

Chapter 1

INTRODUCTION

1.1 Introduction

The chemical properties of ruthenium(II) complexes with chelating polypyridyl ligand groups have been extensively studied. The polypyridyl ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) were symmetric ligands which have σ -donor and π -acceptor properties. In addition, ruthenium(II) was well recognized as a metal ion capable of entering $d\pi$ - $p\pi$ back bonding with polypyridyl ligands. This gave rise to stabilize ruthenium(II) and their complexes showed some interesting properties. For example, solvent effects on photochemistry of $[\text{Ru}(\text{bpy})_3]^{2+}$ has been investigated and it has been used as a sensitizer in a variety of media (Caspar and Meyer, 1983).

Other applications of ruthenium(II) complexes with polypyridyl ligands were the complexes of $[\text{Ru}(\text{L})_3]^{2+}$, where L = polypyridyl bidentate ligand groups, acting as luminescence probes in DNA. It was useful in optically probing the kind of DNA bases. However, these various applications were related to chemical properties of complexes containing different ligands. The binding of mixed-ligand complexes of the type $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ (L = aromatic diimine) to DNA has been investigated. It was concluded that binding of $[\text{Ru}(\text{bpy})_3]^{2+}$ to DNA was negligible (Kumar, *et al.*, 1985). However, the relatively weak binding and the extent of enhancement on binding complexes as general nonradioactive nucleic acid probes. This probe was $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ (dppz = dipyrido[3,2:*a*-2',3':*c*]phenazine), which showed no photoluminescence in aqueous solution at ambient temperature, but displayed intense

photoluminescence in the presence of double-helical DNA (Friedman, *et al.*, 1990 and Jenkins, *et al.*, 1992).

Besides, bpy and phen ligands containing the azoimine (-N=N-C=N-) moiety are good π -acceptors toward ruthenium(II). Other ligand containing the azoimine moiety is 2-(phenylazo)pyridine (azpy). The azpy ligand is an asymmetric and a stronger π -acidity ligand than bpy (Krause and Krause, 1980). Azpy consists one pyridine ring with a pendent nitrogen donor atom from an azo function has been employed very recently in the development of transition metal coordination chemistry. The chemical and application of ruthenium(II) complexes with the azpy ligand have extensively studied.

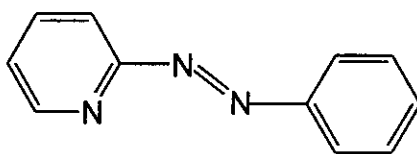
Furthermore, the complexes of $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ (L = 2-(phenylazo)pyridine, azpy and 2-(*m*-tolylazo)pyridine) were studied the chemical properties such as UV-Visible absorption which showed metal-to-ligand charge transfer (MLCT) in the visible region. The infrared spectra displayed the N=N(azo) stretching mode which was the important function group of azoimine ligands. Results from the cyclic voltammetry showed that the azopyridine ligand gave rise to stabilize ruthenium(II) (Goswami, *et al.*, 1981).

Considerable research has focused on the development of nonradioactive probes for nucleic acid. On the basis of the well-characterized photophysical properties of ruthenium polypyridyls, these various applications are related to chemical properties of complexes containing different ligands.

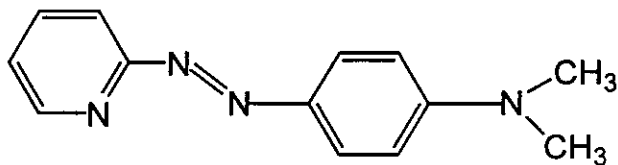
In the present work, ruthenium(II) complexes, $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ (where L = 2-(phenylazo)pyridine (azpy), 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy), 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy), 2-(phenylazo)pyrimidine (azpym) and 2-(4'-*N,N*-diethylaminophenylazo)pyrimidine (deazpym)) were synthesized and characterized. The dmazpy and deazpy ligands are azpy derivatives containing electron

-donating substituents, $-NR_2$ (where $R = -CH_3$ (for dmazpy) and $-C_2H_5$ (for deazpy)). The azpym ligand has pyrimidine ring instead of pyridine ring in azpy. The deazpym ligand is azpym derivative containing electron-donating groups, $-C_2H_5$. The chemical properties of these ligands in complexes were also investigated and compared with those in the $[Ru(bpy)_3]^{2+}$ complex by using spectroscopic and cyclic voltammetric techniques.

