Chapter 1

INTRODUCTION

1.1 Introduction

The ruthenium(II) complexes containing azoimine (\(-N=N-C=C=N-\)) and imine (\(-N=C-C=N-\)) functional units have been chosen to study their chemistry. The advantage of the azoimine functional unit is that it has a strong ability to stabilize ruthenium in the lower oxidation states. 2-(Phenylazo)pyridine (azpy) and 2-(phenylazo)pyrimidine (azpym), containing azoimine functions, are asymmetric bidentate ligands which stronger \(\pi\)-acidity than bpy (Krause and Krause, 1980). The symmetric ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) consist of imine functional group which has \(\sigma\)-donor and \(\pi\)-acceptor properties.

The ruthenium(II) complexes with bpy ligands such as \(\text{cis-Ru}[4,4'(\text{CO}_2\text{H})_2-2,2'-\text{bipyridine}]_2(X)_2\) and \(\text{cis-Ru}[5,5'(\text{CO}_2\text{H})_2-2,2'-\text{bipyridine}]_2(X)_2\) where \(X = \text{Cl}^-, \text{CN}^-\) and \(\text{SCN}^-\), have been anchored to high surface area \(\text{TiO}_2\) electrodes for the conversion of visible light into electricity (Argazzi, et al. 1994). Furthermore, the interaction of \([\text{Ru(phen)}_3]^2+\) with nucleic acids showed two primary modes of binding (intercalation and surface binding) (Barton, et al., 1986).

There were variety of applications of the ruthenium(II) complexes with azoimine ligands. For example, the \([\text{Ru(azpy)}_2\text{Cl}_2]\) complexes showed remarkably high cytotoxicity against a series of tumor-cell lines (Velders, et al., 2000). Besides, the \(\alpha-\)[\(\text{Ru(azpy)}_2(\text{NO}_3)_2\)] complex showed binding to the DNA model (Hotze, et al., 2000). Furthermore, the complexes of \([\text{Ru(azpy)}_2\text{Cl}_2]\) had been used as catalysts in epoxidation reaction (Barf, et al., 1995).
In this work, the complexes of \([\text{Ru(azpy)}_2\text{L}]^{2+}\) where \(\text{L} = 2\)-(phenylazo)pyridine (azpy), 2-(phenylazo)pyrimidine (azpym), 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) have been studied. The ruthenium(II) complexes were synthesized and characterized by FAB mass spectrometry, elemental analysis, Infrared spectroscopy, UV-Visible absorption spectroscopy, NMR spectroscopy, and Cyclic voltammetry. Besides, single-crystal X-ray diffraction technique has been used to explore the structures of the complexes. The structures of ligands are shown in Figure 1.

![2-(phenylazo)pyridine (azpy)](image)

![2-(phenylazo)pyrimidine (azpym)](image)

![2,2'-bipyridine (bpy)](image)

![1,10-phenanthroline (phen)](image)

**Figure 1** The structure of azpy, azpym, bpy and phen
1.2 Literature reviews

Krause and Krause, (1980) studied the chemistry of 2-(phenylazo)pyridine (azpy) ligand and [Ru(azpy)\textsubscript{2}Cl\textsubscript{2}] complexes. Three isomers of these complexes were obtained. The isomers were assigned to be trans-cis-cis (γ), cis-trans-cis (α) and cis-cis-cis (β) with referred to the order of coordination pairs of Cl, N(pyridine), N(azo), respectively. All of three isomers were characterized by infrared spectroscopy, UV-Visible absorption spectroscopy, and \textsuperscript{13}C NMR spectroscopy. The data from cyclic voltammetry showed that the azpy ligand appeared to be a better ligand for stabilizing ruthenium(II) than 2,2'-bipyridine (bpy).

Goswami, et al., (1982) studied the reaction of trans-RuX\textsubscript{2}L\textsubscript{2} (X = Cl, Br, I; L = 2-(phenylazo)pyridine) with tertiary phosphines. The rate of substitution reaction decreased on increasing phosphine bulk : PPhMe\textsubscript{2} > PPh\textsubscript{2}Me >> PPh\textsubscript{3}. These complexes were isolated and structurally characterized with spectroscopic and electrochemical data.

