

## Chapter 5

### CONCLUSION

The  $[\text{Ru}(\text{azpy})_2\text{L}]^{2+}$  complexes where  $\text{L} = \text{azpy}$ ,  $\text{azpym}$ ,  $\text{bpy}$  and  $\text{phen}$  ligands were synthesized by ligand substitution reactions. They were characterized by using elemental analysis, FAB mass, UV-Visible, infrared, 1D and 2D NMR and cyclic voltammetry. Besides, structures of the  $[\text{Ru}(\text{azpy})_3](\text{PF}_6)_2$ ,  $[\text{Ru}(\text{azpy})_2\text{bpy}](\text{PF}_6)_2$  and  $[\text{Ru}(\text{azpy})_2\text{phen}](\text{BF}_4)_2$  complexes were confirmed by X-ray crystallography.

The measured molecular weights using FAB mass spectrometry was consistent with expected value. Result from UV-Visible absorption spectroscopic data displayed  $\pi \rightarrow \pi^*$  and MLCT transition bands. The  $\text{bpy}$  and  $\text{phen}$  complexes showed MLCT band at lower energy than  $\text{azpy}$  and  $\text{azpym}$  complexes. Because  $\text{azpy}$  and  $\text{azpym}$  ligands are good  $\pi$ -acceptor ligand, back-bonding from  $\text{Ru}(\text{II})$  to  $\text{azpy}$  results in stabilization of the  $d\pi$ -levels relative to  $\pi^*$  ( $\text{bpy}$  and  $\text{phen}$ ) and an increase in the MLCT band energy. Besides, the NMR data of complexes showed signals in aromatic region. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR signals of all complexes were shifted to downfield than that of free ligand. The  $\text{bpy}$  and  $\text{phen}$  complexes showed only one set of ligand peaks which was due to the symmetry of molecule. The  $\text{azpy}$  complexes exhibited signals of three  $\text{azpy}$  ligands. Therefore, this complex was not equivalent which was similar to  $\text{azpym}$  complex. Infrared spectroscopic data showed that the  $\text{N}=\text{N}$  (azo) stretching modes in each complex were shifted to lower energy than that of free ligands ( $\text{azpy}$  and  $\text{azpym}$ ). The  $\text{N}=\text{N}$  stretching mode in  $\text{bpy}$  and  $\text{phen}$  complexes occurred at lower energy than  $\text{azpy}$  and  $\text{azpym}$  complexes. As the  $\text{azpy}$  and  $\text{azpym}$  complexes contained more azoimine groups than  $\text{bpy}$  and  $\text{phen}$  complexes. The

azoimine ligands had better  $\pi$ -acceptor properties than imine ligands, bpy and phen. Besides, the employed coligand becomes a better  $\pi$ -acceptor, there was competition with the ruthenium  $t_{2g}$  electron. This resulted in less  $\pi$ -back donation to azpy rising the azo bond order. This result was consistent with the N-N distance in X-ray crystallography. The N-N distances in  $[\text{Ru}(\text{azpy})_3](\text{PF}_6)_2$  complex were shorter than those in  $[\text{Ru}(\text{azpy})_2\text{bpy}](\text{PF}_6)_2$  and  $[\text{Ru}(\text{azpy})_2\text{phen}](\text{BF}_4)_2$  complexes. The average Ru-N(azo) distances were shorter than average Ru-N(py) distances. Besides, the average N-N distances of all the complexes were longer than free azpy. The shortness of Ru-N bond and length of N-N in complexes were attributed to  $d\pi$ - $p\pi$  interactions between ruthenium ( $t_2$ ) and  $\pi^*$ (azo) orbital of azpy ligand. In cyclic voltammetric data, the first reduction couple of azpym complex occurred at lowest negative potential than other complexes. Therefore, the azpym complex accepted electron better than the azpy, and the phen complexes.