Chapter1

INTRODUCTION

1.1 Introduction

The complexes of ruthenium(II) with polypyridyl and azoimine compounds which are π-acceptor ligands have been extensively studied. (Santra, *et al.*, 1999). Ruthenium(II) is well recognized as a metal ion capable of entering into dπ-pπ backbonding with those 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 are symmetric bidentate ligands which have 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 $[Ru(bpy)_3]^{2+}$ and $[Ru(dcb)_2X_2]$ (dcb = 4,4′$(COOH)_2$-2,2′-bipyridine and X = Cl^-, Br^-, I^-, SCN^-, H_2O) used as the most efficient and stable redox sensitizers on nanocrystalline TiO_2 solar cell for conversion light-to-electrical energy (Meyer, 1997). For similar complex, $Ru(bpz)_3^{2+}$ (bpz bipyrazyl) was used as a photosensitizer in solar energy conversion.(Crutchley, *et al.*, 1982). The other useful complexes were the $[Ru(phen)_2L]^{2+}$ complexes where L were 4, 5, 9, 18-tetraazaphenanthreno[9,10-b]triphenylene (taptp) and 2, 3-diphenyl-1, 4, 8, 9-tetraazatriphenylene (dptatp) used as probe in DNA conformation (Zhen, *et al.*, 2000). Besides, the complexes of $[Ru(phen)_2dppz]^{2+}$ (dppz = dipyridophenazine) acted as luminescent probes in DNA. (Nair, *et al.*, 1998). However, these several applications could be due to the different chemical properties of the ligands.

In addition to polypyridyl, the azoimine (-N=N-C=N-) moiety in some ligands have been involved in a π-system and was the potential π-acceptor which could make

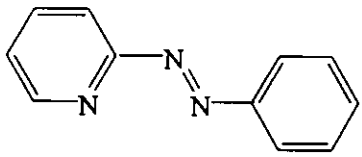
the strong bond with Ruthenium(II). One ligand of this type was 2-(phenylazo)pyridine (azpy). The azpy ligand was an asymmetric bidentate ligand and stronger π-acidity ligand than bpy (Krause and Krause, 1980). Due to asymmetric N-donor sites in the azo imine function, isomeric complexes in ruthenium have been extensively studied (Goswami, *et al.*, 1981). Besides, the azo group was one of the potential function unit which may be photochromatic, pH-responsive, redox active, and mediated electronic communications between photoredox active groups (Misra, *et al.*, 1998). The ruthenium(II) complexes with azpy ligand have been used for several applications. For example, the complexes of $Ru(azpy)_2Cl_2$ have been used as catalyst for epoxidation reactions of olefin to give epoxide (Barf and sheldon, 1995). Besides, The *cis*- and *trans*- isomeric complexes of $Ru(azpy)_2Cl_2$ showed the in vitro cytotoxicity activity in turmor cell lines (Velders, *et al.*, 2000). Furthermore, the complex of α-$Ru(azpy)_2(NO_3)_2$ or *cis*-$Ru(azpy)_2Cl_2$ showed the strong binding of DNA-model bases (Hotze, *et al.*, 2000). The progress in azoimine chemistry of azpy led to further study on other heterocyclic complex such as 2-(phenylazo)imidazole (aai) in $Ru(aai)_2Cl_2$ (Misra, *et al.*, 1998) and 2-(phenylazo)pyrimidine (papm) in $Ru(papm)_2Cl_2$ (Santra, *et al.*, 1999).

Therefore, in this work it interesting to investigate the chemistry of complexes of the type $Ru(L)_2Cl_2$, where L = 2-(*N,N*-dimethylphenylazo)thiazole (dmsazpy) and 2-(*N,N*-diethylphenylazo)thiazole (desazpy). These complexes have been synthesized and characterized by electrospray mass spectrometry (ES-MS), UV-Visible absorption spectroscopy (UV-Visible), ^{1}H NMR spectroscopy (^{1}H NMR), Infrared spectroscopy (IR) and cyclic voltammetry (CV). In addition, X-ray diffraction method has been used to determine the crystal structures of complexes which single crystals were available. The π-accepting properties of these ligands were also investigated and compared with those in $Ru(azpy)_2Cl_2$.

