Synthesis and Characterization of Ruthenium(II) Complexes with 2,2′:6′,2″-terpyridine and 5-chloro-2-(phenylazo)pyridine Ligand

Chanun Phongarthit

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Inorganic Chemistry
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Thesis Title	Synthesis and Characterization of Ruthenium(II) Complexes with 2,2′:6′,2″-terpyridine and 5-chloro-2-(phenylazo)pyridine Ligand
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ชื่อวิทยานิพนธ์ การสังเคราะห์และศึกษาโครงสร้างของสารประกอบเชิงซ้อนของ ruthenium(II) กับลิแกนด์ 2,2′:6′,2″-terpyridine และ 5-chloro-2-(phenylazo)pyridine

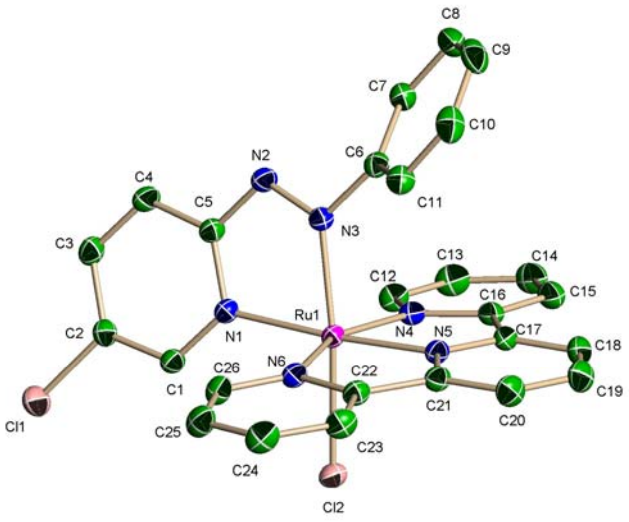
ผู้เขียน นายชนรรค์ พงศ์อาทิตย์

สาขาวิชา เคมีอนินทรีย์

ปีการศึกษา 2553

บทคัดย่อ

ได้มีการสังเคราะห์สารประกอบเชิงซ้อน $[Ru(tpy)(Clazpy)X]PF_6$ (tpy = 2,2′:6′,2″-terpyridine, Clazpy = 5-chloro-2-(phenylazo)pyridine และ X = Cl^-, NCS^-) ได้ทำการศึกษาโครงสร้างของสารแต่ละตัวโดยเทคนิคการวิเคราะห์หาปริมาณธาตุ (elemental analysis) เทคนิคอินฟราเรดสเปกโทรสโกปี (Infrared spectroscopy) เทคนิคนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี (NMR spectroscopy) เทคนิคการวัดการดูดกลืนแสง (UV-Vis spectroscopy) และศึกษาไฟฟ้าเคมีโดยเทคนิคไซคลิกโวลแทมเมทรี (cyclic voltammetry) นอกจากนี้ยังได้ยืนยันโครงสร้างของ $[Ru(tpy)(Clazpy)Cl]PF_6$ โดยเทคนิคการเลี้ยวเบนของรังสีเอกซ์อีกด้วย



$[Ru(tpy)(Clazpy)Cl]^+$

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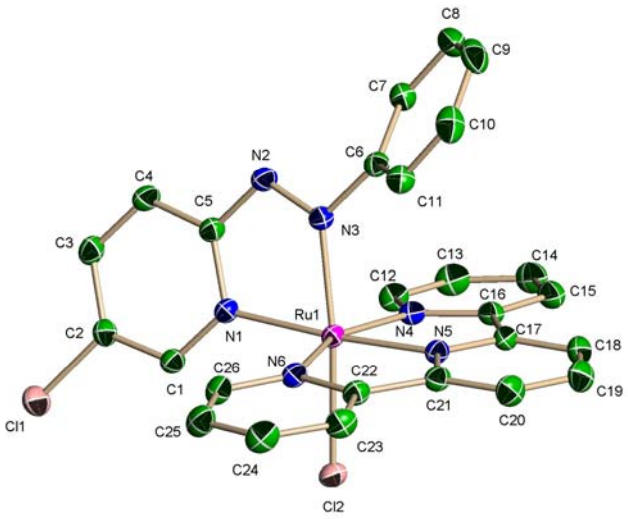
ABSTRACT

The $[Ru(tpy)(Clazpy)X]PF_6$ (tpy = 2,2′:6′,2″-terpyridine, Clazpy = 5-chloro-2-(phenylazo)pyridine and X = Cl^-, NCS^-) were synthesized. The complexes were characterized by elemental analyses, Infrared spectroscopy, NMR spectroscopy, UV-Vis absorption spectroscopy and cyclic voltammetry. The $[Ru(tpy)(Clazpy)Cl]PF_6$ were confirmed by X-ray crystallography.



$[Ru(tpy)(Clazpy)Cl]^+$

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THE RELEVANCE OF THE RESEARCH WORK

In this research, ruthenium(II) complexes with the bidentate ligand, 5-chloro-2-(phenylazo)pyridine (Clazpy) were synthesized and characterized by spectroscopic techniques. The redox properties of these compounds were studied by cyclic voltammetric technique.

Result from this work helps us to understand a variety of techniques used for the synthesis and characterization of compounds. In addition, these compounds may be developed into producing more effective catalysts, medicinal drug and other applications.

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LIST OF ILLUSTRATIONS

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ABBREVIATIONS AND SYMBOLS

Å	= Angstrom unit
A.R. grade	= Analytical reagent grade
azpy	= 2-(phenylazo)pyridine
Clazpy	= 5-Chloro-2-(phenylazo)pyridine
CH_3CN	= Acetonitrile
$CHCl_3$	= Chloroform
CH_2Cl_2	= Dichloromethane
cm^{-1}	= Wave number
COSY	= Correlation spectroscopy
CV	= Cyclic voltammetry
d	= Doublet
dd	= Doublet of doublet
DEPT	= Distortionless Enhancement by Polarization Transfer
DMF	= *N, N*-Dimethylformamide
DMSO	= Dimethyl sulfoxide
g	= Gram
h	= Hour
HMQC	= Heteronuclear Multiple Quantum Correlation experiment
Hz	= Hertz
IR	= Infrared
J	= Coupling constant
K	= Kelvin
mg/mL	= Milligram per milliliter
mL	= Milliliter
MLCT	= Metal-to-ligand charge transfer
mmol	= Millimole
mV/s	= Millivolt per second
MW.	= molecular weight

ABBREVIATIONS AND SYMBOLS (Continued)

nm	= Nanometer
NMR	= Nuclear Magnetic Resonance
s	= Singlet
t	= Triplet
TBAH	= Tetrabutylammonium hexafluorophosphate
TMS	= Tetramethylsilane
tpy	= 2,2′:6′,2″-terpyridine
UV-Vis	= Ultraviolet-Visible
°	= Degree
λ_{max}	= Maximum wavelength
ε	= Molar extinction coefficient
δ	= Chemical shift relative to TMS

1 INTRODUCTION

1.1 Introduction

Ruthenium(II) is well recognized as a metal ion capable of entering into dπ-pπ back bonding with π-acceptor ligands. The π-back bonding, in addition to the conventional σ bonding, gives rise to a number of interesting properties (Krause, *et al*., 1980). This interaction results in the more stability of ruthenium(II) center. There has been considerable interest in ruthenium complexes that contain azoimine (-N=N-C=N-) and imine (-N=C-C=N-) functional units ligands, such as ruthenium(II) contain 2,2′-bipyridine (Sullivan, *et al*., 1980). The ruthenium(II) azoimine complexes were investigated due to their potential applications in many chemical reactions, i.e., the complexes of $[Ru(azpy)_2Cl_2]$ (azpy = 2-(phenylazo)pyridine) have been used as catalysts in epoxidation reactions (Barf, *et al*., 1995). The structure of azpy is shown in Figure 1.

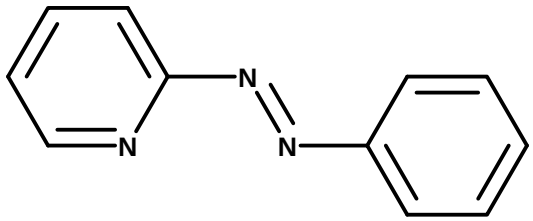
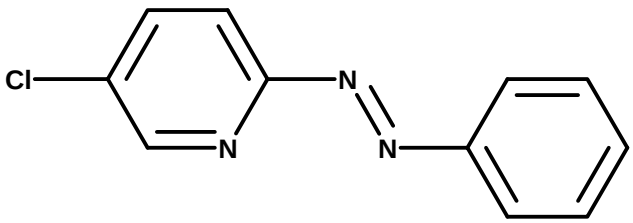


Figure 1. The structure of 2-(phenylazo)pyridine, (azpy)

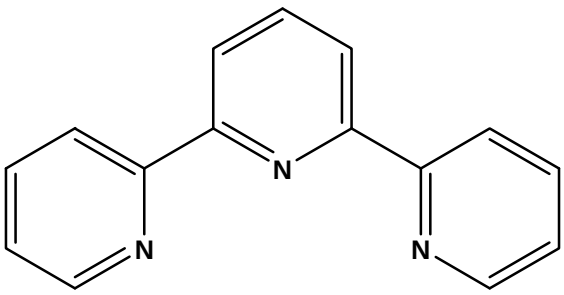
In addition, Ruthenium(II) polypyridyl complexes might be a possible alternative to the use of classical platinum chemotherapy. An example of this compound is the α-$[Ru(azpy)_2Cl_2]$ (azpy = 2-(phenylazo)pyridine) (Reedijk, *et al*., 2003). Furthermore, ruthenium(II) polypyridine complexes are widely used as photosensitizers in covalently linked multicomponent systems. Their photophysical properties make them ideal candidates as building blocks for designing of supra molecular species performing complex light induced functions (Duati, *et al*., 2000).

Complexes of ruthenium(II) with polypyridine ligands, such as ; 2,2′:6′,2″-terpyridine (tpy) and bidentate ligands have been extensively studied. For example, complexes of the type $[Ru(tpy)L_1L_2]^{(2-n)+}$ (L_1= apy (2,2′-azobispyridine), 2-phenylazopyridine, or 2-phenylpyridinylmethyleneamine, L_2= Cl^-, H_2O, or CH_3CN) were found to be able to coordinate to the DNA model base 9-ethylguanine. All compounds were screened for anticancer activity in variety of cancer cell lines. It was shown that in some cases activities are comparable to that of cisplatin (Corral, *et al.*, 2009). The oxoruthenium(IV) complex $[Ru(tpy)(bpy)O]^{2+}$ (bpy = 2,2′-bipyridine) is capable of DNA cleavage agent (Grover and Thorp., 1991).

In this research, 5-Chrolo-2-(phenylazo)pyridine (Clazpy) was chosen as the bidentate ligand. The Clazpy ligand is a derivative of known azo compound like 2-(phenylazo)pyridine. The Clazpy ligand is a better π-acceptor than azpy for stabilizing ruthenium(II) (Hansongnern and Sahavisit., 2005). The structures of Clazpy and tpy ligands are shown in Figure 2.



5-Chrolo-2-(phenylazo)pyridine, (Clazpy)



2,2′:6′,2″-terpyridine (tpy)

Figure 2. The structures of Clazpy and tpy ligands.

Therefore, in this work, it is our interest to investigate the chemistry of $[Ru(tpy)(Clazpy)X]^+$ type of complexes, where X = Cl^- and NCS^-. These complexes have been synthesized and characterized by elemental analysis, infrared spectroscopy, UV-Visible absorption, NMR spectroscopy and cyclic voltammetry. Furthermore, X-ray diffraction method has been used to determine the single crystal structure of complex. In addition, we hope that results from characterization of these complexes will be beneficial to insight information of these complexes and other researches.

1.2 Review of Literatures

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

Tokel-Takvoryan, *et al*., (1973) reported the electrochemistry and electrogenerated chemiluminesence (ecl) of four ruthenium(II) chelates, $Ru(L)_x^{n+}$ (X=3, n=2, L=2,2′-bipyridine (bpy); X=3, n=2, L=1,10-phenanthroline (phen); X=2, n=2, L=2,2′:6′,2″-terpyridine (tpy)). All compounds showed evidences of several one-electron reduction and oxidation steps to form products electrogenerated chemiluminesence via redox reactions of oxidized and reduced forms to form emitting species, which have been identified as the triplet state by comparison with their luminescent spectra; the electrogenerated chemiluminesence of the bpy complex is the most intense.

Sullivan, *et al*., (1980) studied the isomers of $[Ru(tpy)(PPh_3)Cl_2]$ complexes. These complexes have been characterized by infrared spectroscopy, UV-Visible absorption spectroscopy, ^1H and ^{31}P NMR spectroscopy and cyclic voltammetry. They reported some rather striking differences in the properties of the cis and trans isomers of the phosphine derivatives.

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

Gupta, *et al*., (1993) studied the new DNA cleavage agents based on $[Ru(tpy)(bpy)O]^{2+}$ 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 electrochemistry, UV-Visible absorption spectroscopy, electrophoresis and single crystal X-ray diffraction.

