Chapter 5

CONCLUSION

The characterization including X-ray structure determination has been made on the dmazpy, deazpy and $[Ru(tpy)(L)X]^{n+}$ (where L = dmazpy and deazpy, X = Cl⁻, CH_3CN and NO_2^-) complexes. The chemical properties of these complexes depend on the effect of vary monodentate (Cl⁻, CH_3CN and NO_2^-) and bidentate ligands (azpy, dmazpy and deazpy). Infrared spectroscopy, X-ray crystallography and cyclic voltammetry exhibit the different chemical properties when changing the monodentate and bidentate ligands .

The chemistry of $[Ru(tpy)(dmazpy)X]^{n+}$ and $[Ru(tpy)(deazpy)X]^{n+}$ (where X = Cl⁻, CH_3CN and NO_2^-) complexes are different when varying monodentate ligands. Infrared spectroscopic data show that the N=N (azo) stretching modes are sensitive to the nature of monodentate ligands. The monodentate ligands with π-accepting behavior result in increasing the $V_{(N=N)}$ vibration frequency. In this series of complexes, the highest N=N (azo) stretching vibration frequency belongs to nitro complex. It relates to X-ray data, the N=N bond distance of $[Ru(tpy)(dmazpy)NO_2]BF_4$ is shorter than that in $[Ru(tpy)(dmazpy)Cl]BF_4$. This result can confirm that the nitro group has strong π-interaction with the ruthenium center. The Ru-N (azo) bond distances in [Ru (tpy)(dmazpy)NO_2]BF_4 is longer than that in $[Ru(tpy)(dmazpy)Cl]BF_4$ due to the greater Ru-NO_2 π-interaction. In addition, the electrochemical results show the redox Ru(II/III) in nitro complex occurred at higher potential than that in chloro complex. It can indicate that the NO_2^- ligand is the best monodentate ligand to stabilize the ruthenium (II) center.

In another point, the chemical properties of $[Ru(tpy)(L)X]^{n+}$ (where L = dmazpy and deazpy) complexes affect on varying bidentate ligands. Dmazpy and deazpy are the derivatives of azpy. The electron donating substituents, $-N(CH_3)_2$ and $-N(CH_2CH_3)_2$, on the para position make the different chemical properties from the azpy. In the case of uncoordinated ligands, the N=N stretching mode of dmazpy and deazpy in infrared spectra are observed at lower energy than that in azpy, because the substituents donate electrons into the π^* orbital of azo function thus the bond order of azo moiety, N=N, is decreased. It corresponds to X-ray data. The N=N bond distance of free dmazpy is longer than that in free azpy. In the case of complexes, the N(py) of $[Ru(tpy)(dmazpy)Cl]BF_4$ shows the strong donation to Ru(II) and leads to decreasing of Ru-N(py) distances related to the results for $[Ru(tpy)(azpy)Cl/I]BF_4$ complex. The Ru-N(azo) bond distance in $[Ru(tpy)(dmazpy)Cl]BF_4$ is longer than that in $[Ru(tpy)(azpy)Cl/I]BF_4$. It give an evidence that the π-backbonding from Ru(II) center is decreased. Therefore, dmazpy and deazpy ligands are stronger σ donors than azpy ligand. It relates to cyclic voltammetry data. The first reduction couple of dmazpy and deazpy complexes occur at less positive potential than that in azpy complex. Then, dmazpy and deazpy ligands are weaker π acceptors than azpy. On the other hand, the Ru(II/III) redox of dmazpy and deazpy complexes occur at more positive potential than that of azpy complex. It indicates that the increase of conjugated system in dmazpy and deazpy complexes make the Ru(II) stabilized.