

1 INTRODUCTION

1.1 Introduction

The chemistry of ruthenium(II) complexes containing azoimine (-N=N-C=N) functional unit has been reported. This function is π -acidic in character. The advantage of the azoimine functional unit is that it has a strong ability to stabilize low valent metal redox states, such as Ru(II), Os(II), Pd(II), Pt(II), Ag(I), and Cu(I). Thus the chemistry of azoimine functionalized ligand complexes induced some researcher to take an attempt to develop a new ligand containing an azoimine unit.

The ruthenium(II) complexes with azoimine ligands were investigated because of its potential application in many chemical reactions. For example, the complexes of [Ru(azpy)₂Cl₂] have been used as catalysts in epoxidation reaction (Barf, *et al.*, 1995).

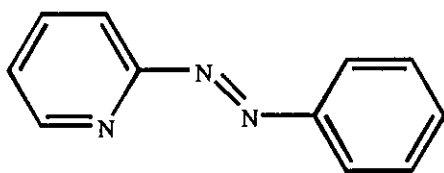


Figure 1. The structure of 2-(phenylazo)pyridine (azpy).

Moreover, the cis-[Ru(azpy)₂Cl₂] showed remarkably high cytotoxicity against a series of tumor-cell lines (Velders, *et al.*, 2000). The pyrimidine ligand is an active component of antibiotics, antimicrobials and anticonvulsants (Santra, *et al.*, 1999).

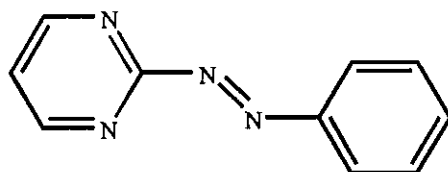


Figure 2. The structure of 2-(phenylazo)pyrimidine (azpym).

For these reasons, there is a continuous pursuit for new ruthenium(II) complexes with derivatives of pyridine ligand or with ligand containing azoimine unit. Like azpy and azpym the 2-(phenylazo)pyrazine or azine derived from the condensation reaction between 2-aminopyrazine and nitrosobenzene provide the π -acidic azoimine fragment for metal coordination. In this work, the ruthenium(II) chemistry with the azine ligand was synthesized and chemical properties of three new ruthenium(II) complexes having the general formula $[\text{Ru}(\text{azine})_2\text{Cl}_2]$ was described. The structure of the azine ligand is shown in Figure 3. Solid state molecular structures of the two complexes with the azine ligand were determined by X-ray crystallography.

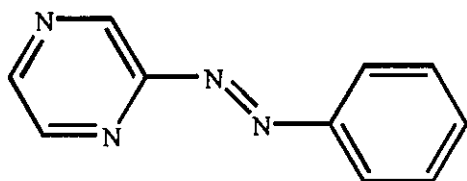


Figure 3. The structure of 2-(phenylazo)pyrazine (azine).

1.2 Review of Literatures

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 two cis-isomers (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 the bpy ligand (bpy = 2,2'-bipyridine).

Sheldon and Barf, (1995) studied the ruthenium-catalyzed epoxidation of olefins using a variety of nitrogen-containing ligands. They reported their finding on the epoxidation of trans-stibene with NaIO_4 as oxygen donor and ruthenium bis[2-(phenylazo)pyridine] (azpy) complexes as catalysts.

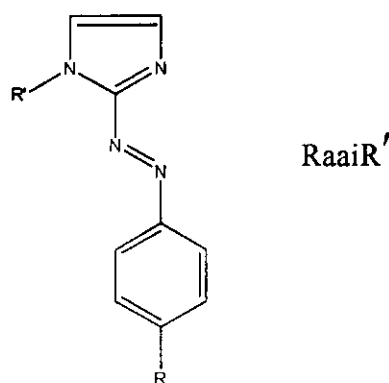
Monica, *et al.*, (1998) studied the synthesis and structural properties of the new mononuclear complex $[\text{Ru}(\text{dpp})(\text{CN})_4]^{2-}$ (dpp = 2,3-bis(2'-pyridyl)pyrazine) and some dinuclear complexes derived from it. They aim to compare the π -backbonding ability of the ligands bpy (bpy = 2,2'-bipyridine), bpz (bpz = 2,2'-bipyrazine) and dpp in the same chemical environment. Both bpz and dpp have the additional capacity (absent in bpy) to incorporate other metallic centers by coordinating through their remote N atoms, so that supramolecular systems can be obtained.