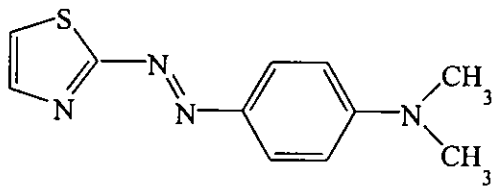
The dmsazpy and desazpy are asymmetric bidentate ligands containing azoimine groups. They can act as π-acceptor like bpy, phen and azpy. Furthermore, the

structures of dmsazpy and desazpy are similar to that of azpy except by the replacement pyridine ring with thiazole ring and phenyl ring containing electron-donating substituents, $-NR_2$ ($R=CH_3$, C_2H_5). Therefore, it is interesting to study the effect of the heterocyclic ring, thiazole and the substituents on the phenyl ring upon the π-acidity and chemical properties of the compounds.

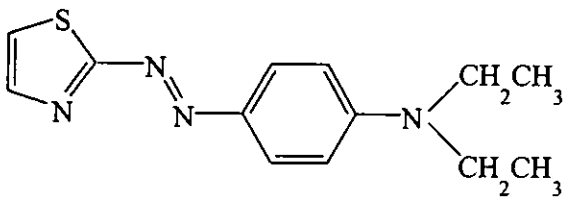
The structures of azpy, dmsazpy and desazpy are shown in Figure 1



2-(phenylazo)pyridine (azpy)



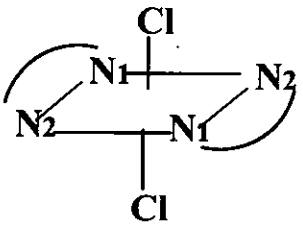
2-(*N,N*-dimethylphenylazo)thiazole (dmsazpy)



2-(*N,N*-diethylphenylazo)thiazole (desazpy)

Figure 1 The structures of azpy, dmsazpy and desazpy ligands

Since the structures, dmsazpy and desazpy are asymmetric bidentate ligands, then in principle, the six coordination of $Ru(L)_2Cl_2$ (L=dmsazpy and desazpy) complexes give five possible geometrical isomers (Figure 2) similar to $Ru(azpy)_2Cl_2$ complexes.



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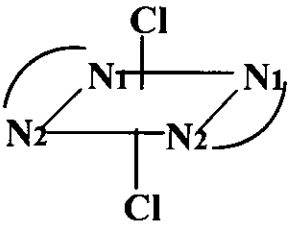

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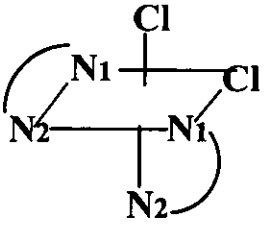

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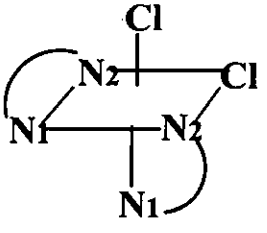

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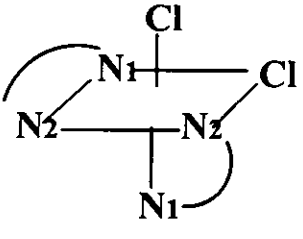
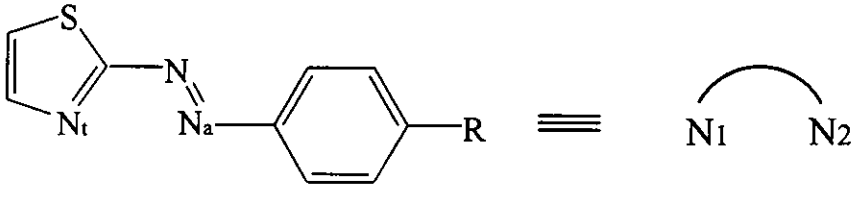


ccc



R = -$NCH_3)_2$ (dmsazpy)

