$	*trans* $Ru(desazpy)_2Cl_2$	*cis* $Ru(dmsazpy)_2Cl_2$	*cis* $Ru(desazpy)_2Cl_2$
4,4′	7.90	7.89	8.16	8.14	8.53	8.51
5,5′	7.25	7.23	7.92	7.86	7.90	7.86
6,6′	7.94	7.92	7.53	7.68	6.89	6.88
7,7	6.73	6.72	6.17	6.23	6.29	6.26
8,8′	3.12	1.25	3.01	1.16	2.99	1.14
9,9′	-	3.48	-	3.34	-	3.33

In *trans*-$Ru(dmsazpy)_2Cl_2$ complex, the proton on thiazole ring, H4,4′ and H5,5′, are shifted to downfield while the proton on phenyl ring, H6,6′ and 7,7′, are shifted to upfield compared to free dmsazpy. The shifting is due to coordinated ligand to ruthenium ion. Each of proton showed the different chemical shift values correspond to the electron density around it.

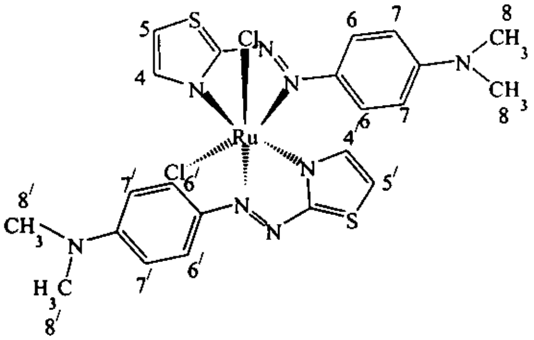


trans-Ru(dmsazpy)$_2$Cl$_2$ complex

The geometry of this complex shows the Cl atoms are in the *trans* position and located in with different plane from chelate rings. In addition, the dihedral angles between thiazole and chelate ring are different values (9.0(1)° and 10.4 (1)°. This effect leads to strong bond of Ru-N(th). The average Ru-N(th) bond distance is 2.068 (2) Å. This bond is shorter than that of Ru(azpy)$_2$Cl$_2$ complex which has the average bond length of Ru-N(py) is 2.108 Å (Velders *et al.*, 2000). This may result in shifting H4, 4′ and H5, 5′ to downfield. In contrast to H6, 6′ and 7, 7′, they are shifted to upfield. One can explain that the dihedral angle between substituent and phenyl is less than 5.0°. Thus, the electrons from substituents (-NR$_2$, R = CH$_3$ and C$_2$H$_5$) can easily flow into phenyl rings. However, the dihedral angles between phenyl ring and chelate is significantly different values (37.1(1) and 36.9(1)°). Therefore, the population of electrons on phenyl proton have not got much interaction from N(azo) which bound to Ru ion. These signal are thus move to upfield compared to free ligands. However, H6,

$6'$ on thiazole ring (*trans*-isomer) are shifted to downfield than *cis*-isomer. It results from interaction through space between chlorine atom with H6, $6'$.

The *cis*-Ru(dmsazpy)$_2$Cl$_2$ complex exhibits similar pattern of *trans*-Ru(dmsazpy)$_2$Cl$_2$ but the chemical shift of each proton is significantly different from *trans* complex.

