Chapter 5

CONCLUSION

The 2,6-(diphenylazo)pyridine (diazpy) ligand which was azo compound, -N=N-C=N-, like azpy but had two azo functions, was synthesized by ligand substitution reactions. Then the $[Ru(diazpy)Cl_2]$ complex, where diazpy acted as a tridentate ligand and $[Ru(diazpy)(L)_2]^{2+}$ (L = azpy, bpy and phen) complexes, where diazpy acted as a bidentate ligand were also synthesized. They were characterized by using elemental analysis, FAB mass, UV-Visible, infrared, 1D and 2D NMR and their electrochemical properties were studied by cyclic voltammetry. Besides, the structure of the diazpy ligand and $[Ru(diazpy)(bpy)_2](BF_4)_2$ complex were confirmed by X-ray crystallography.

The measured molecular weights using FAB mass spectrometry was consistent with expected value. From UV-visible spectroscopic data, The $[Ru(diazpy)(L)_2]^{2+}$ (L = bpy and phen) complexes exhibited MLCT transition bands at lower energy than that of $[Ru(diazpy)(azpy)_2]^{2+}$ complex. Since, azpy is better π-acceptor than bpy and phen. Then π-back bonding from Ru(II) to azpy results in stabilization of the dπ-levels and increase in the MLCT energy. The MLCT band of $[Ru(diazpy)(L)_2]^{2+}$ (L = bpy and phen) complexes were red shifted from those of $[Ru(L)_3]^{2+}$ (L = bpy and phen) complexes. This result for $[Ru(diazpy)(azpy)_2]^{2+}$ was similar to $[Ru(azpy)_3]^{2+}$. Moreover, the NMR data of the free diazpy ligand and the precursor $[Ru(diazpy)Cl_2]$ complex showed a symmetric diazpy molecule. Whereas, it displayed asymmetric molecule in $[Ru(diazpy)(L)_2]^{2+}$ complexes. The ^1H NMR, ^{13}C NMR and DEPT signals of all complexes were shifted to lower field than those of free ligands due to coordination results of positive ruthenium center. Results of 2D NMR experiments,

^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC supported and agreed with 1D NMR data. The infrared spectroscopic data showed remarkable different N=N stretching frequencies of free ligands and complexes. The N=N stretching mode in each complex was shifted to lower energies than that of free ligand (diazpy and azpy). Besides, the N=N stretching mode of coordinated N=N appeared at lower energies than free N=N of diazpy in $[Ru(diazpy)(L)_2]^{2+}$ complexes because of π-back bonding result. These results were corresponded to the N-N distance in X-ray crystallography. In the case of the $[Ru(diazpy)(bpy)_2]^{2+}$ complex, the N-N distance of coordinated N=N was longer than free N=N and free. The bpy and phen complexes showed the N=N stretching modes at lower energy than azpy complex because the azpy complex contained more azoimine functions than bpy and phen complexes. As the azoimine ligands had better π-acceptor properties than imine ligands, bpy and phen, there was competition with the ruthenium t_{2g} electron. This result is less π-back donation to azpy and diazpy rising the azo bond order.

Results of the cyclic voltammetric data in the diazpy and azpy ligands, the first cathodic peak of diazpy occurred at higher positive potential than reduction couple of azpy. Whereas, in the $[Ru(diazpy)(azpy)_2]^{2+}$ complex, azpy could accept electron from $d\pi$ orbital of Ru better than diazpy due to decrease conjugation system in diazpy. Therefore, in this case azpy was better π-acceptor than the asymmetric diazpy ligand. Moreover, in the case of $[Ru(diazpy)(bpy)_2]^{2+}$ and $[Ru(diazpy)(phen)_2]^{2+}$ complexes the first and the second cathodic peaks were reduction peaks of diazpy and they occurred at less positive potential than the first couple of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes. The evidence of Ru-N (azo) distance in $[Ru(diazpy)(bpy)_2]^{2+}$ was shorter than Ru-N(pyridine) of bpy. Therefore, the diazpy ligand accepted electron better than the bpy and phen ligands.