

Chapter 1

INTRODUCTION

1.1 Introduction

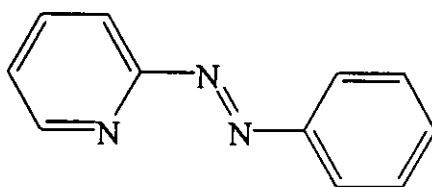
Ruthenium (Ru) is a rare element with atomic number 44. The melting point of Ru is 2546 °C and they are a brittle gray-white metal. The electronic configuration is [Kr] (4d)⁷ (5s)¹. The ruthenium metal is not oxidized by air at room temperature but it is oxidized at high temperature (>900 °C).

Ruthenium (II) complexes have been chosen for studying because of the kinetically inert character of the low-spin d⁶ species and well recognized as a metal ion capable of entering into dπ-pπ back bonding with polypyridyl and azoimine ligands. This phenomena could lead to stabilize Ru(II) center and gave rise to a number of interesting properties (Krause and Krause, 1980). The polypyridyl ligand is a symmetric bidentate ligand, which has σ-donor and π-acceptor properties such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen). The ruthenium(II) complexes with bpy and phen ligands had a lot of applications such as the chiral metal complexes of [Ru(bpy)₃]Cl₂, [Ru(phen)₃]Cl₂ and [Ru(DIP)₃]Cl₂ (DIP = 4,7-diphenyl-1,10-phenanthroline) bound to double helical DNA by intercalation (Kumar, *et al.*, 1985). Furthermore, the interaction of [Ru(phen)₃]²⁺ with nucleic acids showed two primary modes of binding (intercalation and surface binding) (Barton, *et al.*, 1986). The [Ru(phen)₂taptp]²⁺ and [Ru(phen)₂dptatp]²⁺ complexes, where taptp = 4,5,9,18-tetraazaphenanthreno[9,10-b]triphenylene and dptatp = 2,3-diphenyl-1,4,8,9-tetraaza-

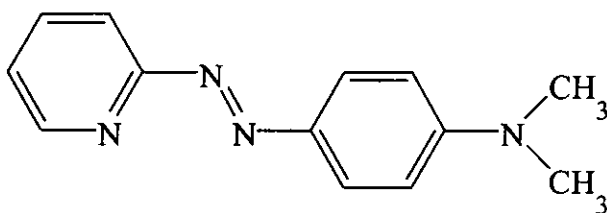
triphenylene, were used as probes in DNA conformation (Zhen, *et al.*, 2000). Besides, the $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ complex (dppz = dipyrrophenazine) acted as luminescent probes in DNA (Nair, *et al.*, 1998).

In addition, the azoimine ligand such as 2-(phenylazo)pyridine (azpy) is an asymmetric bidentate ligand and stronger π -acidity ligand than bpy (Krause and Krause, 1980). The ruthenium(II) complexes with azpy ligand have been used for several applications. For example, the complexes of $\text{Ru}(\text{azpy})_2\text{Cl}_2$ had been used as catalyst for epoxidation reactions of olefin to give epoxide (Barf and Sheldon, 1995). Besides, the complexes of $\alpha\text{-Ru}(\text{azpy})_2(\text{NO}_3)_2$ or *cis*- $\text{Ru}(\text{azpy})_2\text{Cl}_2$ showed the strong binding to DNA-model bases (Hotze, *et al.*, 2000)

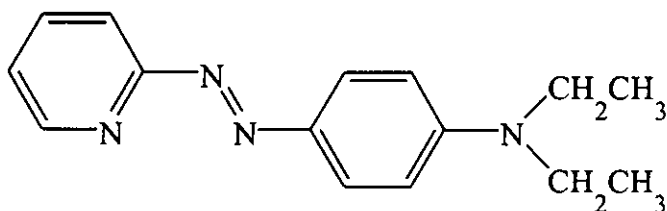
In this work, 2-(phenylazo)pyridine (azpy), 2-(4'-*N,N*-dimethylamino phenylazo)pyridine (dmazpy), 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy), 2-(phenylazo)pyrimidine (azpym) and 2-(4'-*N,N*-diethylaminophenylazo)pyrimidine (deazpym) ligands have been chosen as the bidentate ligands in $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$ complexes where L are azpy, dmazpy, deazpy, azpym and deazpym ligands (the structures of ligands are shown in Figure 1). These ruthenium (II) complexes have been synthesized and characterized by the electrospray and the fast-atom bombardment mass spectrometry, infrared spectroscopy, UV-visible absorption spectroscopy, NMR spectroscopy and cyclic voltammetry. Furthermore, single-crystal X-ray diffraction method has been used to determine the crystal structure of azpy ligand.