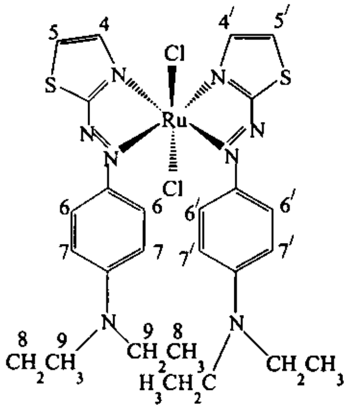


cis-Ru(dmsazpy)$_2$Cl$_2$ complex

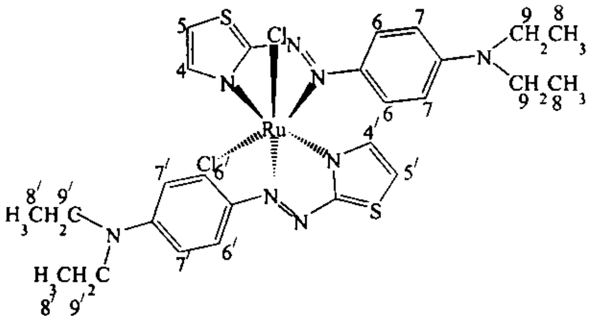
The H4, $4'$ in *cis*-Ru(dmsazpy)$_2$Cl$_2$ appeared at the higher chemical shifts relative to *trans*-Ru(dmsazpy)$_2$Cl$_2$ about 0.46 ppm. It may be due to the inductive Cl atom and N(th) which bound to metal. Whereas H5, $5'$ are similar to those in *trans* complex. On the other hand, the signals of H6, $6'$ and H7, $7'$ move upfield. Especially, $6,6'$-H are shifted about 0.79 ppm upfield relative to *trans* complex.

It is concluded that the chemical shifts of proton 4, $4'$ and 6, $6'$ used to identify different between the *trans*- and *cis*-isomers. In case of the *cis*-isomer, the signal of H4, $4'$ moves downfield than that of *trans*-isomer. Meanwhile, the signal of H6, $6'$ in *cis*-isomer also moves to upfield. These results of *trans* are in opposite direction which is due to different position of Cl atoms in their structures.

Since the single crystal of *trans*- and *cis*-Ru(desazpy)$_2$Cl$_2$ are not obtained but result from this technique can be used to characterize their structures. The ^{1}H NMR spectra of *trans*- and *cis*- Ru(desazpy)$_2$Cl$_2$ can confirm the isolated greenish-blue and pink-purple complexes. That are *trans-cis-cis* and *cis-trans-cis* configuration according to the similar pattern of the ^{1}H NMR of *trans* and *cis*-Ru(dmsazpy)$_2$Cl$_2$. Furthermore, the chemical shifts of these complexes are also observed nearly to values in *trans*- and *cis*-Ru(dmsazpy)$_2$Cl$_2$.



trans-Ru(desazpy)$_2$Cl$_2$ complex



cis-Ru(desazpy)$_2$Cl$_2$ complex

4.4 UV-Visible absorption spectroscopy

The appearances of absorption spectra arise from a part of molecules, which function to absorb light. It is abbreviated to chromophore. The chromophore is π bond system such as C=C, N=N and aromatic ring. In this work, the absorption spectra of free ligands and the complexes are recorded in the range 200-820 nm of various solvents. The absorption bands of ultraviolet and visible regions are in the range 200-400 nm and 400-820 nm, respectively.

The dmsazpy and desazpy ligands show two absorption bands at ~320 nm (~3000 M^{-1}cm^{-1}) and at ~480 nm (~40,000 M^{-1}cm^{-1}). These can be assign to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions centered primarily on the azo group and the conjugated π system. The $\pi \rightarrow \pi^*$ absorption band occurs at the lowest energy. In contrast to azpy ligand, the $n \rightarrow \pi^*$ transition at 450 nm (~950 M^{-1}cm^{-1}) is the lowest energy. The different of these ligands is the substituents (-NR$_2$, R = CH$_3$ and C$_2$H$_5$). The substituents of dmsazpy and desazpy are the auxochrome which effect on absorption of bonded chromophore. Indeed, the substituents are electron donating groups which can donate electrons to greater conjugated system. It leads to the HOMO level increased and close to LUMO, the energy transition is decreased. Therefore, the $\pi \rightarrow \pi^*$ transition is shifted to lower energy and gives more intense band than azpy ligand. Besides, the higher polarity of solvents give rise to bathochromic shift of $\pi \rightarrow \pi^*$ transitions. Because the π^* orbital is stabilized in higher polarity of solvent by increasing the electron donating group of the substituents. In case of dmsazpy and desazpy, the excited state (π^*) is stabilized while the ground state of azpy (n) is destabilized when the polarity of solvents increased.

Major absorption bands of all four isomers, *trans*- and *cis*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) appear above 450 nm and show highly intense allowed transitions in the visible region. There are assigned to $t_{2g}(Ru) \rightarrow \pi^*$ (L) transitions (MLCT) where the π^* level has large ligand character. The absorption spectra of *trans*-isomers differ from *cis*-isomers. The spectrum consists of two MLCT intense bands with different molar extinction coefficients. In general, *cis*-$Ru(L)_2Cl_2$ complexes exhibit intense absorption in the lower energy region compared to *trans*-$Ru(L)_2Cl_2$. This transition is absent in the free ligand.