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

Pramanik, *et al*., (1998) studied the chemistry of $[Ru(tpy)(azpy)Cl]^+$ complex and the monodentate ligand (CH_3CN, 4-picoline and N_3^-). $[Ru(tpy)(azpy)CH_3CN](ClO_4)_2$ was characterized by X-ray crystallography showed that the azpy ligand was bound to ruthenium with the azo-nitrogen trans to CH_3CN. Furthermore, $[Ru(tpy)(azpy)OH_2]^{2+}$ 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-chlorophenyl cyanamide 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 pentaaminеruthenium(III) analogues.

Hansongnern, *et al*., (2001) synthesized and characterized the complex [Ru(tpy)(L)Cl]Cl (where L is 2-(phenylazo)pyridine = azpy). [Ru(tpy)(azpy)Cl]Cl was characterized by X-ray crystallography. The chlorine atom is trans to the nitrogen atom of the pyridine ring.

Konno, *et al*., (2002) reported the chemistry of $[Ru(tpy)(N\text{-}N)Cl]^{+}$ 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 2-(2′-dimetylamino -ethyl)-pyridine (DMAEPy) and 2-(2′-diethylaminoethyl)-pyridine (DEAEPy) had stronger electron donating abilities than 2-(2′-aminoethyl)-pyridine (AEPy).

Hansongnern, *et al*., (2003) studied the polypyridine complex of type $[Ru(tpy)(L)X]^{n+}$ (where tpy = 2,2′:6′,2″-terpyridine, L = a bidentate ligand (azpy), X = Br and n = 1). They synthesized the $[Ru(tpy)azpyBr]BF_4$. Then it was characterized by X-ray crystallography. It was found that the bromine atom is trans to the nitrogen atom of the pyridine ring.

Fabre, *et al*., (2005) synthesized the type [Ru(tpy)(acac)L] where tpy = 2,2′:6′,2″-terpyridine, acac = acetylacetonate, L = hmbpcyd = 4-(3-hydroxy-3-methylbutynyl)phenylcyanamide anion and epcyd = 4-ethynylphenylcyanamide anion. The complexes were characterized by UV-Vis, IR, ES-MS, electrochemistry and ^{1}H, ^{13}C NMR. The single crystal X-ray structure of the [Ru(tpy)(acac) hmbpcyd]$\cdot H_2O$ was determined.

Corral, *et al*., (2006) synthesized and characterized the complexes $[Ru(tpy)(apy)L^{n-}](ClO_4)_{(2-n)}$ (apy = 2,2′-azobispyridne; tpy = 2,2′:6′,2″-terpyridine; L = Cl, H_2O, CH_3CN). These complexes were characterized by 1D and 2D ^1H NMR spectroscopy, as well as spectrometry and elemental analysis. The molecular structures of the compounds were elucidated by single-crystal X-ray diffraction.

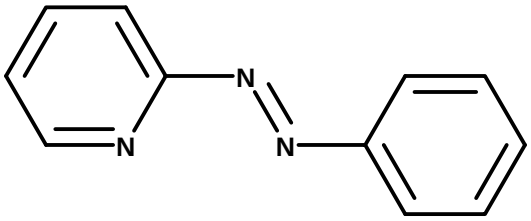
Karidi, *et al*., (2007) reported the DNA-binding properties of a number of ruthenium oligopyridine complexes with conjugated amino acids having the general formula $[Ru(tpy)(4\text{-}COY\text{-}4'\text{-}Mebpy)(X)]^{n+}$, X = NO (n = 3), X = Cl (n = 1) and NO_2 (n = 1) and Y = $AlaCONH_2$. The complexes were spectroscopically characterized and their DNA-binding properties were studied by circular dichroism (CD), ^{23}Na and ^{31}P NMR spectroscopy.

Hamaguchi, *et al*., (2008) prepared the $[Ru(tpy)(bpy)(2\text{-}OpyS)]PF_6$ (where bpy = 2,2′-bipyridine; tpy = 2,2′:6′,2″-terpyridine; 2-OpyS = 2-mercaptopyridine *N*-oxide). The complex contained a $2\text{-}OpyS^-$ ligand coordinating only with the sulfur atom. Electrochemically induced linkage isomerisation was examined for this complex.

Corral, *et al*., (2009) studied the various interaction modes between a group of six ruthenium polypyridyl complexes and DNA. Five mononuclear species were selected with formula $[Ru(tpy)L_1L_2]^{(2-n)+}$, and one closely related dinuclear cation of formula $[\{Ru(apy)(tpy)\}_2\{\mu\text{-}H_2N(CH_2)_6NH_2\}]^{4+}$. The ligand tpy is 2,2′:6′,2″-terpyridine and the ligand L_1 is a bidentate ligand, namely, apy (2,2′-azobispyridine), 2-phenylazopyridine, or 2-phenylpyridinylmethyleneamine. The ligand L_2 is a labile monodentate ligand, being Cl^-, H_2O, or CH_3CN. All six species containing a labile L2 able to coordinate to the DNA model base 9-ethylguanine. These compounds were studied by ^1H NMR and mass spectrometry.

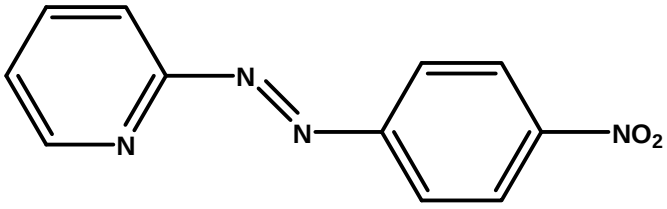
Synthesis and characterization of related compounds with azpy ligand and ruthenium(II) with azpy ligand have been reported;

Krause and Krause, (1980) studied dichlorobis(2-(phenylazo)pyridine)-ruthenium(II) complexes, $[Ru(azpy)_2Cl_2]$. Three isomers of $[Ru(azpy)_2Cl_2]$ were obtained from reaction between 2-(phenylazo)pyridine (azpy) and $RuCl_3.3H_2O$. 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).



azpy

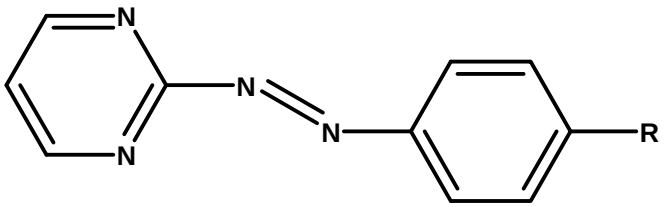
Krause and Krause, (1984) synthesized and characterized the complexes of $Ru(Naz)_2Cl_2$ (Naz = 2-((4-nitrophenyl)azo)pyridine by infrared spectroscopic, UV-Vis absorption spectroscopic and differential pulse voltammetric techniques. In comparison with $Ru(azpy)_2Cl_2$ complexes, the Naz ligand can stabilize ruthenium(II) better than the azpy ligand. This was due to the inductive of the nitrogen group in Naz ligand as it is stronger π-acceptor property than the azpy ligand.



Naz

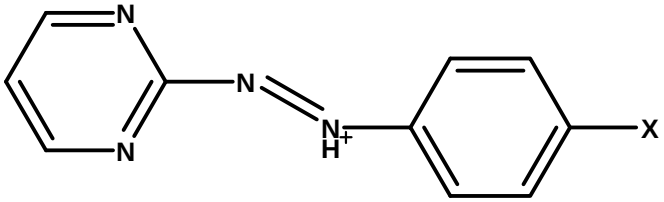
Sheldon and Barf, (1995) studied the ruthenium-catalyzed epoxidation of olefins using a variety of nitrogen-containing ligands. They reported that in the epoxidation of *trans*-stibene with $NaIO_4$ as oxygen donor and $Ru(azpy)_2Cl_2$ complexes was used as catalysts.

Santra, *et al*., (1999) describe the synthesis, spectral studied, redox properties and single crystal X-ray structure of $[Ru(aapm)_2Cl_2]$ (aapm = 2-(arylazo)pyrimidine). They synthesized a new member of azoimine family, 2-(arylazo)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.



aapm

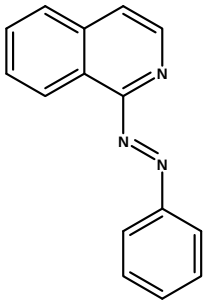
Peneerselvam, *et al*., (2000) reported the crystal structure of the [protonated 2-(phenylazo)pyridine and protonated 2-(4-hydroxyphenylazo) pyridine -(3:1)]tetrafluoroborate compound. The results from X-ray data showed that the protonation occurred at N(azo) atom and it was more basic than N(pyridine). The azpy compound was normally liquid at room temperature but intramolecular hydrogen bonding, N-H-N, and van der waals forces stabilized this crystal structure.



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

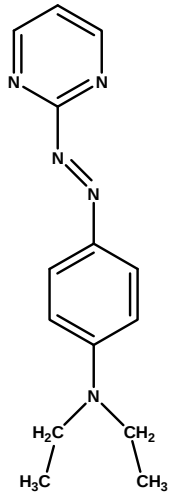
Hotze, *et al*., (2000) reported the new water-soluble compound α-$[Ru(azpy)_2(NO_3)_2]$. The solid-state structure of this compound has been determined by X-ray crystallography. The binding of DNA-model bases 9-ethylguanine (9egua) and guanosine (guo) to this complex has been studied.

Lu, *et al*., (2003) described the synthesis and X-ray characterization of *tcc*- and *ccc*-$[Ru(paiq)_2Cl_2]$ (paiq = 1-phenylazoisoquinoline) complexes. A study of some coordinated bond lengths of these complexes with other similar complexes of ruthenium(II) has been summarized and compared.



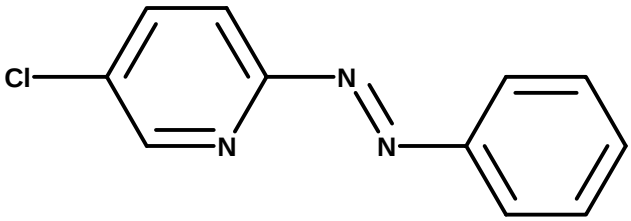
paiq

Hansongnern, *et al*., (2003) reported the synthesis and single-crystal X-ray structure of 2-(4'-*N*,*N*-diethylaminophenylazo)pyrimidine (deazpym). This compound containing pyridine with the azo moiety.



deazpym

Sahavisit and Hansongnern, (2005) synthesized as a new bidentate ligand, containing an azo moiety. Structure of the 5-Chloro-2-(phenylazo)pyridine (Clazpy) was similarly to 2-(phenylazo)pyridine (azpy) but the hydrogen atom on the fifth position on the pyridine ring was replaced by a chlorine atom. They reported the bidentate Clazpy ligand is a better π-acceptor than azpy in order to stabilize Ru(II) center.



Clazpy

1.3 Objective

1. To synthesize the $[Ru(tpy)(Clazpy)X]^{+}$ complexes, where X = Cl^{-} and NCS^{-}.
2. To characterize and to analyze the chemistry of the $[Ru(tpy)(Clazpy)X]^{+}$ complexes.

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Fluka

5-Chloro-2-aminopyridine, $C_5H_7N_3$, A.R. grade

Nitrosobenzene, C_6H_5NO, A.R.grade

Lithium chloride anhydrous, LiCl, A.R. grade

Tetrabutylammonium hexafluorophosphate, $[NBu_4]PF_6$, A.R.grade

2,2´:6´,2´´-terpyridine, $C_{15}H_{11}N_3$, A.R.grade

Materials from Merck

Silica gel 60 (0.063-0.200 nm) GF_{254}

Sodium hydroxide, NaOH, A.R. grade

Materials from Aldrich

Ruthenium(III) chloride hydrate, $RuCl_3.3H_2O$, A.R. grade

2.1.2 Solvents

Solvent from BHD Laboratory Supplies

Chloroform, $CHCl_3$, A.R. grade

Solvents from Lab.Scan Analytical Science

Acetonitrile, CH_3CN, A.R. grade

Dichloromethane, CH_2Cl_2, A.R. grade

Dimethyl sulfoxide, DMSO, A.R. grade

Hexane, C_6H_{14}, A.R. grade

Solvents from Merck

Methanol, CH_3OH, A.R grade

Ethanol, C_2H_5OH, A.R. grade

Hydrochloric acid, HCl, A.R. grade

Solvent from M&B Laboratory Chemical

Dimethylformamide, $HCON(CH_3)_2$, A.R. grade

2.2 Instruments

2.2.1 Melting Point Apparatus

Melting points of all compounds were measured on the Thomas Hoover Capillary melting point, range in 30 - 300˚C.

2.2.2 Elemental Analysis

Elemental analytical data were obtained by using a CE Instruments Flash 1112 Series EA CHNS-O Analyzer

2.2.3 Infrared Spectroscopy

Infrared spectra were collected by using KBr pellets on a Perkin Elmer Spectrum BX FT-IR Spectrophotometer from 400 - 4,000 cm^{-1}.

2.2.4 UV-Visible Absorption Spectroscopy

UV-Visible absorption spectra were recorded in the range 300-800 nm by Hewlett Peckard 8425A diode array spectrophotometer.