R = -$N(C_2H_5)_2$ (desazpy)

N1 = N(th)

N2 = N(azo)

Figure 2 Five possible isomers of $Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) complexes

The structural configuration of possible isomers are considered with reference to three pairs of sequence of Cl, N(th) and N(azo), respectively. In the present work, the four isomeric complexes of *cis*- and *trans*-$Ru(L)_2Cl_2$ were synthesized. The molecular structures of *cis*- and *trans*-$Ru(dmsazpy)_2Cl_2$ have been confirmed by X-ray diffraction. One of these isomers, *trans*-$Ru(dmsazpy)_2Cl_2$, was *trans-cis-cis* (*tcc*) configuration and the other, *cis*-$Ru(dmsazpy)_2Cl_2$, was *cis-trans-cis* (*ctc*) configuration. However, The *cis*- and *trans*-$Ru(desazpy)_2Cl_2$ was characterized by other methods. In the case of $Ru(azpy)_2Cl_2$ only three isomers were isolated (Krause and Krause, 1980), which were *trans-cic-cis* (*tcc*), *cic-trans-cis* (*ctc*) and *cic-cis-cis* (*ccc*) complexes, whereas, the isomeric complexes of *ccc*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) were not obtained.

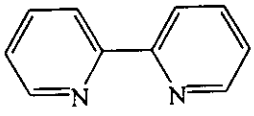
1.2 Literature reviews

Evans *et al.*, (1973) studied the complexes of dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) complexes, $Ru(DMSO)_4Cl_2$, which is an useful starting material for other ruthenium(II) complexes. $Ru(DMSO)_4Cl_2$ was characterized by IR and NMR techniques. The results from data show that there were mixed sulfur and oxygen coordination sites. Triphenylphosphine, diethyl dithiocarbamato, carbonyl, pyridine, 1,10-phenanthroline and other ligands were used to replace Me_2SO in starting material to give new ruthenium(II) complexes. The synthesized complexes were characterized by IR, ^1H NMR and elemental analysis.

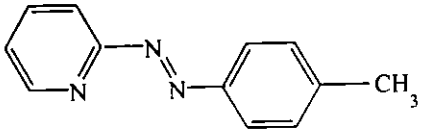
Krause and Krause, (1980) studied 2-(phenylazopyridine) (azpy) ligand and dichlorobis(2-phenylazopyridine)ruthenium(II)complexes, ($Ru(azpy)_2Cl_2$). Three isomers of $Ru(azpy)_2Cl_2$ were obtained from either starting material, $Ru(DMSO)_4Cl_2$

or $RuCl_3.3H_2O$ complexes. Two forms of *cis*-isomers (α and β) and one *trans*-isomer (γ) were obtained. Those complexes were characterized by IR spectroscopy, UV-Visible absorption spectroscopy and ^{13}C NMR techniques. The results from cyclic voltammetric data showed azpy ligand was a better π–acceptor than that of 2,2′-bipyridine (bpy) ligand which could stabilize ruthenium(II) center.

Goswami *et al.*, (1981) studied two types of ruthenium(II) complexes, $Ru(L)_2X_2$ and $[Ru(bpy)_2L](ClO_4)_2.H_2O$ where X = Cl, Br, I; L = 2-(phenylazo)pyridine (azpy) or 2-(*m*-tolylazo)pyridine (tap); 2,2′-bipyridine (bpy). Both types of complexes were characterized by IR, UV-Visible absorption spectroscopy, ^1H NMR spectroscopy and cyclic voltammetry (CV). The results from CV data showed that both $Ru(L)_2X_2$ and $[Ru(bpy)_2L](ClO_4)$ complexes exhibited reversible or quasi-reversible Ru(III/II) couples at higher potential when L was azpy ligand. In addition, the Ru(III/II) redox potentials of $Ru(L)_2Cl_2$ were higher than that of *cis*-$Ru(bpy)_2Cl_2$ and several other dichlororuthenium(II) species. Therefore, the azopyridine ligand stabilized (in the respect of oxidation) ruthenium(II) better than bpy.