In *trans*-forms, there are two absorption bands with similar molar extinction coefficient (ε ~30,000 $M^{-1}cm^{-1}$) in the range 490-516 nm and 680-712 nm. In contrast, *cis*-forms show two absorption bands with the different molar extinction coefficient values. One of these is observed in the range 500-510 nm, which is the most intense bands (ε ~40,000-50,000 $M^{-1}cm^{-1}$). The other is observed in the range 674-690 nm with the less intense band (~20,000 $M^{-1}cm^{-1}$). The colors of *trans*- and *cis*-isomers are greenish-blue and pink-purple, respectively.

The wavelength of 680-712 nm (ε ~30,000 $M^{-1}cm^{-1}$) are the absorption of the orange-red wave and desorption is green-blue wave. Thus, the *trans*-isomer are greenish-blue. For the *cis*-isomers, they absorb the blue-green colors (500-510 nm, ε ~40,000-50,000 $M^{-1}cm^{-1}$) and desorb the purple-red. Therefore, the *cis*-isomers are pink-purple.

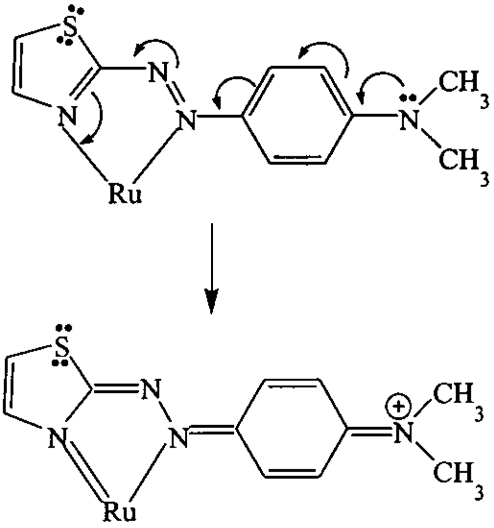
The *trans*- and *cis*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) give the absorption spectra at the lower energy than that of *trans*- and *cis*-$Ru(azpy)_2Cl_2$ complexes. Thus, it is expected that N-coordination of dmsazpy and desazpy ligands would stabilize the $Ru(t_2)$ level better than that in the case of N-coordination of azpy ligand. Furthermore, the dmsazpy and desazpy complexes show the solvent effect in various solvents when the polarity of solvents increased, the bathochromic shift was observed.

4.5 X-ray structures determination

The four isomeric complexes of $Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) are obtained from the reaction. However, only two of them are available single crystals suitable for X-ray technique. They are *trans*- and *cis*-$Ru(dmsazpy)_2Cl_2$ complexes. Although the *trans*- and *cis*-$Ru(desazpy)_2Cl_2$ could not crystallize to give single crystals. They are characterized from spectroscopic techniques, ^1H NMR spectra and electrospray mass spectra.

The structures of those complexes contain a six-coordinated ruthenium atom with two dmsazpy and two chloride atoms and distorted octahedral. The *trans*- and *cis*-$Ru(dmsazpy)_2Cl_2$ complexes are *tcc* and *ctc* configuration. The configuration is referred to Cl atom, N(th) and N(azo), respectively.

Results from table 29 indicated that the different values of the several planes of *trans*-complexes. It leads to the some delocalization of electrons through the metal center. However, *cis*-complexes gives less different values of planarity between two dmsazpys. This mean that they have differed delocalization of electron. In addition, the Table 32 showed the planarity of azo and phenyl are observed with dihedral angle (14.3(2)°) less than in *trans*-complex (28.8(2)° Table 29). Therefore, donating electrons of nitrogen atom from substituent into conjugated system can occur and increase electron density in thiazole ring. Thus, the N(th) bounded to Ru(II) with stronger σ donation. The conjugated structure is suggested in scheme III. The thiazole ring donates more σ-electrons to ruthenium(II) center. Therefore, Ru-N(th) bonds are stronger. Ruthenium(II) are rich of electron then it gives electrons back to the π^* orbital of azo character of ligand (π-backbonding). This results in shortening of the Ru-N(th) bond distances.