2.2.5 Nuclear Magnetic Resonance Spectroscopy

1D and 2D NMR spectra were recorded in DMSO-d_6 solution with Fourier Transform NMR spectrometer 500 MHz, Model UNITY INOVA, Varian. Tetramethylsilane ($Si(CH_3)_4$) was used as an internal standard.

2.2.6 Cyclic Voltammetry

Electrochemical experiments were carried out using cyclic voltammetric technique. The program was Echem 1.5.1. Cyclic voltammograms were obtained using a glassy carbon as a working electrode, a platinum wire as an auxiliary electrode and a platinum disc as a reference electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate, $[NBu_4]PF_6$ **,** (TBAH) in acetonitrile. At the end of each experiment, ferrocene was added as an internal standard. The argon gas was bubbled through the solution prior to each measurement.

2.2.7 X-ray Diffractometry

The structure of $[Ru(tpy)(Clazpy)Cl]PF_6$ was determined by Smart APEX CCD diffractometer with the Xtal 3.7.1 program system.

2.3 Synthesis of ligand

The 5-chloro-2-(phenylazo)pyridine ligand was prepared by literature methods (Sahavisit and Hansongnern, 2005).

5-Chloro-2-(phenylazo)pyridine ligand (Clazpy)

5-chloro-2-aminopyridine (378 mg, 2.94 mmol) and nitrosobenzene (318 mg, 2.97 mmol) were added to the benzene solution with the presence of sodium hydroxide. The mixture was refluxed with stirring continuously for 15 h. The green solution gradually turned to dark brown. The product was extracted with benzene and purified by column chromatography on a silica gel. The orange band was collected after elution with dichloromethane and hexane (1:9 by volume) and evaporated to dryness. The yield was 323 mg (50%).

2.4 Syntheses of complexes

$Ru^{III}(tpy)Cl_3$ complex was synthesized by published procedures (Sullivan, *et al*., 1980). The $[Ru(tpy)(Clazpy)Cl]PF_6$ complex was prepared by modified literature methods (Takeuchi, *et al.*, 1984). The $[Ru(tpy)(Clazpy)NCS]PF_6$ was prepared by modified published procedures (Hecker, *et al.*, 1991).

Trichloro(2,2´:6´,2´´-terpyridine)ruthenium(III) complex, $Ru^{III}(tpy)Cl_3$

The 40 mL of ethanol in a 250 mL round-bottom flask was added to a 0.399 g (1.53 mmol) of $RuCl_3.3H_2O$ and 0.349 g (1.50 mmol) of 2,2´:6´,2´´-terpyridine. The mixture was refluxed for 4 h. After this time the reaction was cool to room temperature. The fine brown powder precipitated and was filtered from the reddish yellow solution. The product was washed with 30 mL of ethanol followed by 30 mL of ether and dried in air at room temperature. The yield was 584 mg (87%).

Chloro(5-chloro-2-(phenylazo)pyridine)(2,2′:6′2″-terpyridine)ruthenium (II) hexafluorophosphate, [Ru(tpy)(Clazpy)Cl]PF_6

$Ru^{III}(tpy)Cl_3$ (0.203 g, 0.454 mmol), 5-Chloro-2-(phenylazo)pyridine (Clazpy) (0.118 g, 0.545 mmol) and LiCl (0.065 g, 1.53 mmol) were added to 40 mL of a 3:1 (V/V) ethanol:H_2O solvent mixture. Triethylamine (0.7 mL) was added as a reductant. The solution was refluxed with stirring continuously for 4 h. Then the reaction mixture was filtered while it was hot. The NH_4PF_6 was added into the dark red solution. After 2 days, black solid was collected by vacuum filtration and washed with cooled water, and ether, respectively. The precipitate was dried and recrystallized with acetone and ethanol. The yield was 288 mg (88%).

(5-chloro-2-(phenylazo)pyridine)(isothiocyanato)(2,2′:6′2″-terpyridine) ruthenium(II) hexafluorophosphate, [Ru(tpy)(Clazpy)NCS]PF_6

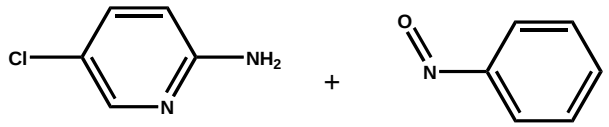
[Ru(tpy)(Clazpy)(NCS)]PF_6 was prepared from the reaction between $Ru^{III}(tpy)Cl_3$ (0.203 g, 0.454 mmol) and 5-chloro-2-(phenylazo)pyridine (Clazpy) (0.118 g, 0.545 mmol). The mixture was refluxed for 4 h in 40 mL of ethanol: H_2O (3:1 by volume) containing 0.065 g (1.53 mmol) of LiCl and 0.7 mL of triethylamine (Et_3N). Then the reaction mixture was filtered while it was hot. The solution was allowed to evaporate for a few days, then the black red solid came out. A 100 mg of the black red solid and 0.030 g of $AgNO_3$ (0.1762 mmol) was refluxed for 1 h in 40 mL of acetone: H_2O (3:1 by volume). Then the reaction mixture was filtered while it was hot. A 52 mg of KSCN (0.5286mmol) was added to the filtrate, and the mixture was heated and refluxed for 1 h. NH_4PF_6 was added to the solution. After 3 days, black red solid was collected by vacuum filtration and washed with cold water and ether, respectively. The precipitate was dried and recrystallized with acetone and ethanol. The yield was 94 mg (78%).

3 RESULTS AND DISCUSSION

3.1 Syntheses and characterization of ligand

3.1.1 Syntheses of ligand

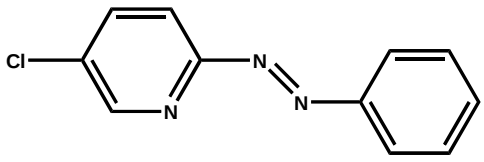
The 5-Chloro-2-(phenylazo)pyridine ligand was synthesized by using the literature procedure (Sahavisit and Hansongnern, 2005). This ligand was generally obtained by the condensation of nitrosobenzene with 5-chloro-2-aminopyridine in 1:1 mole ratio in the mixture of sodium hydroxide and benzene solution. The reaction was refluxed for 15 h. Then, the mixture was extracted with benzene and purified by column chromatography. The orange band was collected. The reaction is shown in equation (1)



5-chloro-2-aminopyridine nitrosobenzene

NaOH

Benzene



(1)

The yield of Clazpy is 50 %.

Table 1. The physical property of Clazpy ligand.

Compound	Physical properties		
	Appearance	Color	Melting point (°C)
Clazpy	solid	orange	98-99

The melting point of the Clazpy ligand was in the range of 98-99°C. The solubility of 10 mg of ligand was tested in 5 mL of various solvents. The ligand was very soluble in the hexane, benzene, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), ethanol (EtOH), methanol (MeOH), acetonitrile (CH_3CN), ethyl acetate (EtOAc), acetone (CH_3COCH_3) and *N*,*N*-dimethyl sulfoxide (DMSO). The Clazpy ligand is insoluble in water (Sahavisit and Hansongnern).

3.1.2 Characterization of ligand

The chemistry of the Clazpy ligand was determined by using these techniques.

3.1.2.1 Infrared spectroscopy
3.1.2.2 UV-Visible absorption spectroscopy
3.1.2.3 Nuclear Magnetic Resonance spectroscopy (1D and 2D)
3.1.2.4 Cyclic Voltammetry

3.1.2.1 Infrared spectroscopy

Infrared spectroscopy is a technique to study the functional groups of compounds. Infrared spectra were collected by using KBr pellets in the range of 4000-400 cm^{-1}. The important vibrational frequencies are C=C, C=N, N=N (azo) stretching modes and C-H bending in monosubstituted benzene.

Infrared spectroscopy of the Clazpy ligand

The infrared spectroscopic data of the Clazpy ligand are listed in Table 2.

Table 2. Infrared spectroscopic data of the Clazpy ligand

Vibration modes	Frequencies (cm^{-1})
C=N, C=C stretching	1565 (m) 1441 (s)
N=N stretching	1364 (s)
C-H bending in monosubstituted benzene	776 (s) 685 (s) 638 (m)
C-Cl stretching	547(s)

s = strong, m = medium

The infrared spectrum of Clazpy exhibited intense bands at 1600-400 cm^{-1}. The ligand showed strong peaks at 1565, 1441 cm^{-1}, corresponding to C=C and C=N stretching in the pyridine ring of the ligand. The sharp band at 1364 cm^{-1} was assigned to the N=N stretching, which was had a lower frequency than that in azpy (1420 cm^{-1}) (Krause and Krause, 1980). This stretching mode was used to be considered the π-acid property in azo complexes. It was found that the N=N bond of the free azpy ligand is stronger than that of Clazpy ligand (Sahavisit and Hansongnern). The infrared spectrum is shown in Figure 3.

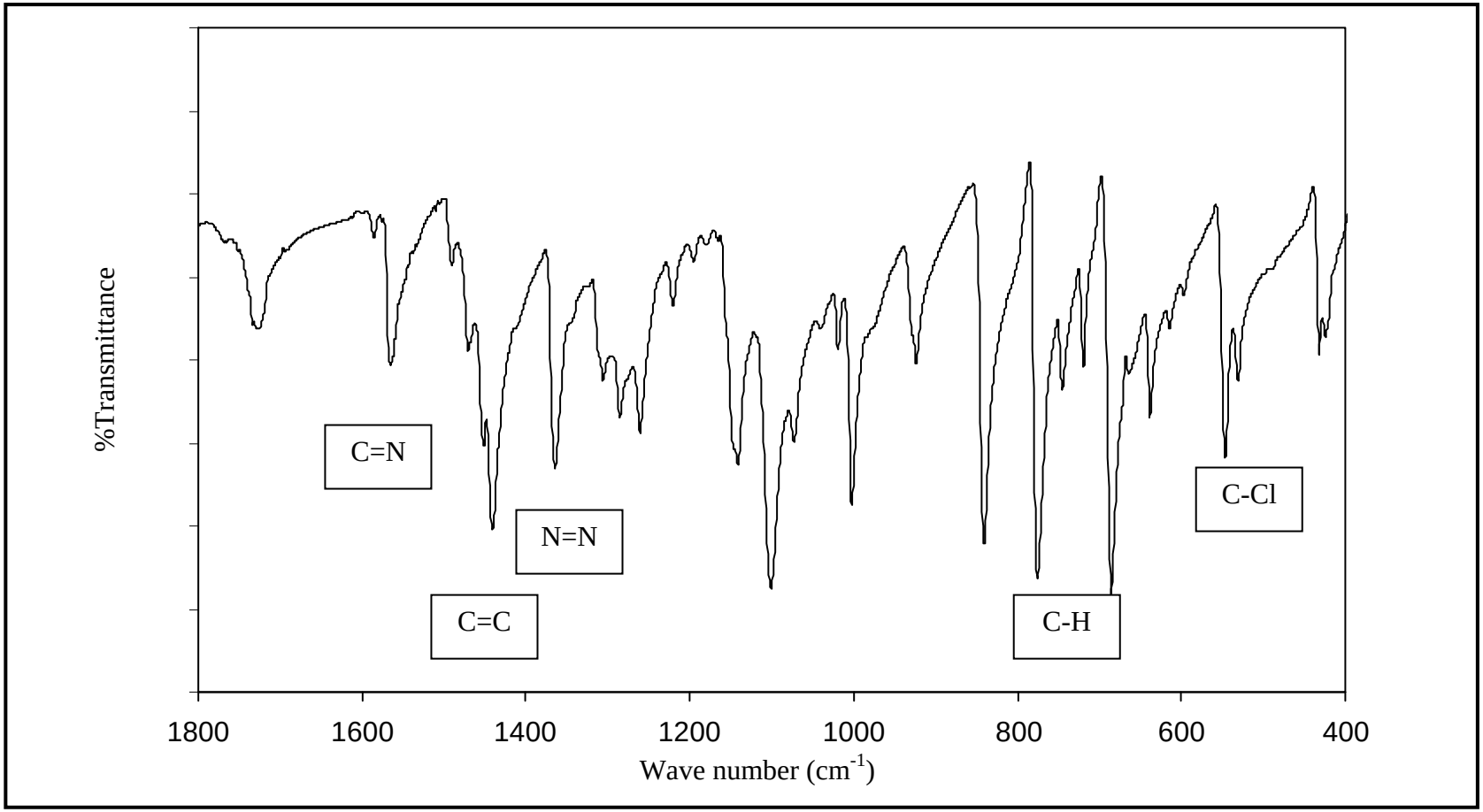


Figure 3. IR spectrum of Clazpy.

3.1.2.2 UV-Visible absorption spectroscopy

UV-Visible absorption spectroscopy is a technique to study the electronic transitions of compounds. The electronic absorption spectrum of the compound in three solvents were recorded in the range of 300-800 nm. The spectral data are given in Table 3. The absorption spectrum of Clazpy in CH_3CN is shown in Figure 4.

Table 3. UV-Visible absorption spectroscopic data of the ligand.

