Chapter 1

INTRODUCTION

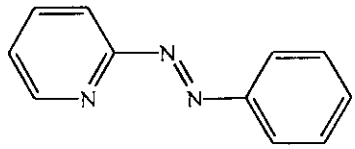
1.1 Introduction

The ruthenium(II) complexes containing azoimine (-N=N-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 π-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 σ-donor and π-acceptor properties.

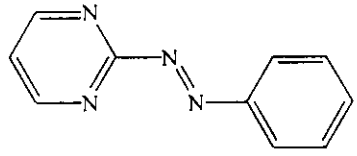
The ruthenium(II) complexes with bpy ligands such as *cis*-Ru[4,4′-$(CO_2H)_2$-2,2′-bipyridine]$_2(X)_2$ and *cis*-Ru[5,5′-$(CO_2H)_2$-2,2′-bipyridine]$_2(X)_2$ where X = Cl^-, CN^- and SCN^-, have been anchored to high surface area TiO_2 electrodes for the conversion of visible light into electricity (Argazzi, *et al.* 1994). 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).

There were variety of applications of the ruthenium(II) complexes with azoimine ligands. For example, the $[Ru(azpy)_2Cl_2]$ complexes showed remarkably high cytotoxicity against a series of tumor-cell lines (Velders, *et al.*, 2000). Besides, the α-$[Ru(azpy)_2(NO_3)_2]$ complex showed binding to the DNA model (Hotze, *et al.*, 2000). Furthermore, the complexes of $[Ru(azpy)_2Cl_2]$ had been used as catalysts in epoxidation reaction (Barf, *et al.*, 1995).

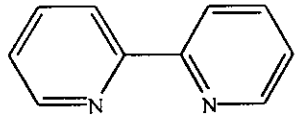
In this work, the complexes of $[Ru(azpy)_2L]^{2+}$ where L = 2-(phenylazo) pyridine (azpy), 2-(phenylazo)pyrimidine (azpym), 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) have been studied. The ruthenium(II) complexes were synthesized and characterized by FAB mass spectrometry, elemental analysis, 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



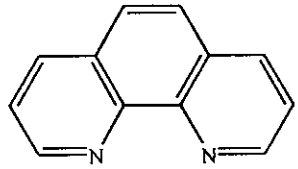
2-(phenylazo)pyridine (azpy)



2-(phenylazo)pyrimidine (azpym)



2,2′-bipyridine (bpy)



1,10-phenanthroline (phen)

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 $[Ru(azpy)_2Cl_2]$ 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 ^{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_2L_2 ($X = Cl^-, Br^-, I^-$; L = 2-(phenylazo)pyridine) with tertiary phosphines. The rate of substitution reaction decreased on increasing phosphine bulk : $PPhMe_2$ > PPh_2Me >> PPh_3. These complexes were isolated and structurally characterized with spectroscopic and electrochemical data.

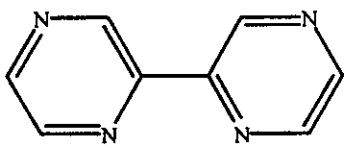
Krause and Krause, (1982) synthesized and characterized the complexes of $[Ru(azpy)_2(AB)]^{n+}$ (AB = 2-(phenylazo)pyridine (azpy), 2,2′-bipyridine (bpy), 4,4′-bithiazole, 1,2-diaminoethane, 2,4-pentanedione). Results from infrared spectroscopy showed the azpy azo stretching mode to be diagnostic of 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_2Cl_2 (L = 2-(phenylazo)pyridine). Both isomers undergo facile and stereoretensive displacement of Cl^- by H_2O, affording the corresponding of $[Ru(OH_2)_2L_2]^{2+}$. The ^1H NMR technique was used to establish

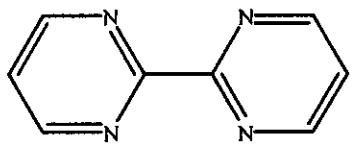
stereochemistry of the isomeric cations. Results from UV-Visible absorption spectra was blue shifted in going from $RuCl_2L_2$ to $[Ru(OH_2)_2L_2]^{2+}$ for all isomers. Besides, cyclic voltammetry was used to studied their redox properties.

