

Chapter 1

INTRODUCTION

1.1 Introduction

There is an intense research interest in the chemistry of ruthenium(II) complexes with polypyridyl and azoimine ligands due to σ -donor and π -acceptor properties of these ligands. The functional units of polypyridyl (-N=C-C=N-) and azoimine (-N=N-C=N-) had a strong ability to stabilize the low valent ruthenium center.

The polypyridyl ligands are symmetric bidentate ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen). The ruthenium(II) complexes with bpy and phen such as the $[\text{Ru}(\text{phen})_2(\text{taptp})]^{2+}$ and $[\text{Ru}(\text{phen})_2(\text{dptatp})]^{2+}$ complexes, where taptp = 4,5,9,18-tetraazaphenanthreno[9,10-b]triphenylene and dptatp = 2,3-diphenyl-1,4,8,9-tetraazatriphenylene had a lot of applications. For example, they were used as probes in DNA conformation (Zhen, *et al.*, 2000). Besides, the $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$, where dppz = dipyrido[3,2: a-2',3':c]phenazine showed no photoluminescence in aqueous solution at ambient temperature, but displayed intense photoluminescence in the presence of double-helical DNA (Friedman, *et al.*, 1990). The 2-(phenylazo)pyridine (azpy) containing azoimine function was an asymmetric bidentate ligand and stronger π -acid than bpy and other family of N-N donor ligands (Krause and Krause, 1980). There were variety of applications of the ruthenium(II) complexes with azoimine ligands. For example, the complexes of $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$ have been used as catalysts in epoxidation reaction (Barf, *et al.*, 1995). Moreover, the *cis*-isomeric complex of $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$ showed remarkably high cytotoxicity against a series of tumor-cell lines (Velders, *et al.*, 2000).

Some pyridine base had a bidentate property. Furthermore, some pyridine-based tridentate ligands are interesting to be investigated. This is primarily due to their ability to stabilize metal center under a variety of oxidative and reductive conditions and the fact that pyridine ligands are on the borderline between hard and soft Lewis bases. For example, the well-known 2,2': 6',2''-terpyridine (tpy) ligand. Besides, 2,6-pyridiyl-diimines (pydim) has emerged as an alternative to tpy (Cetinkaya, *et al.*, 1999). The pydim behaved as a tridentate ligand in complexes such as five-coordinate $[MX_2(\text{pydim})]$ ($M = \text{Mn, Fe; Co, Ni, Cu, Zn, Cd; X = Cl, Br}$) complexes and six-coordinate $[M(\text{pydim})_2]X_2$ ($X = \text{BF}_4^-, \text{ClO}_4^-$) complexes. Pydim has been observed to function as a bidentate chelating ligand in certain carbonyl derivatives (Albon, *et al.*, 1989).

In recent years, several researcher extensively studies the chemistry of ruthenium(II) complexes with three electron-donating ligands such as the 3,6-di-(4-methylpyrid-2-yl)pyridazine (4,4'-dppi) acting as a bidentate ligand. Ruthenium(II) complexes with 4,4'-dppi, the *in*- and *out*- $[\text{Ru}(\text{tpy})(4,4'\text{-Me}_2\text{dppi})(\text{OH}_2)]^{2+}$ used as catalysts in oxidation reaction of benzyl alcohol (Catalano, *et al.*, 2000).

Therefore, in this work it is interesting to synthesize and to investigate the chemistry of a new ligand, which is 2,6-(diphenylazo)pyridine (diazpy). This compound has two azo groups as shown in Figure 1.

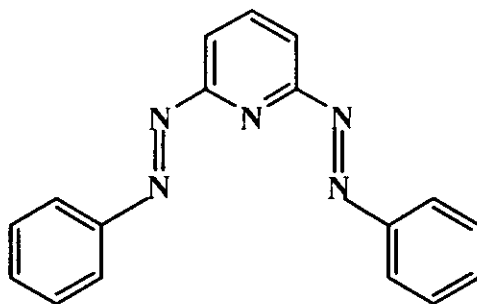
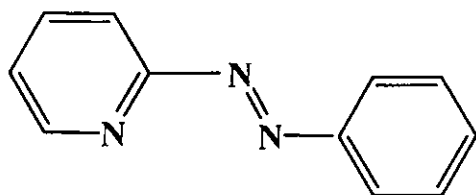
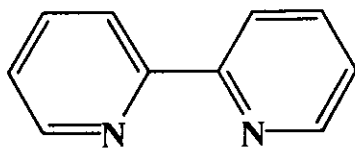


Figure 1 The structure of 2,6-(diphenylazo)pyridine (diazpy).