Solvent	λ_{max} nm, ($\varepsilon^a \times 10^4$ $M^{-1}cm^{-1}$)
CH_3CN	320 (2.11), 446 (0.06)
CH_3OCH_3	450 (0.05)
DMSO	327 (1.96), 449 (0.06)

[a] Molar extinction coefficient

UV-Visible spectral studies of the free ligand displayed two intense bands in range 300-460 nm. The absorptions at 320 and 327 nm ($\varepsilon \approx$ 21100 and 19600 $M^{-1}cm^{-1}$) were assigned to $\pi \longrightarrow \pi^*$ transition and the bands in visible region at 446 and 450 nm ($\varepsilon \approx$ 600 and 500 $M^{-1}cm^{-1}$) were assigned to $n \longrightarrow \pi^*$.

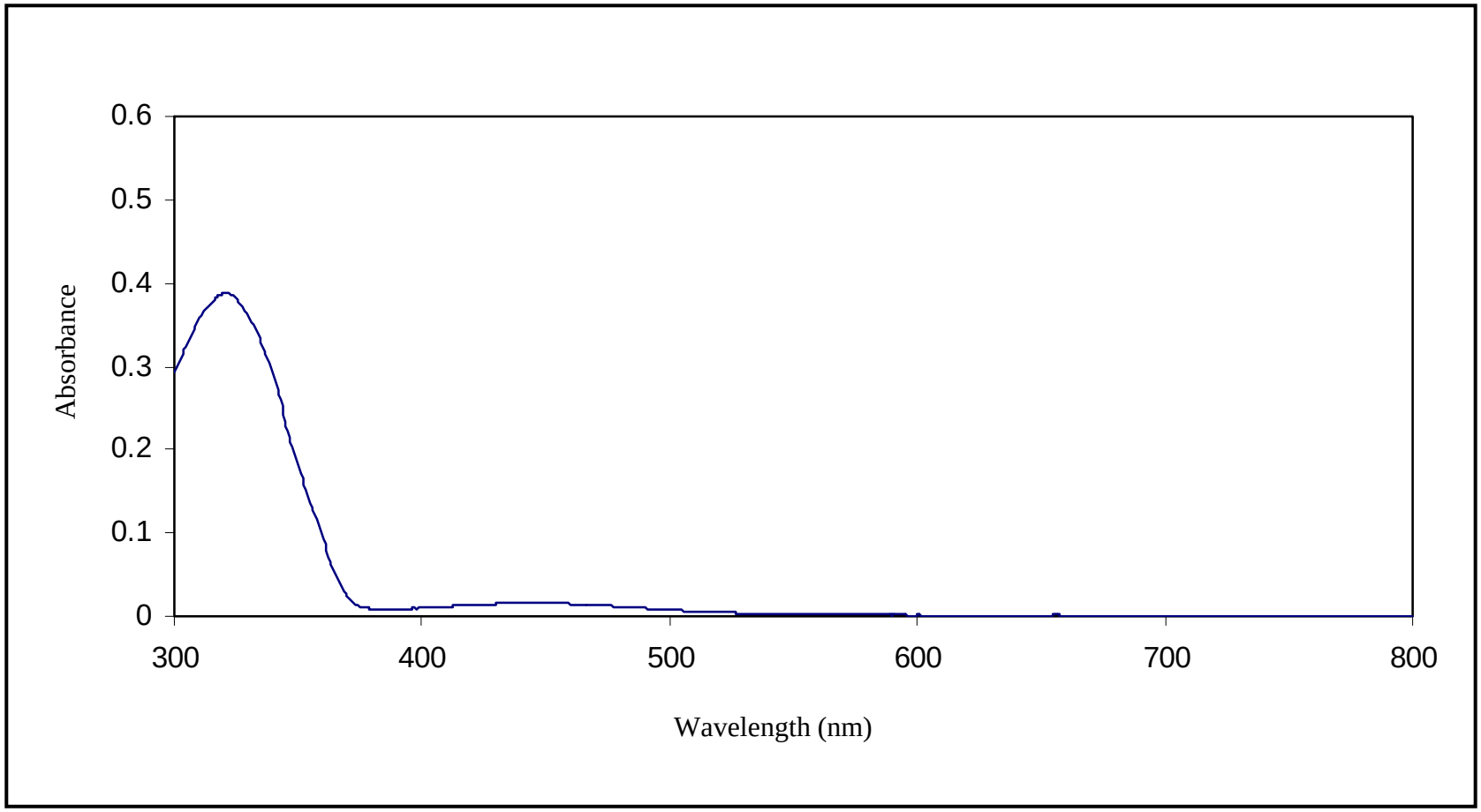


Figure 4. UV-Visible absorption spectrum of Clazpy in CH_3CN.

3.1.2.3 Nuclear Magnetic Resonance spectroscopy (1D and 2D)

Nuclear Magnetic Resonance (NMR) spectroscopy is an important technique to determine the molecular structure of a compound. The structure of Clazpy ligand was investigated by using 1D and 2D NMR spectroscopic techniques (^{1}H NMR, ^{1}H-^{1}H COSY NMR, ^{13}C NMR, DEPT NMR and ^{1}H-^{13}C HMQC NMR). The NMR spectra of the compound were recorded in DMSO-d_6 on UNITY INOVA 500 MHz. The tetramethylsilane ($Si(CH_3)_4$) was used as an internal reference.

Nuclear Magnetic Resonance spectroscopy of the 5-Chloro-2-(phenylazo)pyridine ligand

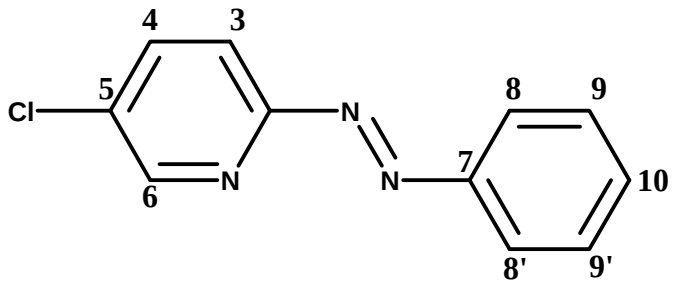


Table 4 showed the chemical shift and *J*-coupling constant data of Clazpy and NMR spectra are shown in Figure 5 to Figure 10.

Table 4 ^{1}H and ^{13}C NMR spectroscopic data of the Clazpy ligand

H-position	^{1}H NMR			^{13}C NMR
	δ (ppm)	*J* (Hz)	Number of H	δ (ppm)
6	8.76 (*d*)	2.5	1	148
4	8.16 (*dd*)	9.0, 2.5	1	138

d = doublet, t = triplet, dd = doublet of doublet

Table 4 ^{1}H and ^{13}C NMR spectroscopic data of the Clazpy ligand (Continued)

H-position	^{1}H NMR			^{13}C NMR
	δ (ppm)	J (Hz)	Number of H	δ (ppm)
8, 8′	7.94 (*m*)	-	2	123
3	7.76 (*d*)	9.0	1	114
9, 9′, 10	7.63 (*m*)	-	3	129, 133
Quaternary carbon (C)			C2 C5 C7	161 151 133

d = doublet, dd = doublet of doublet, m = multiplet

The 5-Chloro-2-(phenylazo)pyridine (Clazpy) has eight protons on the molecule. The ^{1}H NMR spectrum of Clazpy showed five resonance signals for eight protons (Figure 5).

The most downfield of proton H6 was due to the effect of nitrogen and chlorine atom on the pyridine ring. The proton H6 resonance appeared at 8.76 ppm as doublet (d) due to the coupling with the proton H4 (J = 2.5 Hz).

The proton 4 resonance appeared at 8.16 ppm as doublet of doublet (dd) due to the coupling with the proton H3 (J = 9.0 Hz) and long range coupling with the proton H6 (J = 2.5 Hz).

The proton 3 resonance appeared at 7.76 ppm as doublet (d) due to the coupling with the proton H4 (J = 9.0 Hz).

The proton 8 was two equivalent protons on phenyl ring. The proton 8 resonance appeared at 7.94 ppm as multiplet (m). The proton 8 located next to the azo nitrogen, so it appeared at lower than that the proton 9 and the proton 10.

The proton 9 was two equivalent protons located next to the proton 8. The proton 9 resonance appeared at 7.63 ppm as multiplet (m).

The proton 10 located next to the proton 9. The proton 10 resonance appeared at the same position of the proton 9 (7.63 ppm) as multiplet (m).

In addition, the peak assignments was confirmed using ^{1}H-^{1}H COSY NMR spectrum, which showed the correlation of ^{1}H-^{1}H coupling. The ^{1}H-^{1}H COSY NMR signals are presented in Figure 6.

The results from ^{13}C NMR spectrum (Figure 7) was shown. The result of DEPT NMR (Figure 8, 9), showed only signals of CH and CH_3 groups, respectively. The ^{13}C NMR spectrum of the Clazpy ligand gave 9 signals for 11 carbons. The signal of quaternary carbon C2 of the pyridine ring appeared at the most downfield (161 ppm) due to its position between nitrogen of the pyridine ring and nitrogen of the azo function. The signal at 151 ppm was due to the quaternary carbon C5 on the pyridine ring. The intense peak at 133 ppm referred to the quaternary carbon C7. The signal of carbon C6 occurred at 148 ppm, which it the lower field than that of other methane carbons because it is located next to the nitrogen atoms. The carbon signals at 123 and 129 ppm were attributed to the two equivalent carbon C8 and C9. The signals of carbon C3, C4, and C10 appeared at 114, 138, and 133 ppm, respectively. The ^{13}C NMR signals assignments were based on the ^{1}H-^{13}C HMQC NMR spectrum (Figure 10), which exhibited a correlation between ^{1}H NMR spectrum and ^{13}C NMR spectrum. Therefore, the result of 1D and 2D NMR spectra were good evidence to confirm the structure of the Clazpy ligand.

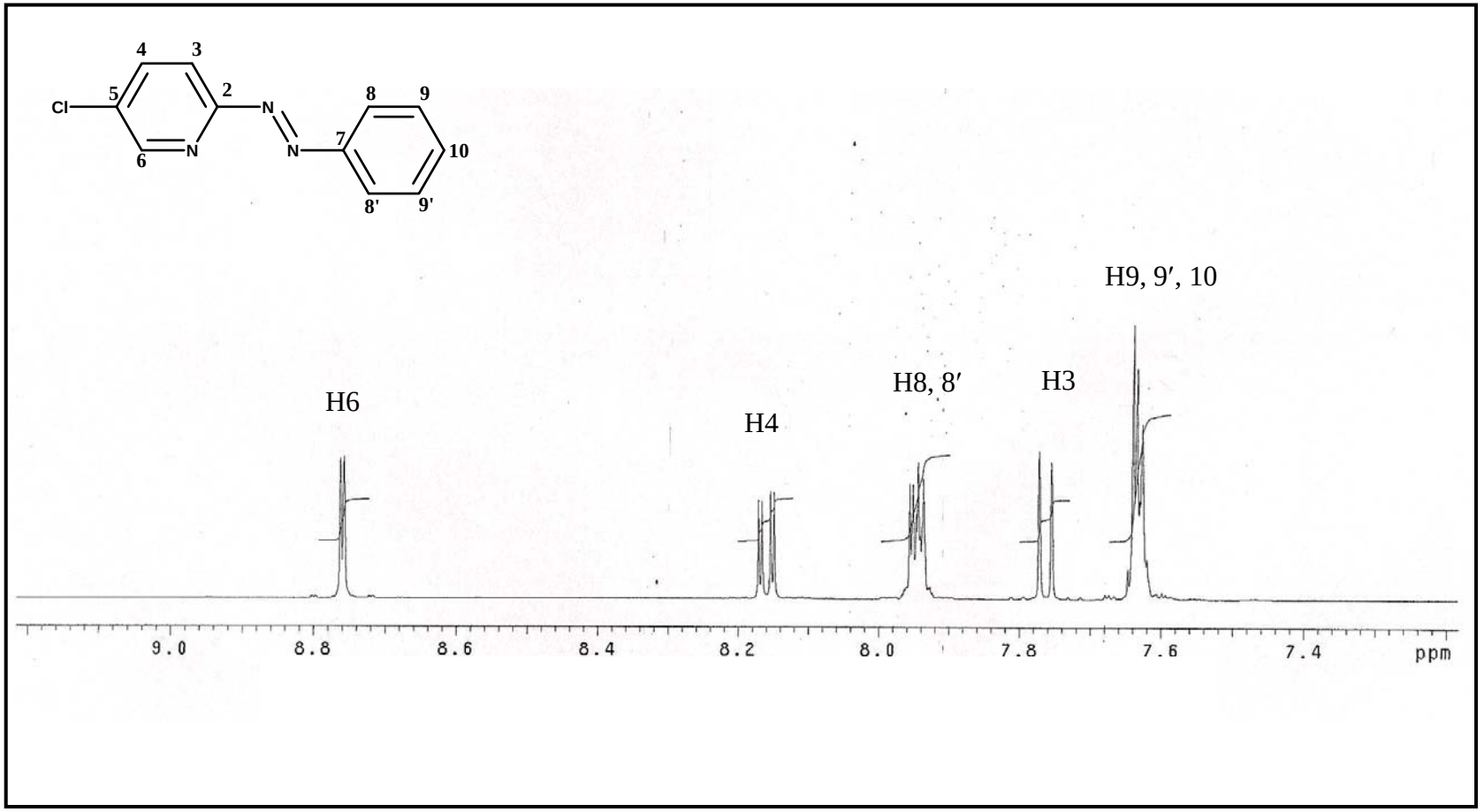


Figure 5. ^{1}H NMR spectrum of Clazpy in DMSO-d_6.