Scheme III

The results from the conjugated system in their structure showed that the Ru-N(th) bond distances become shorter. Whereas, the Ru-N(azo) bonds should be longer related to the azpy complexes. The substituent can donate electrons into dmsazpy structure which leads to extend conjugated system longer than that of azpy complex. These results are shown in Table 39.

Table 39 Bond distances of all complexes (Å)

Bonds	*trans* $Ru(dmsazpy)_2Cl_2$	*trans* $Ru(azpy)_2Cl_2$	*cis* $Ru(dmsazpy)_2Cl_2$	*cis* $Ru(azpy)_2Cl_2$
Ru-N(th)	2.063(2)	2.116(6)	2.040(2)	2.051(4)
N(py)	2.073(2)	2.099(5)	2.030(2)	2.045(4)
Ru-N(azo)	2.024(2)	1.986(5)	2.012(2)	1.984(4)
	2.014(2)	1.988(5)	2.041(2)	1.977(4)
N=N	1.326(3)	1.302(8)	1.324(3)	1.283(6)
	1.321(3)	1.306(7)	1.314(3)	1.279(7)
Ru-Cl	2.380(7)	2.377(15)	2.416(7)	2.401(1)
	2.379(7)	2.368(16)	2.402(6)	2.397(7)

4.5.1 X-ray data of Ru-N(th) bond

The substituents $-NR_2$ ($R = CH_3$ and C_2H_5) on the structures of ligands show sinificantly effect on the Ru-N(th) bond distances in the *trans*- and the *cis*-$Ru(dmsazpy)_2Cl_2$ complexes. This results are due to the delocalization of electrons followed by scheme III. In this work, the average Ru-N(th) bond distance in *trans*-form (2.068(2) Å) is longer than that of *cis*-form (2.035(2) Å). It is due to nitrogen atom of thiazole (Nth) are *trans* to azo function of different ligand which can compete electron density from Ru(II) center although they become stronger σ–donors. In contrast the *cis*-complex, both of nitrogen atoms of thiazole (Nth) are *trans*. They can be bounded to metal with electron density involving the same fill dπ orbital therefore, they become shorter than expected according to the average N(py) and N(th) distances, it can be arranged in order: *trans*-Ru(azpy)$_2$Cl$_2$ > *trans*-Ru(dmsazpy)$_2$Cl$_2$ > *cis*-Ru(azpy)$_2$Cl$_2$ > *trans*-Ru(dmsazpy)$_2$Cl$_2$. Thus, dmsazpy is ligand which gives more the σ donation ability to metal than azpy ligand.

4.5.2 X-ray data of Ru-N(azo) bond

In general, the Ru-N(azo) bond distances are shorter than Ru-N(th) bond distances. It is due to π-backbonding from Ru(II) to azo function. The *trans*-Ru(dmsazpy)$_2$Cl$_2$ complex shows the average Ru-N(azo) distance (2.019(2) Å) shorter than the average Ru-N(azo) of the *cis*-Ru(dmsazpy)$_2$Cl$_2$ (2.026(2) Å). However, this bond distance in the Ru(azpy)$_2$Cl$_2$ complexes are shorter. It is indicated that the Ru-N(azo) bonds of Ru(azpy)$_2$Cl$_2$ are stronger than that of Ru(dmsazpy)$_2$Cl$_2$ complexes Because of the donated electrons of substituent into the π^* orbital of azo function, Then, the π-backbonding from Ru(II) is decreased. This gives rise to the lengthening of Ru-N(azo) bonds in *trans*- and *cis*-Ru(dmsazpy)$_2$Cl$_2$ complexes relative to those in azpy complexes. It demonstrates that azpy is a π- acceptor than that of dmsazpy.

4.5.3 X-ray data of N=N bond

All of complexes showed the N=N bond distances are increased compared to that of free azpy ligand (N=N 1.248 (2) Å, Panneerselvam *et al.*, 2000). This may be due to stronger π-backbonding of $t_{2g}(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{L})$ orbital.