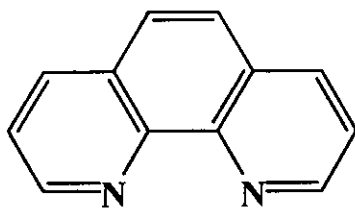
Moreover, ruthenium(II) complex with diazpy, $[\text{Ru}(\text{diazpy})\text{Cl}_2]$ (where diazpy as tridentate ligand), was synthesized and characterized. This complex was used as a precursor for synthesis of the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ (where diazpy as bidentate ligand; $\text{L} = \text{azpy}$, bpy and phen). These ruthenium(II) complexes with diazpy ligand have been synthesized and characterized by FAB mass spectrometry, elemental analysis, Infrared spectroscopy, UV-Visible absorption spectroscopy, NMR spectroscopy, and cyclic voltammetry. Besides, X-ray diffraction technique has been used to explore the structures of the diazpy ligand and the $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ complex. The structures of azpy, bpy and phen are shown in Figure 2.



2-(phenylazo)pyridine (azpy)



2,2'-bipyridine (bpy)



1,10-phenanthroline (phen)

Figure 2 The structures of azpy, bpy and phen ligands.

1.2 Review of Literatures

Tokel-Takvoryan, *et al.*, (1973) studied the electrochemistry and electrogenerated chemiluminescence (ecl) of four ruthenium(II) chelates, Ru(L)_x^{n+} ($x = 3, n = 2, L = 2,2'$ -bipyridine (bpy); $x = 3, n = 2, L = 1,10$ -phenanthroline (phen); $x = 2, n = 2, L = 2,2':6',2''$ -terpyridine (tpy)). All compounds showed evidence of several one-electron reduction and oxidation steps to form products stable during cyclic voltammetric scans. The bpy, phen and tpy complexes produced ecl via redox reactions of oxidized and reduced forms to form emitting species, which have been identified as the triplet state by comparison with their luminescence spectra; the ecl of the bpy complex was the most intense.

Krause and Krause, (1980) studied dichlorobis(2-phenylazo)pyridine 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 $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. There were *cis*-isomer (α and β) and one *trans*-isomer (γ). These complexes 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.

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

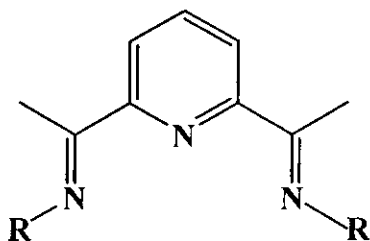
Thorp, *et al.*, (1993) studied the new DNA cleavage agents based on $[\text{Ru}(\text{tpy})(\text{bpy})\text{O}]^{2+}$ complex, oxoruthenium(IV), which 1,10-phenanthroline (phen), 2,4,6-

tripyrindyl-triazine (tpt) and N,N,N',N' -tetramethylethylenediamine (tmen) replaced 2,2'-bipyridine (bpy). These complexes were investigated by electrochemistry, UV-Visible absorption spectroscopy, electrophoresis and single crystal X-ray diffraction.

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, electrospray mass spectrometry, ^1H NMR, ^{13}C NMR and elemental analysis.

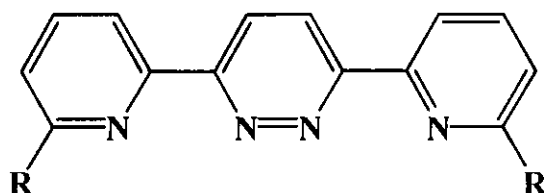
Pramanik, *et al.*, (1998) studied the chemistry of $[\text{Ru}(\text{tpy})(\text{azpy})\text{Cl}]^+$ complex and the monodentate ligand was varied. In addition, $[\text{Ru}(\text{tpy})(\text{azpy})(\text{OH}_2)]^{2+}$ complex acted as a catalyst for the oxidation of water to oxygen via $[\text{Ru}(\text{tpy})(\text{azpy})(\text{O})]^{2+}$ complex.

Cetinkaya, *et al.*, (1999) studied the reaction of $[\text{RuCl}_2(p\text{-cymene})]_2$ with tridentate N,N',N'' ligands, 2,6-pyridyl-diimines. This led to substitution of p -cymene. These complexes exhibited efficient activity for epoxidation of cyclohexene in the presence of iodosobenzene (PhIO). The molecular structure for one of complexes, (acetonitrile){2,6-bis[1-(4-methoxyphenylimino)ethyl]pyridine}dichlororuthenium(II) has been determined by X-ray diffraction.



Pydim (R = alkyl or aryl)

Catalano, *et al.*, (2000) synthesized the geometric isomers, *in*- and *out*-[Ru(tpy)(4,4'-Me₂dppi)(OH₂)]²⁺, where 4,4'-dppi = 3,6-di-(4-methylpyrid-2-yl)pyridazine. The redox properties in aqueous solution of both complexes showed pH-dependent corresponding to the formation of Ru(IV)=O complexes. They acted as catalysts in oxidation reaction of benzyl alcohol.