Wolfgang, *et al.*, (1984) studied spectral and photophysical properties of $[Ru(azpy)_2L_2]^{n+}$ 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.

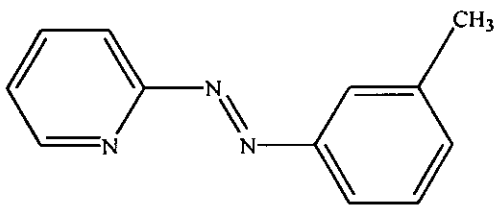
Mallick, *et al.*, (1994) reported a series of $[ML'L_2](ClO_4)_2.H_2O$ (M= Ru or Os; L′ = 2,2′-bipyrazine (bpyz) or 2,2′-bipyrimidine (bpym) and L = 2-(phenylazo) pyridine (papy) or 2-(*m*-tolylazo)pyridine (tapy). These complexes were determined stereochemistry by using ^1H NMR spectroscopy. Besides, 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)

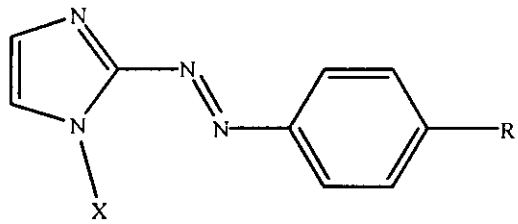


2-(*m*-tolylazo)pyridine (tapy)

Boelrijk, *et al.*, (1995) studied the $[Ru(azpy)_2(H_2O)_2]^{2+}$ and $[Ru(naz)_2(H_2O)_2]^{2+}$ 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 α-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, $[Ru(terpy)(azpy)(H_2O)](ClO_4)_2$ and $[Ru(terpy)(naz)(H_2O)](ClO_4)_2$ were synthesized and less active than the first two compounds.

Barf and Sheldon, (1995) studied the isomeric complexes of $[Ru(azpy)_2Cl_2]$ which were two *cis*-isomers (α, β) and one *trans*-isomer (γ). These complexes were used as catalysts for epoxidation reactions of olefin to give epoxide. The different isomers showed different activity and selectivity. The β and γ-$[Ru(azpy)_2Cl_2]$ complexes gave better yields than the α-$[Ru(azpy)_2Cl_2]$ 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 $RuCl_3.3H_2O$ with these ligands in ethanol under refluxing condition afforded RuL_2Cl_2. Two isomers of complexes were chromatographi- cally separated. The configurations of these isomers were supported by infrared and ^1H 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 π-acidity of the five-membered heterocycle imidazole compared to the six-membered pyridine.



R = H, Me, OMe, Cl, NO_2

X = CH_3

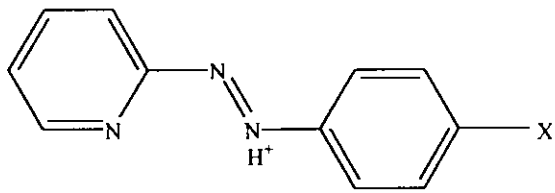
1-methyl-2-(arylazo)imidazoles ligand

Santra, *et al.*, (1999) synthesized 2-(arylazo)pyrimidine (aapm) ligand and complexes of $[Ru(aapm)_2Cl_2]$. Three isomers of $Ru(aapm)_2Cl_2$ 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-$[Ru(azpy)_2(NO_3)_2]$ (azpy = 2-(phenylazo)pyridine; α indicated that isomer in which the coordinating pairs ONO_2, 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-$Ru(azpy)_2Cl_2$. 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 (α-$[Ru(azpy)_2Cl_2]$; β-$[Ru(azpy)_2Cl_2]$; γ-$[Ru(azpy)_2Cl_2]$ which α, β, γ referred to *ctc*, *ccc*, *tcc* configuration). They found that these complexes showed different in vitro cytotoxicity activity. The α-$[Ru(azpy)_2Cl_2]$ showed high cytotoxicity against a series of tumor-cell lines, which was in contrast to the low cytotoxicity of its isomeric complexes β-$[Ru(azpy)_2Cl_2]$ and γ-$[Ru(azpy)_2Cl_2]$. 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 $[Ru(azpy)_2L]^{2+}$ complexes where L = azpy, azpym, 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 $[Ru(azpy)_2L]^{2+}$ complexes.