The N=N bond distances of *trans*-Ru(dmsazpy)$_2$Cl$_2$ complex is 1.323(2) Å longer than the *cis*-Ru(dmsazpy)$_2$Cl$_2$ (1.319(2) Å). It is due to the azo function, -N=N-, accepts more electrons from Ru(II) and from substituent. In contrast, the N=N bonds in Ru(azpy)$_2$Cl$_2$ complexes (1.304(2) Å for *trans*- and 1.281 (2) Å for *cis*-complexes) are shorter than that of dmsazpy complex. The reason is due to more conjugated structure of dmsazpy which allowed electrons continually delocalize in azo π^* orbital. Thus, it is not easy to arrange the π-acid properties of the ligand base on the azo distance. Furthermore, the role of π bonding of Ru-N(azo) is also evident in the long N-N distance and appear in lowered N=N stretching frequencies(Table 40).

Table 40 Bond distances and stretching mode of N=N in *trans*- and *cis*-Ru(L)$_2$Cl$_2$ (L = dmsazpy and desazpy) complexes

Complexes	*trans* Ru(dmsazpy)$_2$Cl$_2$	*trans* Ru(azpy)$_2$Cl$_2$	*cis* Ru(dmsazpy)$_2$Cl$_2$	*cis* Ru(azpy)$_2$Cl$_2$
N=N bond distance (Å)	1.323	1.304	1.319	1.281
N=N stretching mode (cm^{-1})	1244	1291	1247	1295

From the Table 40, the average N=N bond distance is increased, thus the N=N stretching frequencies is decreased.

4.5.4 X-ray data of Ru-Cl bond

The average Ru-Cl bond distances are 2.380(7) Å and 2.409(1) Å for *trans*-Ru(dmsazpy)$_2$Cl$_2$ and *cis*-Ru(dmsazpy)$_2$Cl$_2$, respectively.

The lengthening of Ru-Cl bond in *cis*-isomer is longer due to the repulsions between chlorides and strong interaction with electron clouds from the thiazole ring. Each chlorine atom is the opposite position with N(azo) that coordinated with stronger bond to Ru(II). It leads to lengthening of Ru-Cl bond distance. Furthermore, two chelate planes are deviated from orthogonality (dihedral angle 92.4 (1)°) possibly due to steric interaction. These results also consistent with in *trans*- and *cis*-$Ru(azpy)_2Cl_2$ complexes.

4.6 Electrochemistry

The metal oxidation and ligand reduction behaviors of the complexes have been studied by using cyclic voltammetry (CV) in acetonitrile (0.1 M TBAH). The potential range –2.0 to +2.0 V was applied by using a platinum-working electrode. All potentials are referenced to $Ag/AgNO_3$.

4.6.1 Reduction range (negative potential)

The reductive responses were scanned in the potential range 0.0 to –1.8 V. The reduction potential of dmsazpy and desazpy ligands display one reversible couple at scan rate 50 mV/s. This peak shows at –1.54 V ($\Delta Ep = 58$ mV) for dmsazpy and –1.56 V ($\Delta Ep = 78$ mV) for desazpy. The reduction is referred to the electron acceptance of the azo function, which is represented by Equation (3).

$$\begin{aligned} \text{dmsazpy} + e^- &\rightleftharpoons \text{dmsazpy}^- \\ \text{desazpy} + e^- &\rightleftharpoons \text{desazpy}^- \end{aligned} \qquad (3)$$

It is similar characters from free azpy ligand but the azpy showed the reversible couple of two electron transfer in one process at $E_{1/2}$ = -1.577 V (ΔEp = 171 mV) which suggested the following mechanism of the azpy reduction in equation (4) (Goswami *et al.*, 1983).

$$\text{azpy} + 2e^- \rightleftharpoons \text{azpy}^{2-}$$

will occur in two steps also follow:

$$[\text{-N=N-}] + e^- \rightleftharpoons [\text{-N-N-}]^-$$

$$[\text{-N-N-}]^- + e^- \rightleftharpoons [\text{-N-N-}]^{2-} \qquad (4)$$

The reduction potential represents the electron accepting ability of the ligand. The more positive potential are greater electron accepting ability. The reduction potential of azpy, dmsazpy and desazpy are compared and showed that dmsazpy and desazpy can accept the electron as well as azpy ligand. Therefore, it is interesting to compare the electron accepting ability of these ligand when coordinated to a metal atom further.