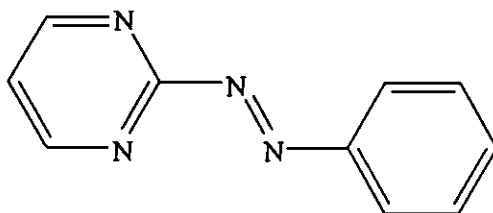
2-(phenylazo)pyridine (azpy)



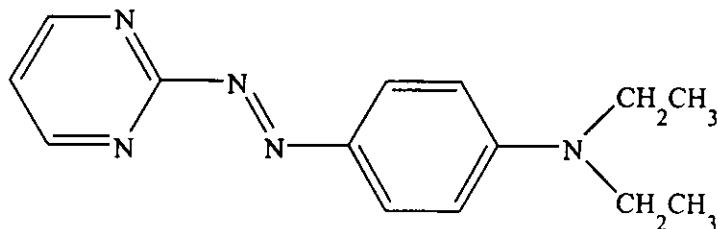
2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy)



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 ligands.

1.2 Literature reviews

Dwyer, *et al.*, (1963) studied the reaction of the $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$ and $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ complexes ($\text{L} = \text{Cl}^-, \text{Br}^-, \text{I}^-$, water, pyridine, acetylacetonone) have been prepared by the pyrolysis of $[\text{phen H}][\text{Ru}(\text{phen})_2\text{Cl}_4]$ or $[\text{bpy H}][\text{Ru}(\text{bpy})_2\text{Cl}_4]$ at 300°C .

Tokel-Takvoryan, *et al.*, (1973) studied the electrochemistry and electro-generated chemiluminescence (ecl) of the $[\text{Ru}(\text{phen})_3]^{2+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{terpy})_2]^{2+}$ and $[\text{Ru}(\text{TPTZ})_2]^{2+}$ complexes where phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine, terpy = 2,2':6',2''-terpyridine and TPTZ = 2,4,6-tripyridyl-*s*-triazine in acetone solution. All complexes showed evidence of several one-electron reduction and oxidation steps to form stable products.

Sullivan, *et al.*, (1978) synthesized the two types of mixed complexes, e.g., $[\text{Ru}(\text{bpy})_2(\text{PPh}_3)\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]^{2+}$ complexes and studied the electronic spectra and redox properties. These results indicated that phosphorus ligands stabilize the Ru (II) of these ions to a greater extent than pyridine type ligands.

Krause and Krause, (1980) studied dichlorobis(2-phenylazopyridine) ruthenium(II) complexes, $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$. Three isomers of $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$ were obtained from reaction between 2-(phenylazo)pyridine (azpy) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. Two forms of *cis*-isomers (α and β) and one *trans*-isomer (γ) were characterized by IR spectroscopy, UV-visible absorption spectroscopy and ^{13}C NMR techniques. The results from cyclic voltammetric data showed that the azpy ligand was a better π -acceptor than bpy ligand.

Bonneson, *et al.*, (1983) synthesized the complexes of *trans*- $[\text{Ru}(\text{phen})_2\text{L}_2]$ (PF_6)₂, ($\text{L} = \text{H}_2\text{O}, \text{CH}_3\text{CN}$ and py) by photolysis of the *cis*- $[\text{Ru}(\text{phen})_2\text{Cl}_2]$ complex in aqueous HPF_6 solution with complete retention of the stereochemistry. Photolysis of the *trans* complexes resulted in efficient rearrangement to the *cis* geometry. These complexes were characterized by IR spectroscopy, UV-visible absorption

spectroscopy, ^{13}C NMR spectroscopy and cyclic voltammetry techniques. Furthermore, the *trans*- $[\text{Ru}(\text{phen})_2(\text{py})_2](\text{PF}_6)_2$ was characterized by single-crystal X-ray diffraction.

Barton, *et al.*, (1984) studied the chiral complexes of $[\text{Ru}(\text{phen})_3]^{2+}$ bound to DNA by intercalation. The direct comparison between spectroscopic features, binding properties and structural parameters of enantiomers established that the Δ form possesses the greater affinity for a right-handed helix.

