

INTRODUCTION

1.1. Introduction

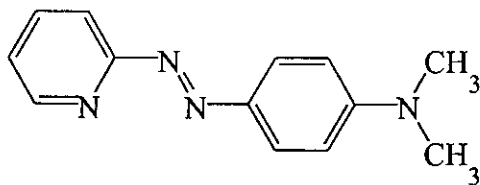
Ruthenium (II) is well recognized as a metal ion capable of entering into $d\pi$ - $p\pi$ back bonding with π -acceptor ligands. π -Back bonding, in addition to the conventional σ bonding, gives rise to a number of interesting properties.

The ruthenium chemistry of unsaturated nitrogenous ligands has been developed in this recent year, primarily due to the wide range of oxidation states, varieties of reactivities of the complexes, directional electron and energy transfer light-to-electrical energy conversion, photochemical properties and DNA intercalation. Furthermore, ruthenium polypyridine complexes are widely used as photosensitisers in covalently linked multicomponent systems. Their photophysical properties make them ideal candidates as building blocks for the design of supramolecular species performing complex light induced functions (Duati, *et al*, 2000). The major work has grown around N,N-chelating pyridine bases and related species. The number of heterocyclic ring significantly modify π -acidity and regulate the physical and chemical properties of the compounds (Misra, *et al.*, 1998).

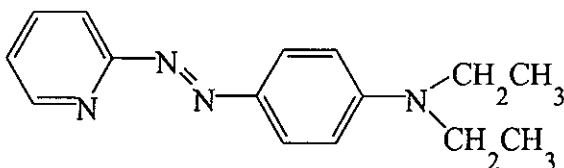
Complexes of ruthenium (II) with polypyridine ligands, such as 2,2':6',2''-terpyridine (tpy) and bidentate ligands have been extensively studied. Thorp and co-workers have demonstrated that the oxoruthenium (IV) complex $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy})\text{O}]^{2+}$ (bpy = 2,2'-bipyridine) is an efficient DNA cleavage reagent (Thorp and Grover, 1991).

The interesting properties of the $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy})\text{X}]^{\text{n}+}$, where X are monodentate ligands, lead to synthesized ruthenium terpyridine complexes with other bidentate ligands which are better π -acceptors than bpy, such as 2-(phenylazo)pyridine (azpy) (Krause and Krause, 1980). Azpy consisting of one pyridine ring with a pendent nitrogen donor atom from an azo function has been employed very recently in the development of transition metal coordination chemistry. Due to unsymmetric N-donor sites in the azo imine function, $-\text{N}=\text{N}-\text{C}=\text{N}-$, isomeric complexes of ruthenium and osmium have been extensively studied (Misra, *et al.*, 1998).

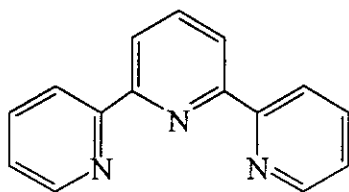
In the present study, 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy) and 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy) have been chosen as the bidentate ligands. The structures of dmazpy and deazpy are shown in Figure 1. Dmazpy and deazpy are the derivatives of azpy. The chemistry of acetonitrile-, chloro-, and nitro-complexes of ruthenium incorporating tpy, dmazpy and deazpy ligands were reported. These complexes have been synthesized and characterized by the electrospray and the fast-atom bombardment mass spectrometry, ^1H NMR spectroscopy, infrared spectroscopy, UV-Visible absorption spectroscopy and cyclic voltammetry. Furthermore, single X-ray diffraction method has been used to determine the crystal structure of ligands and complexes, which single crystals were available. It is interesting to know how the $-\text{NR}_2$ groups of bidentate ligands effect on the chemistry of $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{X}]^{\text{n}+}$ and $[\text{Ru}(\text{tpy})(\text{deazpy})\text{X}]^{\text{n}+}$ where $\text{X} = \text{Cl}^-$, NO_2^- and CH_3CN .



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



2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy)



2,2':6',2''-terpyridine (tpy)

Figure 1 The structures of dmazpy, deazpy and tpy ligands.

