

Chapter 5

SUMMARY

The $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) complexes have been synthesized by ligand substitution reaction. In the comparison with $[\text{Ru}(\text{bpy})_3]^{2+}$, it is found that the chemistry of azopyridine and azopyrimidine complexes are different when varying L ligands. The different of these complexes in UV-Visible absorption properties showed that the energy of $\pi \rightarrow \pi^*$ and MLCT transition bands are red shifted for $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ complexes compared to that of parent $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. The effects of the substituents, $-\text{N}(\text{CH}_3)_2$ and $-\text{N}(\text{C}_2\text{H}_5)_2$ on the para position displayed the different chemical properties from unsubstituted ligands. These substituents are electron donating groups which extend π conjugation of ligands then π^* levels are reduced. The energy of $\pi \rightarrow \pi^*$ transitions of the third ligand in complexes decrease in the order $\text{bpy} > \text{azpym} > \text{azpy} \approx \text{deazpym} > \text{dmazpy} \approx \text{deazpy}$. Infrared spectroscopic data showed that the N=N(azo) stretching modes are sensitive to the nature of the third ligands. In this series of complexes, the substituted azopyridine and azopyrimidine complexes displayed the N=N stretching modes at lower energy than in unsubstituted complexes. Furthermore, the effect of the third ligands in NMR examination showed that the third ligands are affected to each proton on bpy ligands which showed the different chemical shifts. The H3 and H4 in azpy, azpym and deazpym ligands are lower field than H3 onto the pyridine ring of bpy ligands in complexes. Whereas, the chemical shifts of H3 onto the pyridine ring of bpy ligands are lower field than H3 as the third ligands are dmazpy and deazpy in complexes. In addition, The H3 (azpyridine) and H4 (azpyrimidine) of the third ligands in complexes, it found that the chemical shift of unsubstituted ligand is lower

field than substituted ligands. The electrochemical properties of complexes in reduction potential exhibits the electron accepting ability of the ligand. The couples occurred at more positive potentials relative to the reduction of azo function of L while the third and the fourth reductions are related to the reduction of the bpy ligand. The azpym ligand is the best π -acceptor among these ligands. The $[\text{Ru}(\text{bpy})_2\text{azpym}]^{2+}$, $[\text{Ru}(\text{bpy})_2\text{dmazpy}]^{2+}$, $[\text{Ru}(\text{bpy})_2\text{deazpy}]^{2+}$ and $[\text{Ru}(\text{bpy})_2\text{deazpym}]^{2+}$ complexes cannot be observed the Ru(III)/Ru(II) couples within experimental condition. This results could be understood considering the nature of the third ligands. The redox couple of Ru(III)/Ru(II) in azopyrimidine complexes occurred at more positive potential than that of azopyridine complexes. This was in accord with the π -acidity order of the ligands : azopyrimidine > azopyridine > bipyridine.

The chemical properties of $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ complexes (L = azpy, dmazpy, deazpy, azpym and deazpym) depend on the third ligand (L). These complexes are determined by spectroscopic techniques and cyclic voltammetry exhibiting the different chemical properties when changing the third ligands.