Chapter 5

SUMMARY

The bidentate ligands, dmsazpy and desazpy, are azo compounds, -N=N-C=N-, like azpy. When the thiazole system is incorporated into a chelate molecule, its chemical properties are different from pyridine system in azpy since the five-membered heterocyclic ring will impose a greater 'bite' to the chelate ring and thereby introduce some distortion into the metal ion environment (Fitzpatrick and Goodwin, 1982).

The dmsazpy and desazpy reacted with $Ru(dmso)_4Cl_2$ to give the four isomeric complexes of $Ru(L)_2Cl_2$ (L = dmsazpy and desazpy). The structures of $Ru(dmsazpy)_2Cl_2$ complexes were confirmed by X-ray analyses as *trans*- and *cis*- configurations referred to Cl atoms. In addition, the $Ru(dmsazpy)_2Cl_2$ and $Ru(desazpy)_2Cl_2$ complexes were characterized by spectroscopic methods. Although the *trans*- and *cis*-$Ru(desazpy)_2Cl_2$ complexes have not been determined by X-ray diffraction analyses but the electrospray mass spectroscopic, ^1H NMR, UV-Visible data can determine the structures to be the *trans*- and *cis*-configuration similar to the *trans*- and *cis*-$Ru(dmsazpy)_2Cl_2$ complexes.

The different isomers show specific characters in electrospray mass spectra and ^1H NMR results. From the electrospray mass spectra, the *trans*-isomer is preferably protonated, whereas the *cis*-isomer is preferably loss a chlorine atom and the Ru-Cl bond strength of *trans* isomer is greater than that of *cis*-isomer. Furthermore, the ^1H NMR data can determine the binding mode and stereochemistry of *trans*- and *cis*-isomer. In *cis*-isomer, proton-4 on thiazole ring is shifted to downfield, whereas, in *trans*-isomer, proton-6 on phenyl ring is shifted to downfield. It results from the interaction through space between the chlorine atom to these protons in their

structures. In addition, the *cis*-isomer exhibits more intense a MLCT transition with molar absorptivity than *trans*-isomer due to less symmetry of *cis*-isomer.

The effects of 5-membered heterocyclic ring, thiazole, and the substituents on the phenyl ring are studied from X-ray structure, infrared spectroscopic data and cyclic voltammetric technique. The five-membered ring of thiazole and the substituent, $-NR_2$ ($R = CH_3$, C_2H_5) on the para position make the different chemical properties from azpy. These substituents are planar to the phenyl planes (dihedral angle less than 5^o). Thus, it can donate electrons into the phenyl groups. The electrons delocalized in the conjugated system and were through the thiazole ring. These results gave significantly increasing the electron density on thiazole rings. That leads the Ru-N(th) bonds to become strong σ–donor. The Ru-N(th) distances are much shorter than Ru-N(py) in azpy complexes. It is indicated that dmsazpy and desazpy are stronger σ donor than azpy ligand. Besides, the conjugated system in dmsazpy and desazpy complexes make the Ru(II) stabilized. Therefore, the $E_{1/2}$ potentials of Ru(II/III) couple occur at higher potentials than that of azpy complexes.

Nevertheless, the azpy is still the stronger π acceptor ligand. It is agree well with the results data from X-ray and IR techniques. The N=N stretching mode in IR spectra of dmsazpy and desazpy are observed at lower energy than azpy complexes. That is due to the substituents, ($-NR_2$) of dmsazpy and desazpy are possible to donate electrons to the π^* orbital of the azo function thus the bond order of azo, -N=N-, is decreased related to azpy complexes. The results from X-ray and IR data can provide the arrangement of π acceptor properties of those ligands in the order azpy > dsazpy, dmsazpy. Whereas, the σ donating ability of these ligands are assigned in the reverse order of dmsazpy, desazpy > azpy.

One can conclude that the four isomeric complexes of $Ru(L)_2Cl_2$ are stable with the strong σ donating and weaker π-acceptor properties. This is due to ligands being five-membered heterocyclic rings and electron donating substituents.