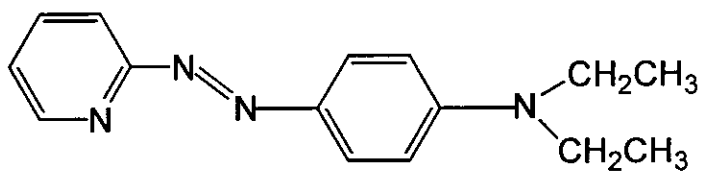
It is interesting to know how the $-NR_2$ groups effect the chemistry of $[Ru(bpy)_2L]^{2+}$. The structures of azpy, dmazpy, deazpy, azpym and deazpym ligands are shown in Figure 1.



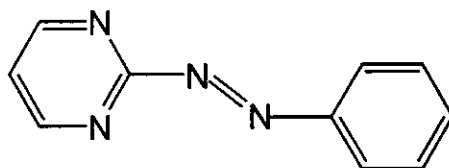
2-(phenylazo)pyridine (azpy)



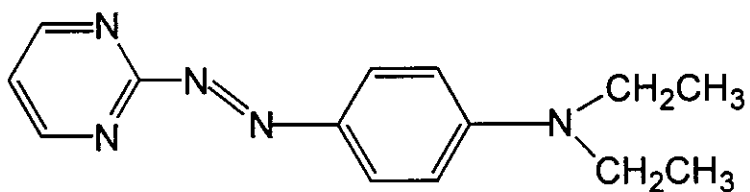
2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy)



2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy)



2-(phenylazo)pyrimidine (azpym)



2-(4'-*N,N*-diethylaminophenylazo)pyrimidine (deazpym)

Figure 1 The structures of azpy, dmazpy, deazpy, azpym and deazpym

1.2 Literatures reviews

Fergusson, *et al.* (1966) studied the electronic spectra of $[M(\text{bpy})_2\text{X}_2]$ and $[M(\text{bpy})_2\text{X}_2]\text{X}'$, where $M = \text{Fe, Ru and Os}$; $\text{X, X}' = \text{Cl, Br and I}$; $\text{X}_2 = 2,2'$ -bipyridine. These complexes were investigated by UV-Visible absorption spectroscopic technique.

Bryant, *et al.* (1971) synthesized complexes of the type $[M(\text{bpy})_3]^{2+}$, $[M(\text{bpy})_2\text{X}_2]^{n+}$, $[M(\text{bpy})_2\text{XY}]^{n+}$, $[M(\text{bpy})\text{X}_4]^{n+}$, $[M(\text{bpy})(\text{X}_2)_2]^{n+}$ and $[M(\text{bpy})\text{X}_2\text{Y}_2]^{n+}$ where $M = \text{Fe, Ru and Os}$; $\text{X, Y} = \text{monodentate ligands}$; $\text{X}_2 = \text{bidentate ligands}$. The charge-transfer and intraligand transition of these complexes have been studied by UV-Visible absorption spectroscopic technique.

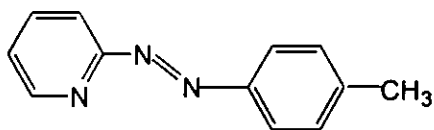
Brown, *et al.* (1976) synthesized complexes of the type $[M(\text{bpy})_2\text{L}]^{2+}$, where $\text{L} = \text{diamine ligands such as ethylenediamine (en)}$. These complexes were characterized by UV-Visible absorption spectroscopic, infrared spectroscopic, NMR spectroscopic and cyclic voltammetric techniques.

Sullivan, *et al.* (1978) synthesized the *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex which used as the starting material for the synthesis of other polypyridyl and phosphene complexes such as $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\text{Cl}]^{2+}$. The electronic spectra and redox properties were studied by UV-Visible absorption spectroscopy and cyclic voltammetry, respectively.

Krause (1978) synthesized the complex of *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ from starting material of $[\text{Ru}(\text{bpy})_2\text{py}_4]^{2+}$ solution ($\text{py} = \text{pyridine}$) and characterized this complex by infrared spectroscopy. Krause and Krause (1980) studied the isomeric complexes of $\text{Ru}(\text{azpy})_2\text{Cl}_2$. The complexes of $\text{Ru}(\text{azpy})_2\text{Cl}_2$ were synthesized from both $\text{Ru}(\text{dmsO})_4\text{Cl}_2$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ complexes and different isomers were obtained. These

complexes were characterized by infrared spectroscopy, ^{13}C NMR spectroscopy, UV-Visible absorption spectroscopy and cyclic voltammetry.