Santra, *et al.*, (1999) described the synthesis, spectral studies, redox properties and single crystal X-ray structures of ruthenium(II) complexes of 2-(arylo)pyrimidines. They synthesized a new member of the azoimine family, 2-(arylo)pyrimidine (aapm). Pyrimidine was chosen because of its higher π -acidity than that found in conventional widely used pyridine bases and also due to its biochemical importance.

Zaki, (2000) studied the nature of metal binding in thymine and its azo derivatives. The DC electrical behavior of 6-(2-thiazolylazo)thymine compound and its cobalt(II), nickel(II) and copper(II) complexes at different temperatures was investigated. The mechanism of conduction was explained. Pyrimidine derivatives constitute a very important class of compounds because they are components of the biologically important nucleic acid.

Das, *et al.*, (2000) interested in the chemistry of osmium in different coordination environment. They have chosen OsBr_2 moiety as the reactive fragment, because the Os-Br bonds were known to undergo dissociation under rather mild conditions. To satisfy the remaining four coordination sites of osmium in this OsBr_2 moiety, two π -acid ligands, i.e. 2-(phenylazo)pyridine and triphenylphosphine (PPh_3), have been utilized. An account of the chemistry of $[\text{Os}(\text{PPh}_3)_2(\text{azpy})\text{Br}_2]$ complex was reported with special references to synthesis, structure and redox properties.

Pal, *et al.*, (2000) reported the synthesis, structural characterization, redox activities of ruthenium complexes of 1-alkyl-2-(arylo)imidazoles (RaaiR') with $\text{Ru}(\text{bpy})_2$ -core.



Velder, *et al.*, (2000) presented the remarkably different cytotoxicity data of three isomeric dichlororuthenium(II) complexes of type $[\text{Ru}(\text{azpy})_2\text{Cl}_2]$, in which azpy stands for the bidentate ligand 2-(phenylazo)pyridine. Although the mechanism of action of antitumor-active ruthenium compounds was not fully understood, it was thought that, similar to the platinum drugs, the chloride complexes can hydrolyze in vivo, allowing the Ru to finally bind to the nucleobases of the DNA.

Hotze, *et al.*, (2000) reported the new water-soluble compound $\alpha\text{-}[\text{Ru}(\text{azpy})_2(\text{NO}_3)_2]$. The solid-state structure of this compound has been determined by X-ray

crystallography. The binding of the DNA-model bases 9-ethylguanine (9egua) and guanosine (guo) to this complex has been studied.

Wang, *et al.*, (2000) reported the synthesis of a series of azo metal chelate dyes whose spectra were capable of matching a semiconductor laser having wavelength of 635-650 nm. Studies of their spectroscopic and thermal properties were also included, azo metal chelate dyes have been developed in view of their excellence in sensitivity and stability as optical recording medium.

Santra, *et al.*, (2001) reported two classes of mixed-ligand ruthenium(II)-arylazopyrimidine complexes incorporating one and two 2-(arylazo)pyrimidine (aapm) ligands. Triphenylphosphine and Cl^- act as coligands. $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ was used as starting complex of ruthenium. In dichloromethane, the mixing of $\text{Ru}(\text{PPh}_3)_2(\text{aapm})\text{Cl}_2$ whereas the reaction in EtOH under reflux yields $[\text{Ru}(\text{PPh}_3)_2(\text{aapm})_2]^{2+}$ as the major species. The complexes were characterized by spectroscopic studies and in one case, $\text{Ru}(\text{PPh}_3)_2(\text{aapm})\text{Cl}_2$, the structure was established by X-ray crystallography.

Santra, *et al.*, (2001) reported first structurally characterized coordination polymer of silver(I) with 2-(arylazo)pyrimidine (aapm). 2-(Arylazo)pyrimidine belonged to neutral binucleating N,N' -chelating ligand. They possess active azoimine function and were efficient agents to stabilise low valent metal redox state. Presence of meta-related pyrimidine-N was responsible for self-assembly to generate coordination polymer.

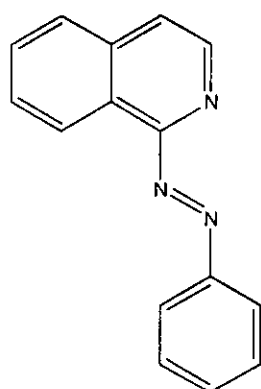
Senapati, *et al.*, (2002) reported the synthesis, spectral studies, redox properties and single-crystal X-ray structure of one of the isomers of osmium(II) complexes of 2-(arylazo)pyrimidines (aapm). The electronic properties of osmium(II) complexes were

different from that of ruthenium(II)-arylazopyrimidine complexes and have been interpreted from theoretical calculations using EHMO approximation.