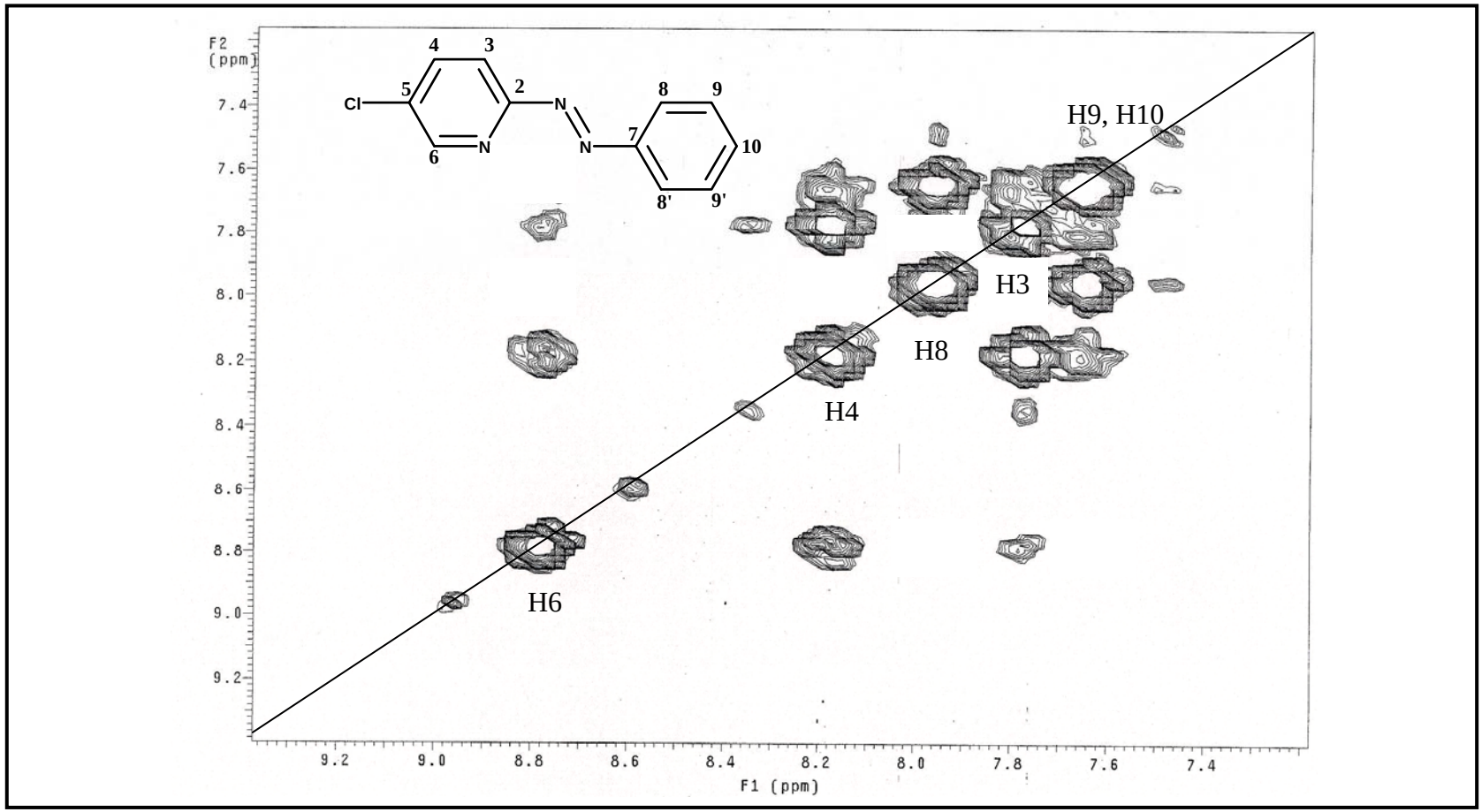


Figure 6. ^{1}H-^{1}H COSY NMR spectrum of Clazpy in DMSO-d_6.

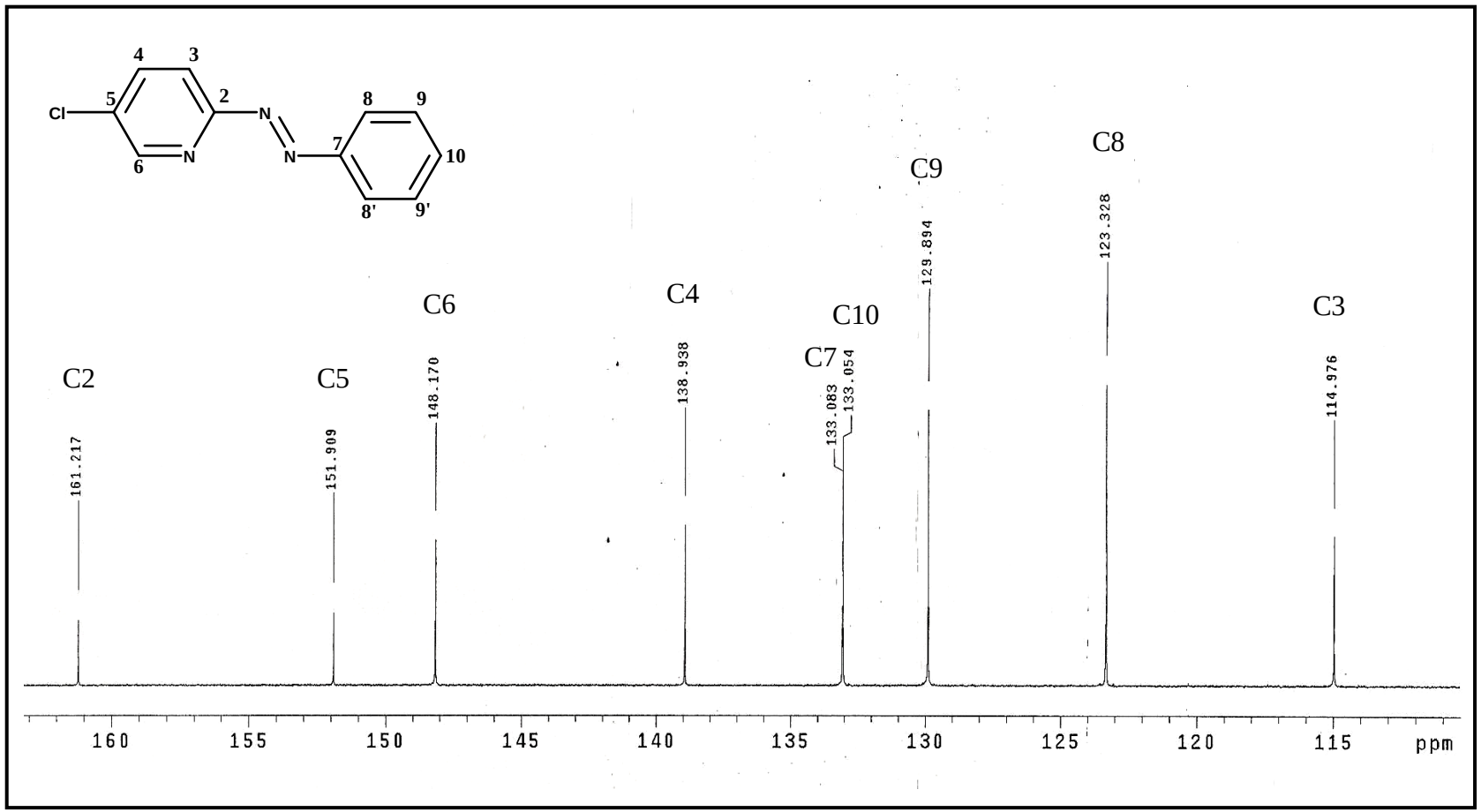


Figure 7. ^{13}C NMR spectrum of Clazpy in DMSO-d_6.

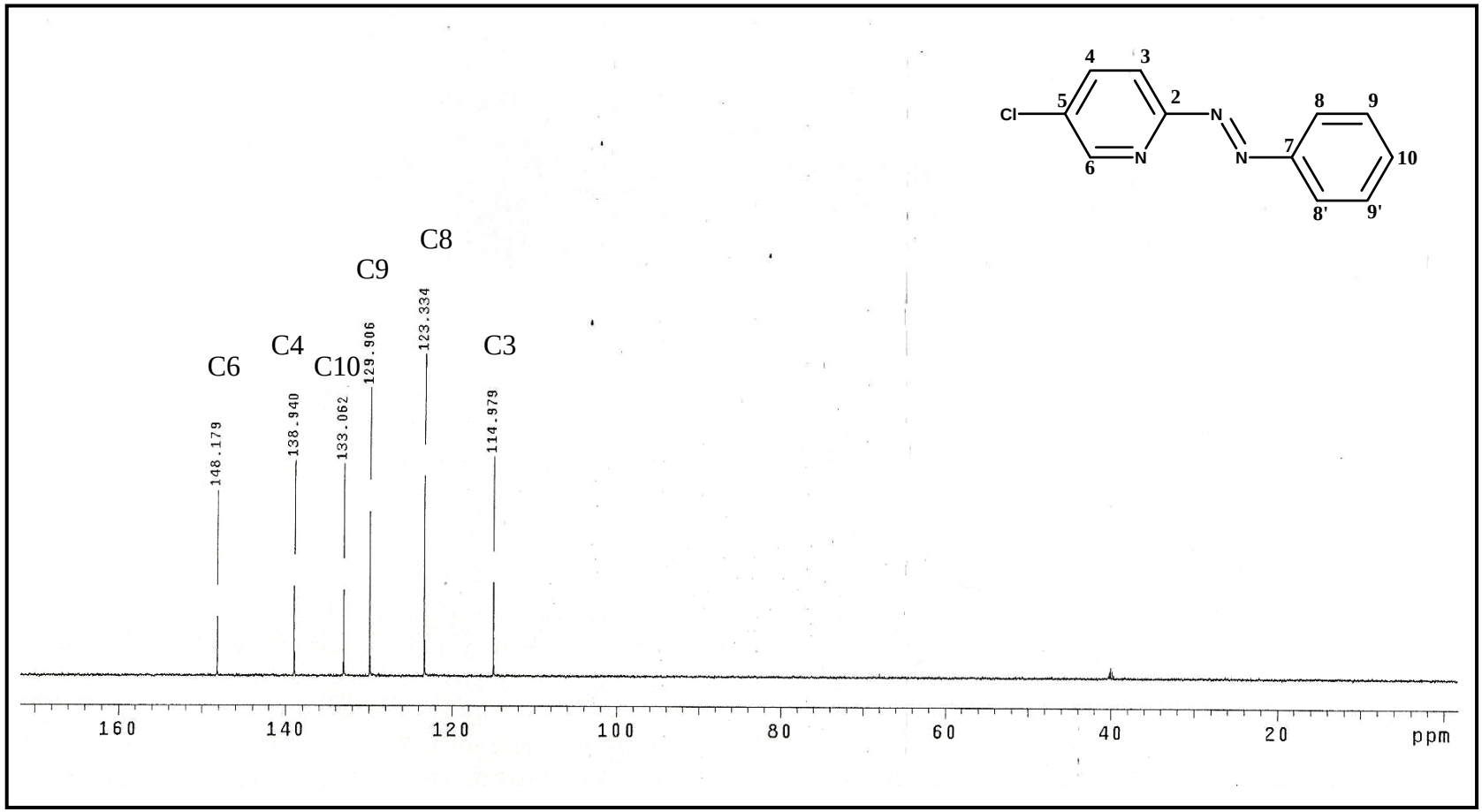


Figure 8. DEPT90 NMR spectrum of Clazpy in DMSO-d_6.