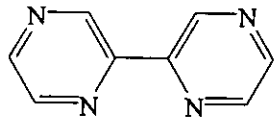
2,2′-bipyridine (bpy)



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

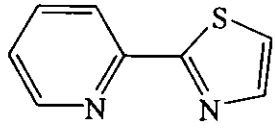
Crutchley and Lever, (1982) reported the synthesis of 2,2′-bipyrazine (bpz) ligand and $Ru(bpz)_3Cl_3.3.5H_2O$, $Ru(bpz)_3.1.5((CH_3)_2CO)$, $[Ru(bpz)_2CH_3CN(Cl)][PF_6]$, $[Ru(bpz)_3Cl_2.H_2O$, $Mo(CO)_4bpz$ and $W(CO)_4bpz$ complexes and studied the protoanation of bipyrazyl complex, $Ru(bpz)_3(PF_6)_2$ in acetronitrile for developing $[Ru(bpz)_3]^{2+}$ used as a photosensitizer in solar energy conversion. These complexes were characterized by spectroscopic and electrochemical methods and compared their

properties with those of their bipyridyl (bpy) analogues. The results from these technique showed that bpz was weaker π-acceptor than bpy. The bpy ligand was the strong σ–donor, which caused an enhancement of π-backdonation with π–donor metals.



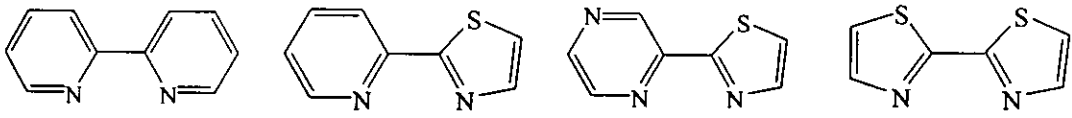
2,2′-bipyrazine (bpz)

Fitzpatrick and Goodwin, (1982) studied the new complexes of $[RuL_3]^{2+}$, $[Ru(L)_2(bpy)]^{2+}$ and $[RuL(bpy)_2]^{2+}$ where L= 2-(2-pyridyl)thiazole that showed a closer similarity to bpy. These complexes were characterized by UV-Visible absorption spectroscopy and electrochemical methods. The results from absorption spectra indicated that these complexes displayed absorption spectra in the visible region at lower energies than those found in $Ru(bpz)_3^{2+}$. These transition were assigned to metal-to-ligand charge transfer (MLCT) transitions shifted to lower energies when the number of coordinated thiazole molecule increased. The ruthenium(II) center was stabilized by the greater π–acceptor nature of thiazole. In addition, the redox studies of these complexes showed that $E_{1/2}$ potential of Ru(II/III) couples occurred at higher potentials with increased coordination of thiazole. The thiazole moiety in L had an important effect on its π–acceptor capacity. The ligand containing the thiazole ring because greater π-acceptor than pyridine moiety in bpy.



2-(2-pyridyl)thiazole

Orellana *et al.*, (1988) reported the chemistry of $[Ru(L)_3]^{2+}$ complexes containing five- and six-membered heterocyclic moiety ligands. These complexes, RuL_3^{2+} (where L= 2,2′-bipyridine (1), 2-(2-pyridyl)thiazole (2), 2-(2-pyrazyl)thiazole (3) and 2,2′-bithiazole (4)) were characterized by using ^{1}H NMR and ^{13}C NMR spectroscopy.