Krause and Krause, (1982) synthesized and characterized the complexes of [Ru(azpy)\textsubscript{2}(AB)]\textsuperscript{2+} (AB = 2-(phenylazo)pyridine (azpy), 2,2'-bipyridine (bpy), 4,4'-bithiazole, 1,2-diaminoethane, 2,4-pentanedione). Results from infrared spectroscopy showed the azpy azo stretching mode to be diagnostic of the coligand (AB) π-accepting behavior, with strongly π-accepting coligands giving the highest azpy N=N stretching mode.

Goswami, et al., (1983) studied ctc, ccc-RuL\textsubscript{2}Cl\textsubscript{2} (L = 2-(phenylazo)pyridine). Both isomers undergo facile and stereoretentive displacement of Cl\textsuperscript{-} by H\textsubscript{2}O, affording the corresponding of [Ru(OH\textsubscript{2})\textsubscript{2}L\textsubscript{2}]\textsuperscript{2+}. The \textsuperscript{1}H NMR technique was used to establish
stereochemistry of the isomeric cations. Results from UV-Visible absorption spectra was blue shifted in going from RuCl₂L₂ to [Ru(OH₂)₂L₂]²⁺ for all isomers. Besides, cyclic voltammetry was used to studied their redox properties.

Wolfgang, et al., (1984) studied spectral and photophysical properties of [Ru(azpy)₂L₂]²⁺ complexes where azpy = 2-(phenylazo)pyridine and L = various monodentate or bidentate ligands. Results from resonance Raman spectra revealed a relatively localized MLCT excited state with large distortions of the azo N=N bond. These complexes were red shifted relative to those for other Ru(II) diimine complexes.

Mallick, et al., (1994) reported a series of [ML′L₂](ClO₄)₂·H₂O (M = Ru or Os; L' = 2,2'-bipyrazine (bpyz) or 2,2'-bipyrimidine (bpym) and L = 2-(phenylazo)pyridine (papy) or 2-(m-tolylazo)pyridine (tapy). These complexes were determined stereochemistry by using 'H NMR spectroscopy. Besides, UV-visible absorption spectroscopy and cyclic voltammetry were used to study electronic transitions and redox properties in the complexes, respectively.

![2,2'-bipyrazine](bpyz)

![2,2'-bipyrimidine](bpym)

![2-(m-tolylazo)pyridine](tapy)
Boelrijk, *et al.*, (1995) studied the [Ru(azpy)$_2$(H$_2$O)$_2$]$^{2+}$ and [Ru(naz)$_2$(H$_2$O)$_2$]$^{2+}$ complexes (azpy = 2-(phenylazo)pyridine, naz = 2-(p-nitrophenyl)azopyridine). These complexes were proved to be active catalysts yielding octyl glucuronic acid and 2,3-glycol cleavage product from octyl $\alpha$-D-glucopyranoside (OGP). Results from reactions with cyclobutanol in combination with spectroscopic data indicated that a Ru (IV)=O species was the active catalytic species. Besides, two new complexes, [Ru(terpy)(azpy)(H$_2$O)](ClO$_4$)$_2$ and [Ru(terpy)(naz)(H$_2$O)](ClO$_4$)$_2$ were synthesized and less active than the first two compounds.

Barf and Sheldon, (1995) studied the isomeric complexes of [Ru(azpy)$_2$Cl$_2$] which were two cis-isomers ($\alpha$, $\beta$) and one trans-isomer ($\gamma$). These complexes were used as catalysts for epoxidation reactions of olefin to give epoxide. The different isomers showed different activity and selectivity. The $\beta$ and $\gamma$-[Ru(azpy)$_2$Cl$_2$] complexes gave better yields than the $\alpha$-[Ru(azpy)$_2$Cl$_2$] complex.