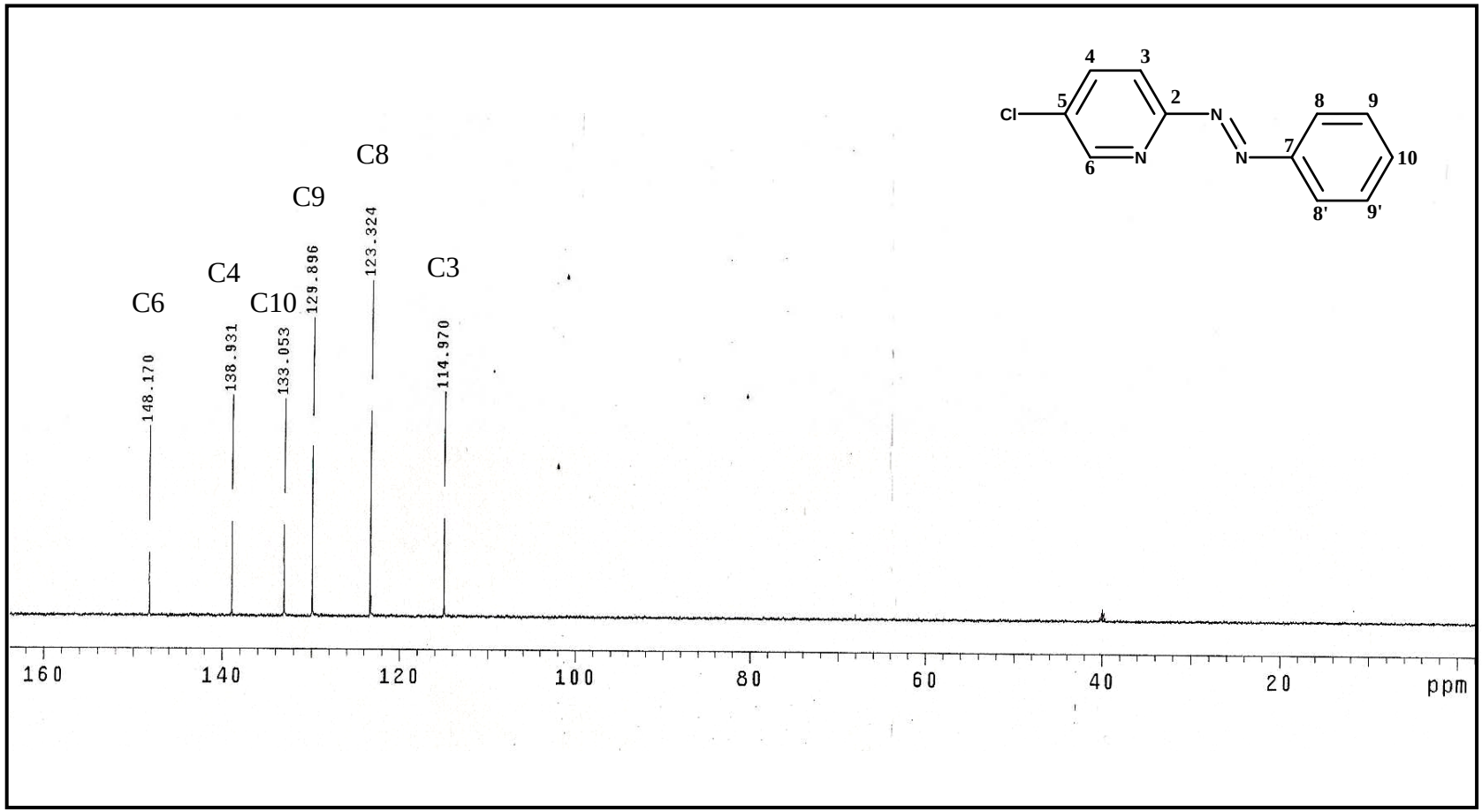


Figure 9. DEPT135 NMR spectrum of Clazpy in DMSO-d_6.

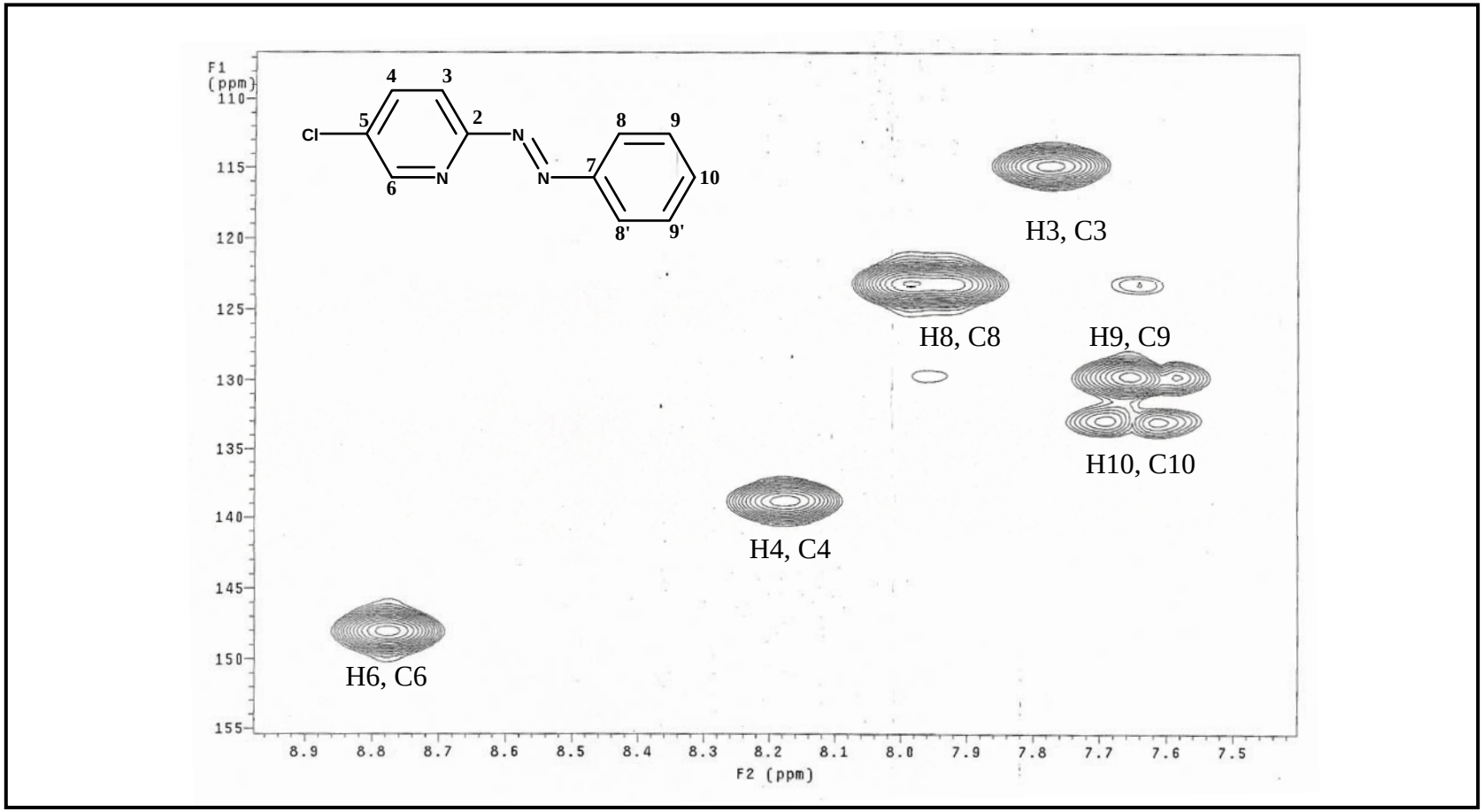


Figure 10. ^{1}H- ^{13}C HMQC NMR spectrum of Clazpy in DMSO-d_6.

3.1.2.4 Cyclic Voltammetry

Electrochemical properties of the Clazpy ligand was studied by cyclic voltammetry with a glassy as a carbon working electrode, platinum wire as a reference electrode, a platinum disk as an auxiliary electrode and was examined in acetonitrile using tetrabutylammonium hexafluorophosphate (TBAH) as a supporting electrolyte at the scan rate of 50 mV/s. All potentials were reported with reference to the ferrocene/ ferrocenium couple.

In this experiment, different scan rates were used to check the couple and the ΔEp of the redox reaction. The couple having equal anodic current (i_{pa}) and cathodic current (i_{pc}) was referred to as a reversible couple. On the other hand, the unequal currents were referred unequally transfer of reduction and oxidation peaks. This led to an irreversible couple. The cyclic voltammogram in acetonitrile solution of the Clazpy ligand is shown in Figure 11. The cyclic voltammetric data are given in Table 5.

Table 5. cyclic voltammetric[a] data of Clazpy ligand in 0.1 M TBAH CH_3CN at scan rate 50 mV/s (ferrocence as an internal standard)

Compound	$E_{1/2}$ (V) (ΔE_p (mV))	
	Oxidation	Reduction
Clazpy	-	-1.05 (120)
azpy	-	-1.15[b]

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa}-E_{pc}$

[b] cathodic peak potential

Oxidation range

The cyclic voltammogram of Clazpy ligand showed no signals in potential range 0.00 to +1.50 V.

Reduction range

The cyclic voltammogram of Clazpy ligand showed one quasi-reversible couple with two electron transfer process at -1.05 V with peak-to-peak separation 120 mV in potential range 0.00 to -2.00 V. The result from above corresponded to the electron acceptor of the azo function in equation (2)

$$\text{Clazpy} + 2e^- \rightleftharpoons \text{Clazpy}^{2-} \qquad (2)$$

The electrochemistry behavior of Clazpy was different from the azpy ligand. The Clazpy ligand showed one quasi-reversible, while azpy showed one irreversible (Sahavisit and Hansongnern).

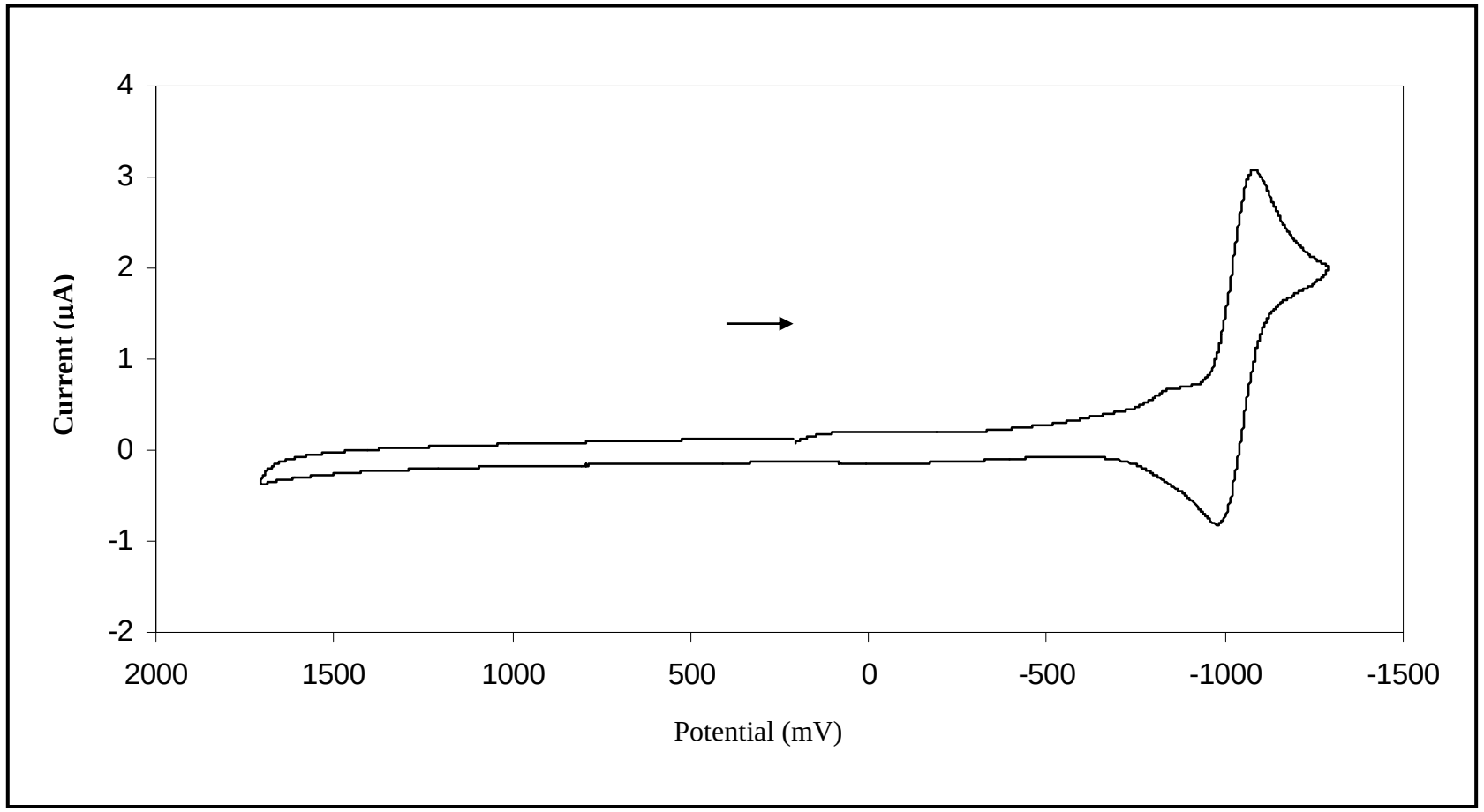
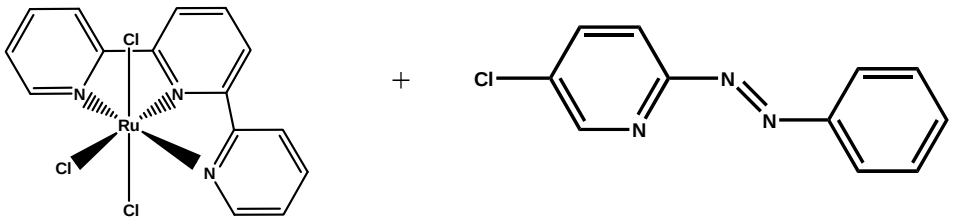


Figure 11. Cyclic voltammogram of Clazpy in 0.1 M TBAH CH_3CN at scan rate 50 mV/s.