1.2. Reviews of Literatures

Synthesis and characterization of ruthenium (II) with tpy ligand have been studied;

Balzani and Tokel-Takvoryan (1973) reported the electrochemistry and electrogenerated chemiluminescence (ecl) of four ruthenium (II) chelates, $\text{Ru}(\text{L})_3^{2+}$ ($\text{L} = 2,2'$ bipyridine (bpy) and $\text{L} = 1,10$ -phenanthroline(phen)) and $\text{Ru}(\text{L})_2^{2+}$ ($\text{L} = 2,2':6',2''$ -terpyridine (tpy) and 2,4,6-tripyridyl-*s*-triazine (TPTZ)). All compounds showed evidence of several one-electron reduction and oxidation steps to form products 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.

Meyer and Sullivan (1980) studied the isomers of $[\text{Ru}(\text{tpy})(\text{PPh}_3)\text{Cl}_2]$ complex. Infrared spectroscopy, UV-Visible absorption spectroscopy, ^1H and ^{31}P NMR spectroscopy and electrochemistry were used to characterize these complexes.

Thorp and Grover (1991) studied the $[\text{Ru}(\text{tpy})(\text{bpy})\text{O}]^{2+}$ complex with electrochemistry, UV-Visible absorption spectroscopy and electrophoresis. This complex showed DNA cleavage agent property.

Gupta and Thorp (1993) studied the new DNA cleavage agents based on $[\text{Ru}(\text{tpy})(\text{bpy})\text{O}]^{2+}$ complex, which 1,10-phenanthroline (phen), 2,4,6-tripyridyl-triazine (tpt) and N,N,N',N' -tetramethylethylenediamine (tmen) replaced 2,2'-bipyridine (bpy). These complexes were investigated by cyclic voltammetry, UV-Visible absorption spectroscopy, electrophoresis and single crystal X-ray diffraction analysis.

Gerli, *et al.* (1995) synthesized complexes of the type $[\text{Ru}(\text{tpy})(\text{bpz})\text{X}]^{n+}$, where bpz = 2,2'-bipyrazine and $\text{X} = \text{Cl}^-$ and H_2O . Bpz ligand led to a dramatic change of the redox behavior when it was compared with bpy ligand. Furthermore, $[\text{Ru}(\text{tpy})(\text{bpz})\text{H}_2\text{O}]^{2+}$ complex was found to be an active catalyst for the oxidation of benzyl alcohol when oxidized to its Ru(IV) oxidation state.

Pramanik, *et al.* (1998) reported the chemistry of $[\text{Ru}(\text{tpy})(\text{azpy})\text{Cl}]^+$ complex and the monodentate ligand (CH_3CN , 4-picoline and N_3^-) was varied. Structure determination of $[\text{Ru}(\text{tpy})(\text{azpy})\text{CH}_3\text{CN}](\text{ClO}_4)_2$ by X-ray crystallography showed that

the azpy ligand was bound to ruthenium with the azo-nitrogen *trans* to CH₃CN. In addition, [Ru(tpy)(azpy)OH₂]²⁺ complex acted as a catalyst for the oxidation of water to oxygen via [Ru(tpy)(azpy)O]²⁺ complex.

Mosher, *et al.*(2001) synthesized and characterized the complexes [Ru(tpy)(bpy)L]⁺ where L is 4-methyl-, 3-chloro-, 2,4-dichloro-, 2,4,5-trichloro-, 2,4,6-trichloro-, 2,3,4,5-tetrachloro-, 2,3,5,6-tetrachloro-, or penta-chlorophenylcyanamide anion ligand. Spectroelectrochemical oxidation to the Ru(III) complexes permitted an analysis of their Ru(III)-cyanamide ligand-to-metal charge transfer (LMCT) spectral properties and metal-ligand coupling elements in comparison to their pentaamineruthenium(III) analogues.

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

Synthesis and characterization of related compounds with azpy ligand and ruthenium (II) complexes with azpy ligand have been reported;

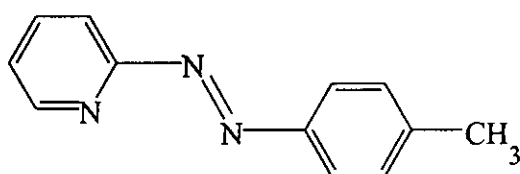
Irving, *et al.* (1953) reported the stability constants of some metal chelates of 2-(4'-*N,N*-dimethylaminophenylazo)pyridine (dmazpy). The dmazpy could act as an indicator in measuring other metal-complex stability constants. Stability constants for 1:1 chelated of dmazpy with metals at 25 °C, pH 6 and ionic strength 0.15 fallen in

order Cu > Hg > Ni > Co > Zn > Mn > Ca > Mg. They also described the protonated forms in different pH.