Goswami, *et al.* (1981) studied two types of ruthenium(II) complexes, RuX_2L_2 (green) and $[\text{Ru}(\text{bpy})_2\text{L}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (red), where $\text{bpy} = 2,2'$ -bipyridine, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $\text{L} = 2$ -(phenylazo)pyridine (azpy) or 2-(*m*-tolylazo)pyridine (tap). These complexes were characterized by infrared and UV-Visible absorption spectroscopy. In addition, the ^1H NMR spectrum of the $\text{Ru}(\text{tap})_2\text{X}_2$ showed methyl signal in CDCl_3 . The redox activities were done by cyclic voltammetric technique in acetonitrile and dichloromethane. The RuX_2L_2 complexes showed $\text{Ru}(\text{II}/\text{III})$ couple at higher potential than that of *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and several other dichlororuthenium(II) species. The azopyridine ligand can stabilize (with respect to oxidation potential) ruthenium(II) better than bpy.



2-(*m*-tolylazo)pyridine (tap)

Kumar, *et al.* (1985) studied the binding of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, of $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ and of $[\text{Ru}(\text{DIP})_3]\text{Cl}_2$ complexes to calf thymus DNA, where DIP = 4,7-diphenyl-1,10-phenanthroline. The photophysical properties of these complexes were investigated by spectroscopic techniques.

Amouyal and Homsí (1990) synthesized the $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ complex, where $\text{dppz} = \text{dipyrido}[3,2\text{:}a\text{-}2',3'\text{:}c]\text{phenazine}$. The chemical properties of this complex was characterized by UV-Visible absorption spectroscopy, emission and cyclic voltammetry.

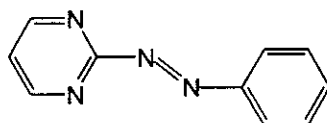
Friedman, *et al.* (1990) studied the binding of $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ to calf thymus DNA, where $\text{dppz} = \text{dipyrido}[3,2\text{:}a\text{-}2',3'\text{:}c]\text{phenazine}$. This complex showed no photoluminescence in aqueous solution at ambient temperature, but displayed intense photoluminescence in the presence of double-helical DNA.

Morgan, *et al.* (1991) studied the binding of $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ to calf thymus DNA, where L = aromatic diimine such as 4',7'-phenanthroline-5',6':2,3-pyrazine (ppz) or 2,3-di-2-pyridylpyrazine (ddp) by using absorption, emission and circular dichroism spectroscopy and equilibrium dialysis binding studies.

Ye, *et al.* (1995) synthesized the complexes of $[\text{Ru}(\text{bpy})_2(\text{phen})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ru}(\text{bpy})_2(\text{Me-phen})](\text{ClO}_4)_2$, where phen = 1,10-phenanthroline and Me-phen = 5-methyl-1,10-phenanthroline. The structures of these complexes were confirmed by X-ray crystallography. Both complexes were studied by UV-Visible absorption spectroscopy, infrared spectroscopy, Electrospray mass spectrometry, ^1H NMR, ^{13}C NMR and elemental analysis.

Santra, *et al.* (1999) synthesized and isolated three isomers of $\text{Ru}(\text{aapm})_2\text{Cl}_2$ (aapm = 2-(arylazo)pyrimidine) complexes. They were determined to have *trans-cis-cis* (tcc), *cis-trans-cis* (ctc) and *cis-cis-cis* (ccc) configurations by X-ray crystallography with referred to the order of coordination pair as Cl, N(pyrimidine), N(azo). In both of these structures, the Ru-N(azo) distances were relatively shorter than those of Ru-N(pyrimidine) distances indicating stronger bonding of the former and the $\text{Ru}(\text{aapm})_2\text{Cl}_2$ π -interaction that was localized in the Ru-N(azo) fragment. The structure of all isomers were supported by infrared and ^1H NMR spectroscopy. In addition, the cyclic voltammetric data showed the Ru(III)/Ru(II) couple at higher potential than those in $\text{Ru}(\text{bpy})_2\text{Cl}_2$, $\text{Ru}(\text{azpy})_2\text{Cl}_2$ and $\text{Ru}(\text{aai})_2\text{Cl}_2$ (aai = 2-aryl

azoimidazole) complexes. Then the order of the π -acidity of ligands can be arranged as; azopyrimidine > azoimidazole > bpy.



2-(arylamino)pyrimidine

Wang, *et al.* (2001) synthesized and characterized the $[\text{Ru}(\text{bpy})_3]\text{N}_3\text{Cl}\cdot 2\text{H}_2\text{O}$ complex by UV-Visible absorption spectroscopy and infrared spectroscopy. The structure of this complex was confirmed by X-ray crystallography.

1.3 Objectives

1. To synthesize the $[\text{Ru}(\text{bpy})_2\text{L}](\text{BF}_4)_2$ complexes, where L = azpy, dmazpy, deazpy, azpym and deazpym.
2. To characterize and study of chemical properties of these complexes and to compare with those of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex.
3. To analyze and summarize the effect of varying the third ligands on those complexes.