3.2 Syntheses and characterization of the complexes

3.2.1 Syntheses of complexes

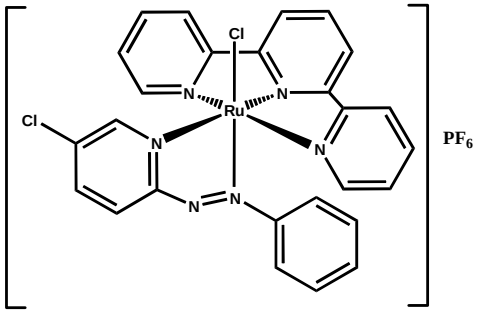
The $[Ru(tpy)(Clazpy)Cl]PF_6$ complex was synthesized by reaction of the free Clazpy ligand with $Ru(tpy)Cl_3$ under the refluxing condition in ethanol/water in a presence of NEt_3 and LiCl. Triethylamine (NEt_3), which functions as a base, is probably the reductant reagent. The NEt_3 reduced Ru(III) to Ru(II). The LiCl is used to prevent any dissociation of Cl^- from the product and thus to increase the yield of the product (Pramanik, *et al*., 1998). The reaction is shown in equation (3).



$Ru^{III}(tpy)Cl_3$ + Clazpy

(1) NEt_3, $EtOH/H_2O$ (3:1) LiCl, reflux

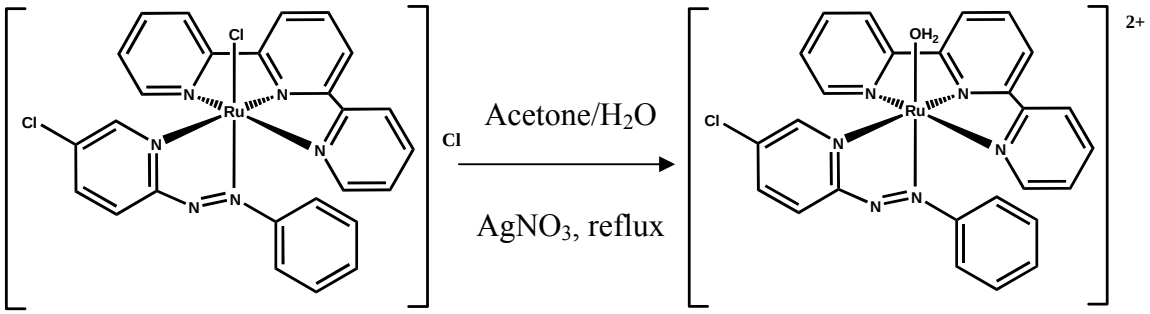
(2) NH_4PF_6



$[Ru^{II}(tpy)(Clazpy)Cl]PF_6$ (3)

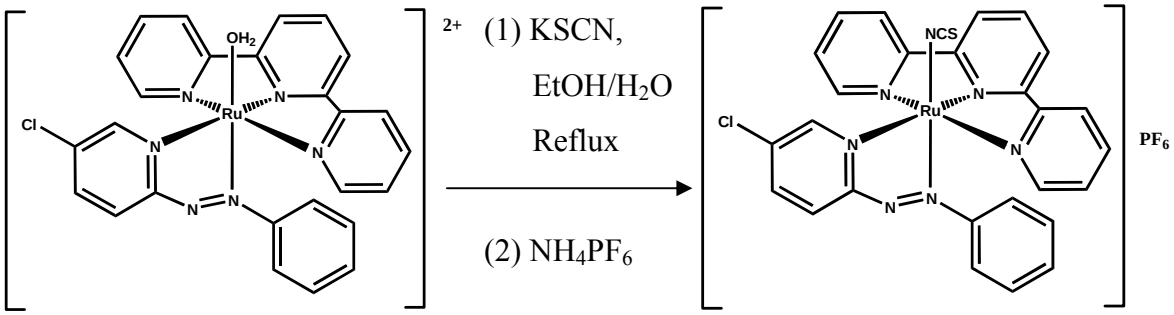
The yield of $[Ru^{II}(tpy)(Clazpy)Cl]PF_6$ is 88%.

The $[Ru(tpy)(Clazpy)NCS]PF_6$ was synthesized by a reaction involving $AgNO_3$ abstraction of chlorine from $[Ru(tpy)(Clazpy)Cl]Cl$ in acetone/water followed by reaction with KSCN and was precipitated by PF_6^- salt. The reactions are shown in equation (4)-(5).



$[Ru(tpy)(Clazpy)Cl]Cl$ $[Ru(tpy)(Clazpy)(H_2O)]^{2+}$

$+ \quad AgCl$ (4)



$[Ru(tpy)(Clazpy)(H_2O)]^{2+}$ $[Ru(tpy)(Clazpy)NCS]PF_6$

(5)

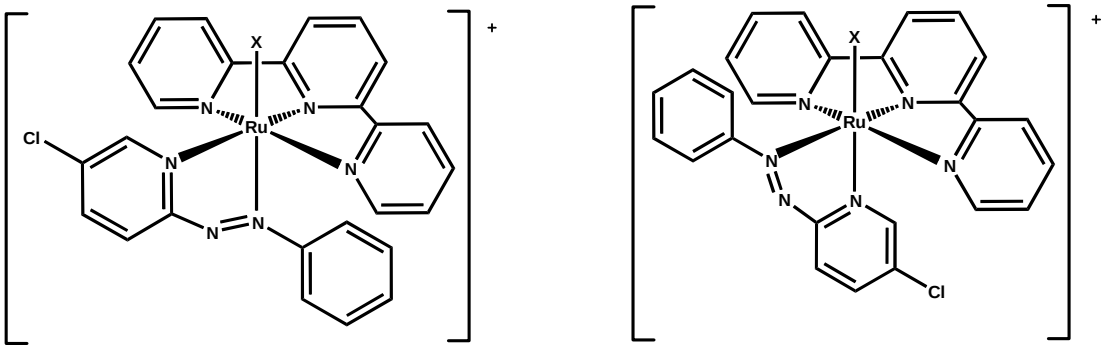
The yield of $[Ru^{II}(tpy)(Clazpy)NCS]PF_6$ is 78%. The physical properties of the complexes are summarized in Table 6.

Table 6. The physical properties of complexes

Complex	Physical properties		
	Appearance	Color	Melting point (°C)
$[Ru(tpy)(Clazpy)Cl]PF_6$	solid	black	> 250
$[Ru(tpy)(Clazpy)NCS]PF_6$	solid	black	238-239

The solubility of 10 mg of $[Ru(tpy)(Clazpy)Cl]PF_6$ and $[Ru(tpy)(Clazpy)NCS]PF_6$ complexes were tested in 10 mL of various solvents. The results showed that complexes were slightly soluble in methanol (MeOH) and ethanol (EtOH). It was completely soluble in acetone (CH_3OCH_3), acetonitrile (CH_3CN) and *N*,*N*-dimethyl sulfoxide (DMSO) but insoluble in hexane, benzene, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), ether and water.

The Clazpy is an asymmetrical bidentate ligand, $[Ru(tpy)(Clazpy)X]^+$ may exist in two geometrical isomeric forms, as shown in Figure 12.



1 2

Figure 12. Two geometrical isomeric forms of $[Ru(tpy)(Clazpy)X]^+$.

3.2.2 Characterization of complexes

The chemistry of the complexes was determined by using these techniques.

3.2.2.1 Elemental analysis
3.2.2.2 Infrared spectroscopy
3.2.2.3 UV-Visible absorption spectroscopy
3.2.2.4 Nuclear Magnetic Resonance spectroscopy (1D and 2D)
3.2.2.5 Cyclic Voltammetry
3.2.2.6 X-ray Crystallography

3.2.2.1 Elemental analysis

Elemental analysis is a technique to study the composition of elements in a compound. It is shown that the analytical data of the compounds corresponded to the calculated values. The elemental analysis data are listed in Table 7.

Table 7. Elemental analysis data of the $[Ru(tpy)(Clazpy)Cl]PF_6$ and the $[Ru(tpy)(Clazpy)NCS]PF_6$ complexes

Compounds	% C		% H		% N	
	Calc.	Found	Calc.	Found	Calc.	Found
$[Ru(tpy)(Clazpy)Cl]PF_6$	42.64	42.88	2.61	2.74	11.47	11.11
$[Ru(tpy)(Clazpy)NCS]PF_6$	42.95	42.08	2.53	2.47	12.98	13.40

3.2.2.2 Infrared spectroscopy

Infrared spectroscopy is an useful technique to study the functional groups of compounds. Infrared spectra were collected by using KBr pellets in the range 4000-400 cm^{-1}. The important vibrational frequencies are C=C, C=N, N=N (azo) stretching modes and C-H bending in monosubstituted benzene and C-Cl. The infrared spectroscopic data of the complexes are listed in Table 8 and these spectra are shown in Figure 13 and Figure 14.

Table 8. Infrared spectroscopic data of $[Ru(tpy)(Clazpy)Cl]PF_6$ and $[Ru(tpy)(Clazpy)NCS]PF_6$ complexes

Vibration modes	Frequencies (cm^{-1})	
	$[Ru(tpy)(Clazpy)Cl]PF_6$	$[Ru(tpy)(Clazpy)NCS]PF_6$
CN stretching	-	2,100
CS stretching	-	780
C=N, C=C stretching	1,599 1,443	1,599 1,449
N=N stretching	1,300	1,320
C-Cl	557	557
C-H bending in monosubstituted benzene	771 733 701	770 732 700
P-F stretching	841	841

Infrared spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 is shown in Figure 13. In the [Ru(tpy)(Clazpy)Cl]PF_6 complex, the infrared spectra exhibited medium peaks at 1,599 cm^{-1} and 1,443 cm^{-1}. These frequencies were assigned to the C=N and the C=C vibrational modes. The N=N(azo) vibrational frequency at 1,300 cm^{-1}, is lower than that of the free Clazpy ligand (ca. 64 cm^{-1}). This is a good indication of N-azo coordination. It was due to the π-back bonding between Clazpy ligand and ruthenium (II) resulted in a decrease of the vibrational energy of the N=N (azo) stretching mode. Infrared spectrum of [Ru(tpy)(Clazpy)NCS]PF_6 is shown in Figure 14. In the [Ru(tpy)(Clazpy)NCS]PF_6 complex, the infrared spectra exhibited medium peaks at 1,599 cm^{-1} and 1,449 cm^{-1}. These frequencies were assigned to the C=N and the C=C vibrational modes. Intense band at 1320 cm^{-1}, is attributed to the N=N (azo) stretching frequencies, the red shifted from Clazpy ligand about 44 cm^{-1}. The NCS^- ligand coordinated through the nitrogen end in [Ru(tpy)(Clazpy)NCS]PF_6 because a strong absorption in the range of 2100 cm^{-1} is observed, which it is consistent with previous work (Xu, *et al*., 2007). Sharp band at 2,100 cm^{-1} is assigned to the CN stretching vibrational. In addition, the most significant feature of these complexes in IR spectrum is the occurrence of band at 841 cm^{-1} due to the presence of ionic hexafluorophosphate. However, the vibration at 325 cm^{-1} of Ru-Cl stretching (Pramanik, et al., 1998) could not be observed because the spectrum was out of range.

It is noted that the N=N stretching modes in the complexes appeared at lower frequency than that in the free ligand. It was due to the π-back bonding occurring from the t_{2g} orbitals of metal to the π* orbitals of azo. From this result, the bond order of N=N (azo) decreased and the bond length increased, therefore, the vibrational energies decreased. In addition, ν(N=N) of the [Ru(tpy)(Clazpy)NCS]PF_6 appeared at the higher frequency than the [Ru(tpy)(Clazpy)Cl]PF_6. It indicated that the NCS^- ligand has greater π-acceptor ability than the Cl^-. It competed with Clazpy for electron density from the metal center. The selected vibrational frequencies of Clazpy ligand and [Ru(tpy)(Clazpy)X]PF_6 complexes are summarized in Table 9.