In reduction range, *trans*-Ru(L)$_2$Cl$_2$ (L = dmsazpy and desazpy) complexes give the quasi-reversible couple at $E_{1/2}$–0.98 V (ΔEp = 54 mV) for dmsazpy complex and –1.00 V (ΔEp = 54 mV) for desazpy complex at 50 mV/s. The electron transfer process is one electron and they also show an irreversible cathodic potential peaks at –1.25, -1.44 V for dmsazpy complex and –1.28, -1.49 V for desazpy complex.

In contrast, the *trans*-Ru(azpy)$_2$Cl$_2$ showed two reversible reduction couples at $E_{1/2}$ –1.03 V (ΔEp = 50 mV) and $E_{1/2}$ –1.63 V (ΔEp = 80 mV) . From the reduction potential, the π–accepting ability of these ligand can be arranged in order: dmsazpy > desazpy > azpy. Nevertheless, these results from X-ray data and IR data supported that the azpy has the greater π–accepting ability.

In case of *cis*-Ru(L)$_2$Cl$_2$ (L = dmsazpy and desazpy) complexes, in the reduction potential the quasi-reversible couple occur at $E_{1/2}$ –1.02 V (ΔEp = 44 mV) and $E_{1/2}$ −1.05 V (ΔEp = 50 mV) for dmsazpy and desazpy complexes at 50 mV/s. Whereas, the electron transfer process is one electron and they also show irreversible cathodic peaks at −1.37 and −1.22 mV for dmsazpy and desazpy complexes, respectively. However, the *cis*-Ru(azpy)$_2$Cl$_2$ showed two quasi-reversible couple at $E_{1/2}$ -1.94 V (ΔEp = 64 mV) and $E_{1/2}$ −1.77 V (ΔEp = 86 mV).

All of *trans*-Ru(L)$_2$Cl$_2$ (L = dmsazpy and desazpy) give more positive reduction potential than that in *cis*-Ru(L)$_2$Cl$_2$ complexes. Because stronger π-backbonding in *trans*-Ru(L)$_2$Cl$_2$ was obtained based on the shortening of Ru-N(azo) distances.

4.6.2 Oxidation range (positive potential)

In free ligands of dmsazpy and desazpy, each showed one irreversible anodic peak eventhough the various scan rate were applied and the other couple was observed at higher scan rate. It is referred to couple I and couple II. However, the appearance is not available for azpy ligand. It is due to the substituent group of dmsazpy and desazpy ligands. In order to prove this reason, the starting materials of *N,N*-dimethylaniline and *N,N*-diethylaniline were performed by cyclic voltammetric method. The cyclic voltammograms of both compounds (Figure 39 Appendix C) were obtained. There was one irreversible anodic peak in oxidation range which similar to the group I of dmsazpy and desazpy voltammograms.

The character of the group I of dmsazpy and desazpy was studied in the range +0.30 to +0.80 V. It showed the one irreversible peak eventhough the high scan rates were applied (200-1000 mV). Besides, the currents of anodic peak was increased when high potential scan rate supplied. The electron transfer process was followed by equation (5). The oxidation reaction occurred at phenyl ring. The available of electron donating groups, R referred to $-N(CH_3)_2$ and $-N(C_2H_5)_2$ provided the ease of redox reaction on phenyl(benzene) ring.

$$NSC_3H_2N{=}NC_6H_5\text{-}N(R)_2 \rightleftharpoons NSC_3H_2N{=}NC_6{}^{+}H_5\text{-}N(R)_2 + e^- \qquad (5)$$

The cyclic voltammogram of this couple of both ligands are shown in Figure 37 Appendix C)

The ligand couple II are studied in the range 0.78-1.10 V. The group II has a specific character that it must be produced from the anodic species of group I at +0.82 V (ΔEp = 40 mV) for dmsazpy and +0.83 V (ΔEp = 30 mV) for desazpy at scan rate 50 mV/s followed the equation (6).

$$NSC_3H_2N{=}NC_6{}^{+}H_5\text{-}N(R)_2 \rightleftharpoons NSC_3H_2N{=}NC_6{}^{2+}H_5\text{-}N(R)_2 + e^- \qquad (6)$$

The four isomeric complexes showed the redox of the three groups in oxidation range, the first was the redox of group I of ligand, the second was the redox of Ru(II/III) and the final was group II of ligand.