Ohlsson, *et al.*, (2002) presented five azo dyes: 4-(phenylazo)-phenol, 4-phenylazo-benzeneamine, 4-phenylazo-benzonethiol, 4-phenylazo-benzoic acid, and 4-phenylazo-pyridine. The dyes with carboxylic acid and thiol gave coloured electrodes both for ZnO and TiO₂ whereas the pyridine had affinity only for TiO₂.

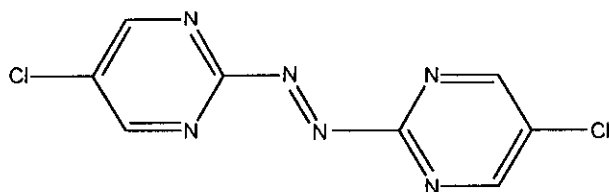
Kamar, *et al.*, (2002) described the synthesis and properties of a series of chromium(II) and chromium(III) complexes of the isomeric 2-[(N-arylamino) phenylazo]pyridine ligands. Optical properties of these were markedly different than those of the parent chromium-pap complexes.

Lu, *et al.*, (2003) described the synthesis and X-ray characterization of *tcc*-(dichloro){bis-(1-phenylazoisoquinoline)}ruthenium(II) and *ccc*-(dichloro){bis-(1-phenylazoisoquinoline)}ruthenium(II) complexes. A study of some coordinated bond lengths of these complexes with other similar complexes of ruthenium(II) has been summarized and compared. It is presumable that the coordination chemistry played an important role in biological molecules such as hemoglobin, chlorophyll and vitamin E.



1-(Phenylazo)isoquinoline

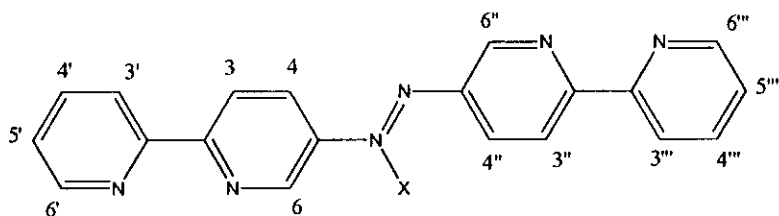
Kaim, *et al.*, (2003) presented the hypochlorite oxidation route for heterocycle amines to form corresponding azo compounds, 2,2'-azobis(5-chloropyrimidine) (abcp). They described efforts to further increase the π acceptor capacity by adding acceptor functions such as chloride substituents and by CH/N replacement.



abcp

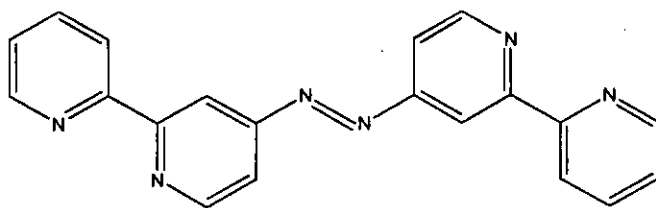
Das, *et al.*, (2003) presented the results on the reaction of ArNH_2 with $[\text{Ru}(\text{pap})_3](\text{ClO}_4)_2$ (pap = 2-(phenylazo)pyridine). In this case all the coordinated pap ligands have undergone amination exclusively at the para-carbon on the phenyl ring.

Otsuki, *et al.*, (2003) reported on the preparation and properties of new entries in bpy family having the 5,5''-substitution pattern, i.e., (1) the 5,5''-azobis(2,2'-bipyridine) or 5,5''-azo (2) the 5,5''-azoxybis(2,2'-bipyridine) or 5,5''-azoxy. Mononuclear and dinuclear ruthenium(II) complexes having one of these bridging ligands and 2,2'-bipyridine terminal ligands were also prepared. The azo or azoxy ligand in these complexes exhibited reduction processes at the less negative potentials than the terminal bpy's due to the low-lying π^* level. The results obtained for these 5,5''-azo derivatives were compared with the results from the 4,4''-azo compounds. It was shown that, the electrochemical properties were quite similar to those of 4,4''-azo. On the other hand, spectroscopic properties were quite different from each other.



X = none 5,5''-azo

X = O 5,5''-azoxy



4,4''-azo

1.3 Objectives

1. To synthesize the 2-(phenylazo)pyridine (azine) ligand and the three complexes of $[\text{Ru}(\text{azine})_2\text{Cl}_2]$
2. To characterize and to study the chemical properties of those compounds
3. To analyze and to summarize the chemistry of the azine ligand and the $[\text{Ru}(\text{azine})_2\text{Cl}_2]$ complexes.