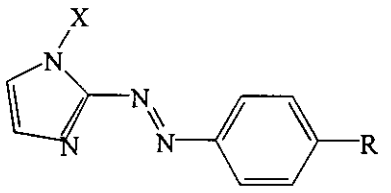
(1) (2) (3) (4)

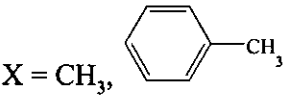
Barf and Sheldon, (1995) studied the isomeric complexes of $Ru(azpy)_2Cl_2$ which were two *cis*-isomers (α, β) and one *trans*-isomer (γ). They were used as catalysts for epoxidation reactions of olefin to give epoxide. The different isomers should different activity and selectivity. The results showed that the β-$Ru(azpy)_2Cl_2$ and γ-$Ru(azpy)_2Cl_2$ complexes gave better yields than the α- $Ru(azpy)_2Cl_2$ complex.

Ye *et al.*, (1995) studied the complexes of $[Ru(bpy)_2(phen)](ClO_4)_2.H_2O$ and $[Ru(bpy)_2(Me\text{-}phen)]\ (ClO_4)_2$. They reported the synthesis, spectra and single crystal X-ray structures of two complexes. The results from X-ray data indicated that the Ru-N(bpy) and Ru-N(phen) bond distances were comparable and as expected of π–backbonding interaction which involved of each ligand in the coordination sphere.

Misra *et al.*, (1998) studied new azoimidazole ligands (L) which belonged to the class of 1-methyl-2-(arylazo)imidazole (R = H, CH_3, OCH_3, Cl, NO_2) as shown below. The reaction of $RuCl_3.3H_2O$ with these ligands in ethanol under refluxed condition giving RuL_2Cl_2 complexes. The isomeric complexes, RuL_2Cl_2, were characterized by spectra, redox behavior and single crystal X-ray structures. These

azoimidazole ligands were better π-acceptor ligands than bpy and phen but they were weaker than that of azpy. Furthermore, the ruthenium-imidazole complexes were of interest for their antitumor activities.





X = CH_3,

R = H, CH_3, OCH_3, Cl, NO_2

1-methyl-2-(arylazo)imidazoles

Velders *et al.*, (2000) investigated the three isomeric of $Ru(azpy)_2Cl_2$ 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* configurations. These complexes showed different in Vitro cytotoxicity activity. The *ctc*-$Ru(azpy)_2Cl_2$ isomer showed high cytotoxicity against a series of tumor cell lines. While the *ccc* and *tcc* showed low to moderate cytotoxicity. In addition, the structure of *tcc* isomer was confirmed by a single crystal X-ray diffraction. The *tcc* had two chloride atoms in *trans* position, but the N(pyridine) and N(azo) groups were in *cis* geometry. Futhermore, the binding of DNA bases 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 *cis*-$Ru(bpy)_2Cl_2$ complex. Therefore the *ctc*-isomer was found to show high cytotoxicity against a series of tumor-cell lines.

Holtze *et al* ., (2000) reported the synthesis and characterization of α-$[Ru(azpy)_2(NO_3)_2]$ complexes. The structure of α-$[Ru)azpy)_2(NO_3)_2]$ were determined by X-ray crystallography. The binding of the DNA-model bases

9-ethylguanine and guanosine has also been studied and compared with *cis*-$[Ru(bpy)_2Cl_2]$ complexes. The binding DNA complexes have been identified by ^1H NMR and 2D NMR spectroscopy.

Panneerselvam *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 occured at N(azo) atom and it was more basic than N(pyridine). The azpy compound was normally liquid at ambient temperature but this crystal structure was stabilizes by intramolecular H-bonding, N-H-N and Van der Waals force.

1.3 Objectives

1. To synthesize the $[Ru(L)_2Cl_2]$ complexes, where L = dmsazpy and desazpy ligands.
2. To characterize and to study of chemistry and electrochemistry of their complexes.
3. To compare the π-acceptor properties of azpy, dmsazpy and desazpy ligands.
4. To analyze and to summarize the chemistry of $[Ru(L)_2Cl_2]$ (L = dmsazpy and desazpy) complexes.