Misra, *et al.*, (1998) synthesized the class of 1-alkyl-2-(arylazo)imidazole (R = H, CH$_3$, OCH$_3$, Cl, NO$_2$). The reaction of RuCl$_3$·3H$_2$O with these ligands in ethanol under refluxing condition afforded RuL$_2$Cl$_2$. Two isomers of complexes were chromatographically separated. The configurations of these isomers were supported by infrared and $^1$H NMR data. Results from cyclic voltammetry showed that the couple of Ru(III)/Ru(II) was shifted to more positive potential and the MLCT bands were blue shifted on going from azoimidazole to azopyridine ruthenium(II) complexes. This was due to the decreased $\pi$-acidity of the five-membered heterocycle imidazole compared to the six-membered pyridine.
Santra, et al., (1999) synthesized 2-(arylazo)pyrimidine (aapm) ligand and complexes of [Ru(aapm)₂Cl₂]. Three isomers of Ru(aapm)₂Cl₂ have been separated by using chromatographic technique. They were determined as trans-cis-cis (tcc,γ), cis-trans-cis (ctc, α) and cis-cis-cis (ccc, β) configurations with referred to the order of coordination pairs as Cl, N(pyrimidine), N(azo). The tcc and ccc-isomers have been confirmed by X-ray crystallography. In both of these structures, the Ru-N(azo) distances were relatively shorter than those of Ru-N(pyrimidine), indicating stronger bonding in the former and the presence of a Ru-(aapm) π-interaction localized in the Ru-azo fragment. Besides, the isomer configuration was supported by infrared and ¹H NMR data. In addition, redox properties of these complexes were studied.

Hotze, et al., (2000) studied the complex of α-[Ru(azpy)₂(NO₃)₂] (azpy = 2-(phenylazo)pyridine; α indicated that isomer in which the coordinating pairs ONO₂, N(py) and N(azo) were cis, trans and cis, respectively). The structure of this complex has been determined by X-ray crystallography. The binding of the DNA-model bases 9-ethylguanine and guanosine also has been studied and compared with the complex of cis-Ru(azpy)₂Cl₂. The binding DNA complexes has been identified by ¹H NMR and 2D NMR spectroscopy.

Peneerselvam, et al. (2000) reported the crystal structures of the [protonated 2-(phenylazo)pyridine and protonated 2-(4-hydroxyphenylazo)pyridine(3:1)]
tetrafluoroborate compound. The results from X-ray showed 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 intramolecular H bonding, N-H-N, and van der waals forces stabilized this crystal structure.

Protonated azpy \( X = H(75\%) \) and \( OH^- (25\%) \)

Velders, et al., (2000) investigated three isomeric \([Ru(azpy)_2Cl_2]\) complexes (\(\alpha\)-[Ru(azpy)_2Cl_2]; \(\beta\)-[Ru(azpy)_2Cl_2]; \(\gamma\)-[Ru(azpy)_2Cl_2]) which \(\alpha\), \(\beta\), \(\gamma\) referred to ctc, ccc, tcc configuration). They found that these complexes showed different in vitro cytotoxicity activity. The \(\alpha\)-[Ru(azpy)_2Cl_2] showed high cytotoxicity against a series of tumor-cell lines, which was in contrast to the low cytotoxicity of its isomeric complexes \(\beta\)-[Ru(azpy)_2Cl_2] and \(\gamma\)-[Ru(azpy)_2Cl_2]. In addition, the binding of DNA base to the ctc-[Ru(azpy)_2Cl_2] was studied and compared with the similar complexes such as cis-[Ru(bpy)_2Cl_2]. The binding of the ctc-isomer with guanine and purine base was sterically less hindered than that in the complex cis-[Ru(bpy)_2Cl_2].
1.3 Objectives

1. To synthesize the \([\text{Ru}(\text{azpy})_2L]^2^+\) complexes where \(L = \text{azpy}, \text{azpym}, \text{bpy} \) and phen ligands.

2. To characterize and to study of chemical properties of those complexes.

3. To analyze and to summarize the chemistry of the \([\text{Ru}(\text{azpy})_2L]^2^+\) complexes.