Krause and Krause (1980) reported the three isomers of $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$ complex such as two of *cis*-isomer (α and β) and a *trans*-isomer (γ). Infrared spectroscopy, ^{13}C NMR spectroscopy, UV-Visible absorption spectroscopy and cyclic voltammetry were used to characterize their isomers. The results exhibited that azpy ligand had the potential to be better π -acceptor than bpy ligand to stabilize ruthenium (II) center.

Chakravorty and Goswami (1982) studied the complexes of $[\text{Ru}(\text{azpy})(\text{P})_2]^{n+}$, (where P = tertiary phosphine) were synthesized via $[\text{Ru}(\text{azpy})(\text{OH}_2)_2]^{2+}$. The results showed that the bulkiness of phosphine ligand decreased the rate of reaction. The important role of aquo-complex, $[\text{Ru}(\text{azpy})(\text{OH}_2)_2]^{2+}$, was precursor to synthesize the derivative complexes of ruthenium(II) with azpy ligand.

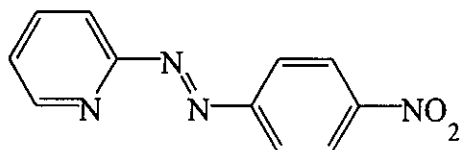
Goswami, *et al.*(1983) studied the $[\text{Ru}(\text{bpy})(\text{L})_2]^{2+}$ complexes, where L = 2-(phenylazo)pyridine (azpy) and 2-(*m*-tolylazo)pyridine (tap). The electrochemical data showed the highly positive metal oxidation potentials. A correlation of MLCT transition energy with the difference between the formal potentials of the Ru(III)-Ru (II) couple and the first ligand reduction couple was noted.



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

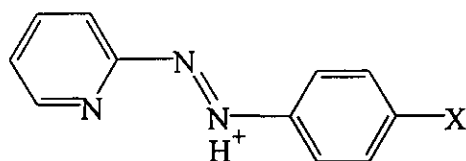
Goswami and Chakravorty (1983) studied the isomers of $[\text{Ru}(\text{azpy})_2(\text{OH}_2)(\text{C}_6\text{H}_5\text{N})]^{2+}$ and $[\text{Ru}(\text{azpy})(\text{OH}_2)_2]^{2+}$ complexes, which were synthesized via $[\text{Ru}(\text{azpy})(\text{OH}_2)_2]^{2+}$. The solvolysis of $[\text{Ru}(\text{azpy})(\text{OH}_2)_2]^{2+}$ showed that the solution of *tc* isomer (N(py), N(py) spanned *trans* positions, N(azo), N(azo) *cis* position) in donor solvent (S) such as benzonitrile ($\text{C}_6\text{H}_5\text{N}$), the MLCT band energy underwent significantly shifts from acidic aqueous solution values due to substitution of coordinated water by solvent molecules. In acetonitrile and benzonitrile, the shifts were hypsochromic as expected from the Dq order ($\text{RCN} > \text{H}_2\text{O}$).

Krause and Krause (1984) synthesized and characterized the complexes of $\text{Ru}(\text{Naz})_2\text{Cl}_2$ complex (Naz = 2-(4'-nitrophenylazo)pyridine) by infrared spectroscopic, UV-Visible absorption spectroscopic and differential pulse voltammetric methods. In comparison with $\text{Ru}(\text{azpy})_2\text{Cl}_2$ complexes, the Naz ligand could stabilize Ru(II) greater than the azpy ligand. This was due to the inductive effect of the nitro group in Naz ligand as it was stronger π -acceptor properties than that in azo complexes.



2-(4'-nitrophenylazo)pyridine (Naz)

Peneerselvam, *et al.* (2000) reported the crystal structure of the [protonated 2-(phenylazo)pyridine and protonated 2-(4-hydroxyphenylazo)pyridine(3:1)] tetrafluoroborate compound. The results from X-ray data 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%)

1.3. Objectives

1. To synthesize $[\text{Ru}(\text{tpy})(\text{dmazpy})\text{X}]^{\text{nt}}$ and $[\text{Ru}(\text{tpy})(\text{deazpy})\text{X}]^{\text{nt}}$ where X = Cl⁻, NO₂⁻ and CH₃CN.
2. To characterize the chemistry of these complexes.
3. To analyze and to summarize the effect of varying bidentate and monodentate ligands on those complexes.