The ligand couple I was shifted to less potential in complexes when compared with free ligands. The potentials were +0.27 V (ΔEp = 34 mV for *trans*-Ru(dmsazpy$_2$)Cl$_2$, +0.24 V (ΔEp = 30 mV) for *trans*-Ru(desazpy$_2$)Cl$_2$, +0.38 V (ΔEp = 34 mV) for *cis*-Ru(dmsazpy$_2$)Cl$_2$ and +0.43 V (ΔEp = 50 mV) for *cis*-Ru(desazpy$_2$)Cl$_2$. The shifts of ligand group I were due to greater conjugation in ligands. This led to lower the π^* level. Therefore, the redox potential of phenyl ring occured at lower potential than that of free ligand.

The redox of Ru(II/III) in all complexes were found to be quasi-reversible couples when scanned in the range +0.70 to +1.10 V. The $E_{1/2}$ potential of *trans*-Ru(dmsazpy$_2$)Cl$_2$ is +0.84 V (ΔEp = 72 mV), +0.85 V (ΔEp = 44 mV) for *trans*-Ru(desazpy$_2$)Cl$_2$, +0.82 V (ΔEp = 60 mV) for *cis*-Ru(dmsazpy$_2$)Cl$_2$ and +0.79 V (ΔEp = 98 mV) for *cis*-Ru(desazpy$_2$)Cl$_2$. One can assign the stability of

Ru(II) in order of *trans*-Ru(desazpy$_2$)Cl$_2$ > *trans*-Ru(dmsazpy$_2$)Cl$_2$ > *cis*-Ru(dmsazpy$_2$)Cl$_2$ > *cis*-Ru(desazpy$_2$)Cl$_2$. Whereas, the *trans*- and *cis*-Ru(azpy)$_2$Cl$_2$ give the potential at +0.55 V (ΔEp = 60 mV) and +0.73 V (ΔEp = 63 mV), respectively.

In azpy complexes, *cis*-isomer is stabilized more than *trans*-isomer. In contrast to dmsazpy and desazpy complexes, which *trans*-isomer is more stabilized in the oxidative range than *cis*-isomer. The results agree well with the X-ray data for dmsazpy but not desazpy and IR results. It is shown in Table 41.

Table 41 The selected bond distances and formal potentials of all Ruthenium(II) complexes

compounds	*trans* Ru(desazpy)$_2$Cl$_2$	*trans* Ru(dmsazpy)$_2$Cl$_2$	*cis* Ru(dmsazpy)$_2$Cl$_2$	*cis* Ru(desazpy)$_2$Cl$_2$
Ru-N(th)	-	2.068	2.035	-
Ru-N(azo)	-	2.019	2.026	-
N=N (Å)	-	1.323	1.319	-
N=N (cm^{-1})	1239	1244	1247	1249
$E_{1/2}$	+0.85 (44)	+0.84 (72)	+0.82 (60)	+0.79 (98)

Data from Table 41 clearly show that $E_{1/2}$ increases as the average Ru-N(azo) bond decreases (increased π–bonding). Thus, the stronger the Ru-N(azo) bond and Ru-N(th) bond, the higher is the potential required to oxidize the metal- a result in consonance with principles of redox thermodynamics (Goswami *et al.*, 1983).

The dmsazpy and desazpy ligands can stabilize the Ru(II) in the complexes more than azpy. It caused from σ donating ability of thiazole ring to the parent molecule and increased the strength of σ bonding at thiazole toward to Ru(II) with more conjugation. Indeed, the desazpy is greater stabilized Ru(II). This redox is given in equation (7).

$$\mathrm{Ru^{III}(L)_2Cl_2} + e^- \rightleftharpoons \mathrm{Ru^{II}(L)_2Cl_2} \qquad (7)$$

The final groups are the ligand group II in all complexes which occur at higher potential than those in free ligands, +1.02 V for *trans*-Ru(dmsazpy$_2$)Cl$_2$, +1.02 V for *trans*-Ru(desazpy$_2$)Cl$_2$, +1.07 V for *cis*-Ru(dmsazpy$_2$)Cl$_2$ and +1.06 V for *cis*-Ru(desazpy$_2$)Cl$_2$. The shifting to higher potentials than that in free ligands caused by the complex is oxidized with two electrons before reaching to the potential of this species I forward scan oxidation side. Those oxidized electrons are from the ligand group I and the other from Ru center. Thus, the losing of one electron is difficult. The supplied potentials are higher than that of free ligands.