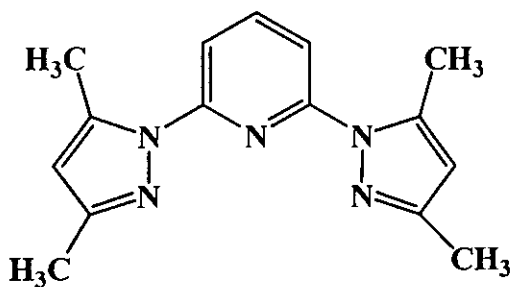
4,4'-dppi (R = H, Cl or CH₃)

Hossain, *et al.*, (2000) synthesized a novel dinuclear ruthenium complex, [(tpy)Ru(tmbimbyH₄)Ru(tpy)](ClO₄)₄, where tpy = 2,2':6',2''-terpyridine and tmbimbyH₄ = 2,6,2',6'-tetra(4,5-dimethylbenzimidazol-2-yl)-4,4'-bipyridine. Both fully protonated and deprotonated forms of the dinuclear Ru complexes were isolated and these compounds were interchangeable by the addition of acid or base. It was observed that when the protonated Ru complex was fully deprotonated, the maximum wavelength became red shift. Besides, a negative oxidation potential shift was also observed.

Zhen, *et al.*, (2000) synthesized the [Ru(phen)₂taptp]²⁺ and [Ru(phen)₂dptatp]²⁺ complexes (taptp = 4,5,9,18-tetraazaphenanthreno[9,10-*b*]triphenylene and dptatp =

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 luminescence in organic solvent but were quenched in water with 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. $[\text{Ru}(\text{phen})_2\text{tapt}]^{2+}$ showed negligible luminescence in water buffer but bright luminescence on binding to DNA, enabling it to be a sensitive probe for DNA conformation.

Chryssou, *et al.*, (2002) synthesized a new complex, $[\text{Ru}(\text{II})(\text{dcbpyH}_2)(\text{bdmpp})\text{Cl}](\text{PF}_6)$ (where $\text{bdmpp} = 2,6\text{-bis}(3,5\text{-dimethyl-N-pyrazoyl})\text{pyridine}$, dcbpyH_2 is 2,2-bipyridine-4,4-dicarboxylic acid). This complex was characterized by mass spectroscopy, IR, ES-MS and ^1H NMR (1D and 2D) spectroscopies. The broad and very high intensity MLCT absorption band in the visible made this dye potentially beneficial for the photosensitization process. Cyclic voltammetry analysis displays a well reversible oxidation-reduction wave. Transparent TiO_2 thin film electrodes could easily be chemically modified by the complex and the incorporation of the resulting photoelectrodes in wet regenerative solar cells produced a stable photovoltage of 550 mV and gave a continuous photocurrent of $140 \mu\text{A cm}^{-2}$.



2,6-bis(3,5-dimethyl-N-pyrazoyl)pyridine (bdmpp)

Konno, *et al.*, (2002) studied the chemistry of $[\text{Ru}(\text{tpy})(\text{N-N})\text{Cl}]^+$ where N-N = 2-(2'-dimethylaminoethyl)-pyridine (DMAEPy) and 2-(2'-diethylaminoethyl)-pyridine (DEAEPy). The spectroscopic, electrochemical and photochemical property of these complexes were studied and compared to those of the corresponding primary-amine complexes, $[\text{Ru}(\text{tpy})(\text{AEPy})\text{Cl}]^+$ where AEPy = 2-(2'-aminoethyl)-pyridine. The electrochemical results showed that DMAEPy and DEAEPy had stronger electron donating abilities than AEPy.

Vedernikov, *et al.*, (2002) synthesized the tripyridinedimethane (tpdm), consisting of three pyridine residues linked at their ortho carbons by two CH_2 groups, was showed to be a sterically flexible ligand capable of binding in a meridional arrangement in trigonal bipyramidal (tpdm) $\text{Cu}^{\text{II}}\text{Cl}_2$ but binding in facial arrangement in tetrahedral (tpdm) $\text{Cu}^{\text{I}}\text{Cl}$. Nucleophilic substitution of chloride by tBuO^- and $\text{PhC}\equiv\text{C}^-$ was possible, and deprotonation of the acidic benzylic protons did not take place because the resulting carbanion cannot achieve coplanarity with the aryl rings. RhCl_3 forms, with tpdm in boiling methanol, a 1:1 kinetic mixture of *fac*- and *mer*-isomers $\text{RhCl}_3(\text{tpdm})$.

1.3 Objectives

1. To synthesize the 2,6-(diphenylazo)pyridine (diazpy) ligand, the $[\text{Ru}(\text{diazpy})(\text{Cl})_2]$ complex and the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes, where L = azpy, bpy and phen.
2. To characterize and to study of chemistry and electrochemistry of diazpy ligand and its complexes.
3. To analyze and to summarize the chemical properties of the diazpy ligand and the $[\text{Ru}(\text{diazpy})(\text{L})_2]^{2+}$ complexes.