Santra, *et al.*, (1999) synthesized and isolated three isomers of $\text{Ru}(\text{aapm})_2\text{Cl}_2$ (aapm = 2-(phenylazo)pyrimidine) complexes. They were determined as *trans-cis-cis* (*tcc*), *cis-trans-cis* (*ctc*) and *cis-cis-cis* (*ccc*) configurations with referred to the order of coordination pairs as Cl, N(pyrimidine), N(azo). The isomers of *tcc* and *ccc* were confirmed by X-ray crystallography. Both of these structures, the Ru-N(azo) distances were shorter than Ru-N(pyrimidine) distances indicating stronger bonding of the former and the presence of a Ru-(aapm) π -interaction that was localized in the Ru-N(azo) fragment. The structures of all isomers were studied by IR 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-arylazoimidazole) complexes.

Ji, *et al.*, (2000) studied the $[\text{Ru}(\text{phen})_2\text{bpm}](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2\text{bpm}](\text{PF}_6)_2$ complexes, where bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline and bpm = 2,2'-bipyrimidine. The characterization were carried out using electrospray mass spectrometry, UV-visible absorption spectroscopy, ^1H and ^{13}C NMR spectroscopy, electrochemistry and X-ray single crystal diffraction analysis. The results showed that the spectroscopic and electrochemical properties of both complexes were similar to those of their parent complexes $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$. The $[\text{Ru}(\text{bpy})_2\text{bpm}](\text{PF}_6)_2$ and $[\text{Ru}(\text{phen})_2\text{bpm}](\text{PF}_6)_2$ complexes could be used as building blocks for the construction of molecular device.

Panneerselvan, *et al.*, (2000) reported the crystal structure of the [protonated 2-(phenylazo)pyridine and protonated 2-(hydroxylazo)pyridine (3:1)] tetrafluoroborate compound. The results from X-ray data indicated that the protonation occurred at N (azo) atom and it was more basic than N(pyridine). The azpy compound was normally liquid at room temperature but this crystal structure was stabilized by intermolecular H-bonding, N-H-N and van der Waals force.

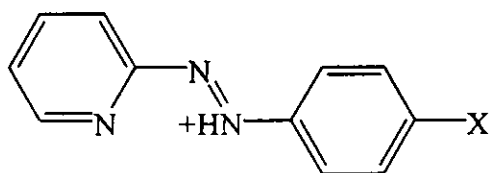


Figure 2 Structure of protonated azpy, X = H(75%) and OH(25%).

Zhen, *et al.*, (2000) synthesized the $[\text{Ru}(\text{phen})_2\text{taptp}]^{2+}$ and $[\text{Ru}(\text{phen})_2\text{-dptatp}]^{2+}$ complexes (taptp is 4,5,9,18-tetraazaphenanthreno[9,10-b]triphenylene and dptatp is 2,3-diphenyl-1,4,8,9-tetraazatriphenylene). These complexes were characterized by elemental analyses, ^1H NMR spectroscopy, UV-Visible absorption spectroscopy and electrochemistry. Both complexes luminesced in organic solvent but were quenched in water to different extents. Furthermore, the interaction of the complexes with calf thymus DNA was studied by absorption and emission spectra and measured viscosity and lifetime. All data indicated that both complexes bound with double stranded calf thymus DNA via intercalative mode. $[\text{Ru}(\text{phen})_2\text{taptp}]^{2+}$ showed negligible luminescence in water buffer but bright luminescence on binding to DNA, enabling it to be a sensitive probe for DNA conformation.

Baranoff, *et al.*, (2002) synthesized and investigated photochemical substitution reactions of $\text{Ru}(\text{phen})_2\text{L}^{2+}$, where L were derivatives of bipyridine and bis-benzonitrile derivatives. In the presence of a bis-benzonitrile derivative, acted as a

bidentate chelate, photoexpulsion of L was performed under the action of visible light, with quantitative formation of new complexes of the type $\text{Ru}(\text{phen})_2\text{L}'^{2+}$ (L' = bis-nitrile ligand). The $\text{Ru}(\text{phen})_2(\text{dCN}_3)(\text{PF}_6)_2$, $\text{Ru}(\text{phen})_2(\text{dCN}_4)(\text{PF}_6)_2$, $\text{Ru}(\text{phen})_2(6,6'\text{-dmbp})(\text{PF}_6)_2$ and $\text{Ru}(\text{phen})_2(\text{biq})(\text{PF}_6)_2$ complexes had been characterized by X-ray crystallography.

1.3 Objectives

1. To synthesize and to characterize the $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$, where L are azpy, dmazpy, deazpy, azpym and deazpym ligands.
2. To study and to summarize the chemistry of $[\text{Ru}(\text{phen})_2\text{L}]^{2+}$, where L are azpy, dmazpy, deazpy, azpym and deazpym ligands compared to those of the $[\text{Ru}(\text{phen})_3]^{2+}$ complex.