Table 9. Selected vibrational frequencies of Clazpy ligand and $[Ru(tpy)(Clazpy)X]PF_6$ complexes

Compound	$\upsilon_{(N=N)}$, (cm^{-1})
Free Clazpy	1,364
$[Ru(tpy)(Clazpy)(Cl)]^+$	1,300
$[Ru(tpy)(Clazpy)(NCS)]^+$	1,320

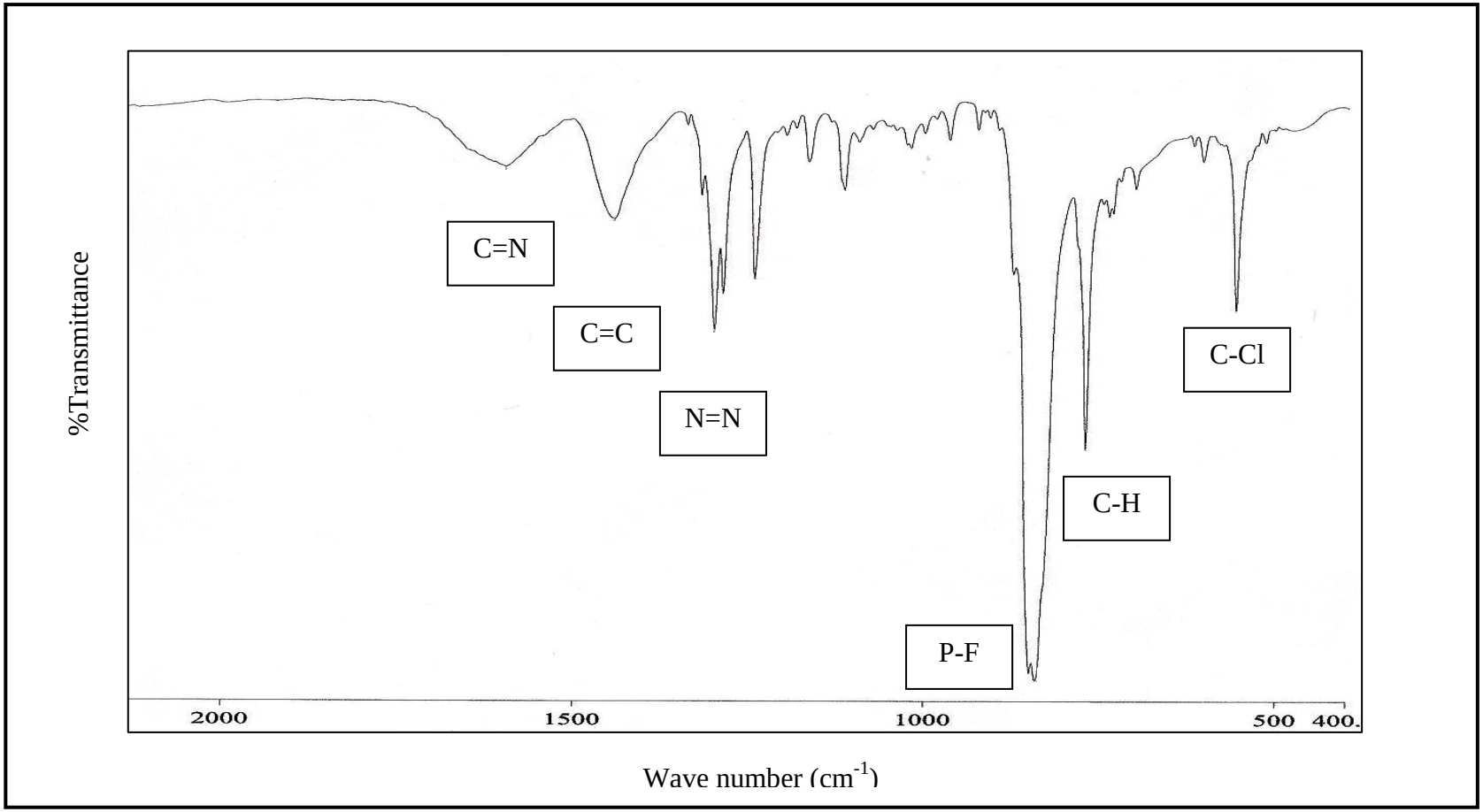


Figure 13. IR spectrum of $[Ru(tpy)(Clazpy)Cl]PF_6$.

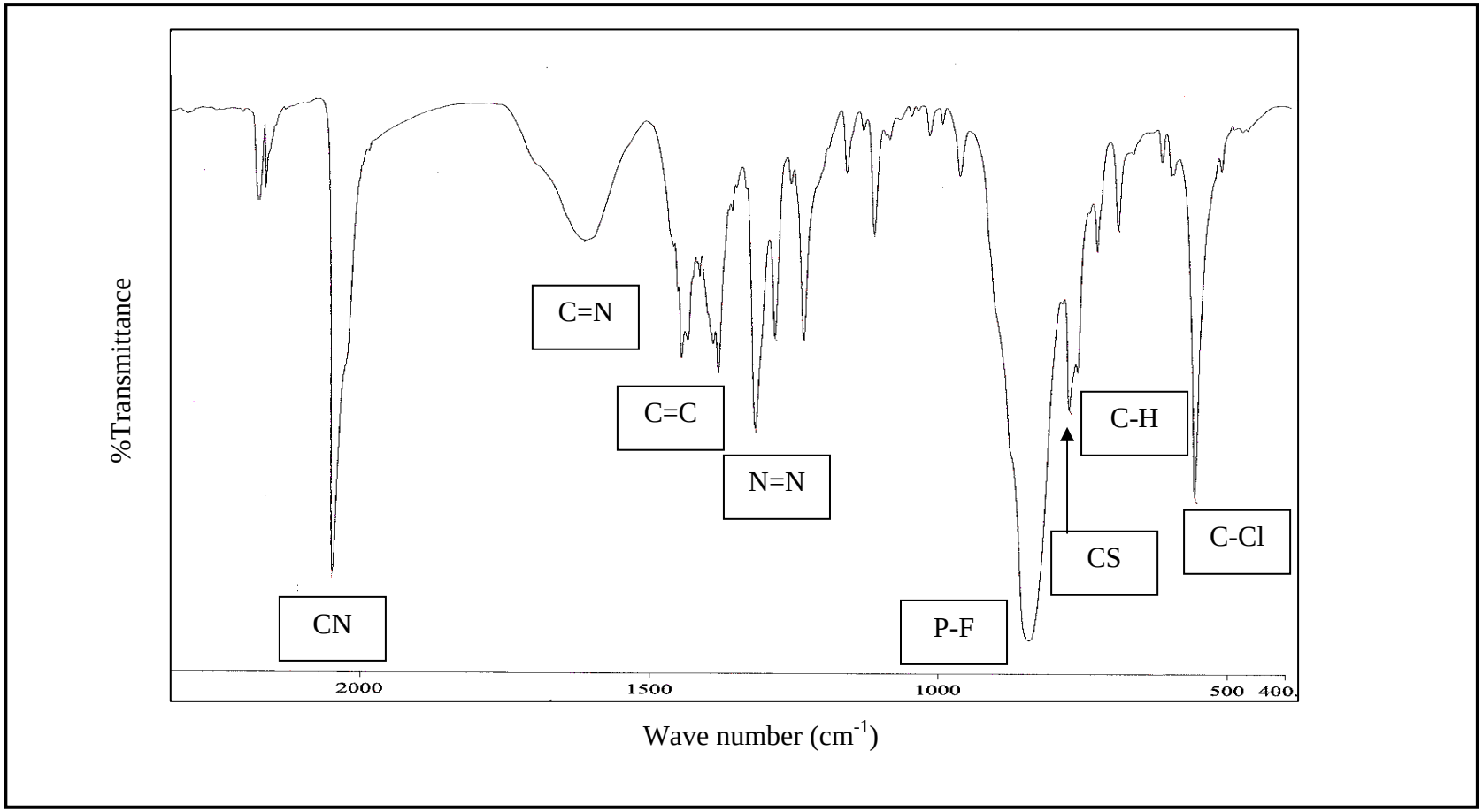


Figure 14. IR spectrum of [Ru(tpy)(Clazpy)NCS]PF_6.

3.2.2.3 UV-Visible absorption spectroscopy

UV-Visible absorption spectroscopy is a technique to study the electronic transitions of compound. The electronic absorption spectra of the complexes in three solvents were recorded in the range of 300-800 nm. The spectral data are given in Table 10. The absorption spectra of complexes in CH_3CN are shown in Figure 15 and 16.

Table 10. UV-Visible absorption spectroscopic data of the complexes.

Complex	Solvent	$\lambda_{max, nm}$ (ε^a, $M^{-1}cm^{-1}$)	
		UV region	Visible region
[Ru(tpy)(Clazpy)(Cl)]PF_6	DMSO	318(39,600)	514(17,800)
	Acetone	-	513(24,600)
	CH_3CN	316(17,400)	511(7,400)
[Ru(tpy)(Clazpy)(NCS)]PF_6	DMSO	318(34,600)	516(15,200)
	Acetone	-	515(10,200)
	CH_3CN	315(26,000)	513(12,400)

[a] Molar extinction coefficient

The [Ru(tpy)(Clazpy)(Cl)]PF_6 and [Ru(tpy)(Clazpy)(NCS)]PF_6 complexes were recorded in UV and visible regions in three different solvents; acetone, acetoitrile (CH_3CN) and dimethyl sulfoxide (DMSO). The spectra of [Ru(tpy)(Clazpy)(Cl)]PF_6 and [Ru(tpy)(Clazpy)(NCS)]PF_6 display two absorption bands in range 315-318 nm and 511-516 nm. They are assigned to intraligand charge transfer in UV region and metal-to-ligand charge transfer transition (MLCT) in the visible range.

In addition, when the solvents have been varied. Absorption spectra show that the intense metal-to-ligand charge transfer (MLCT) in the visible region are not effected. These solvents have slightly difference in polarity. Figure 15 and 16 show the UV-Visible absorption spectra for the [Ru(tpy)(Clazpy)(Cl)]PF_6 and [Ru(tpy)(Clazpy)(NCS)]PF_6 complexes in acetonitrile.

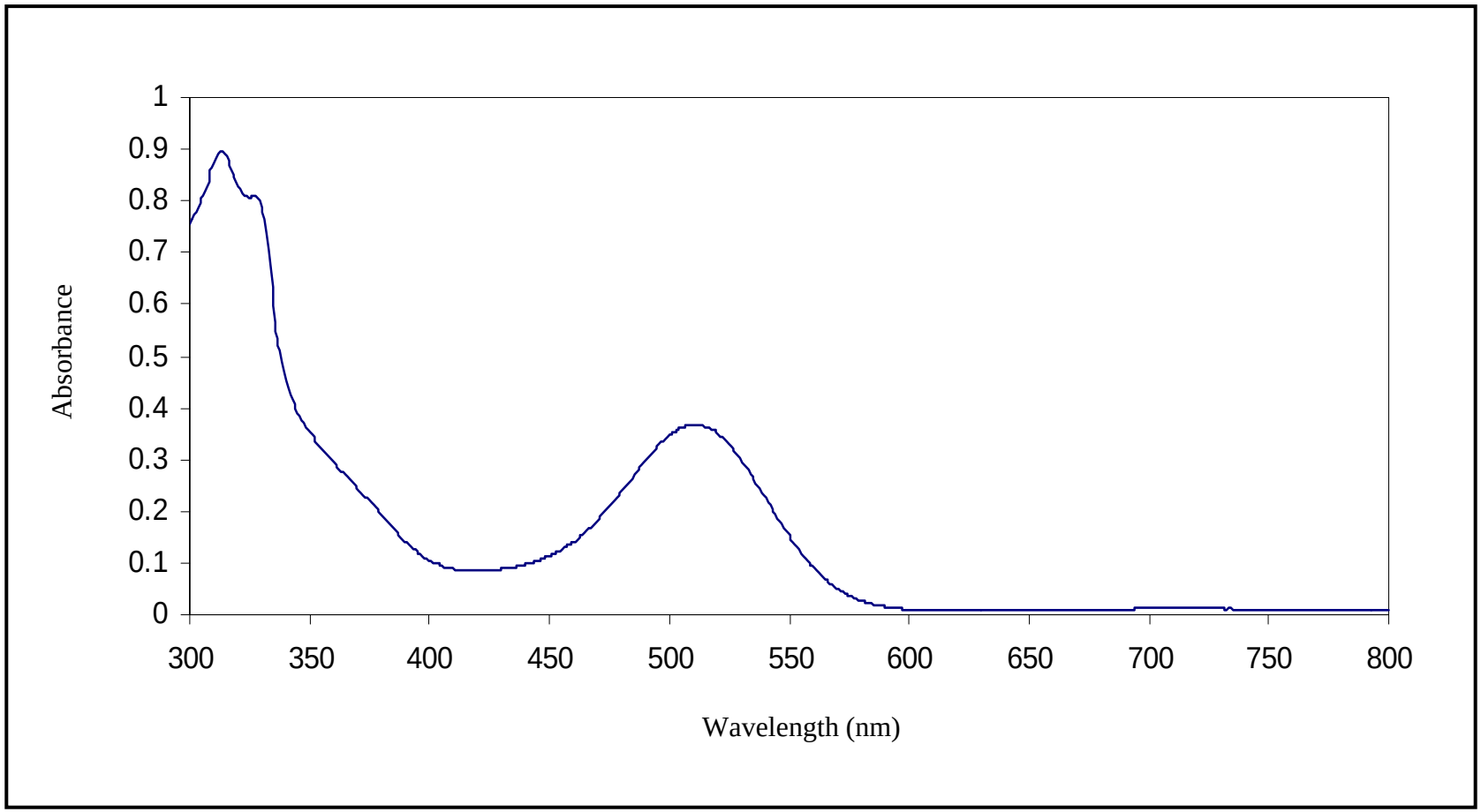


Figure 15. UV-Visible absorption spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in CH_3CN.

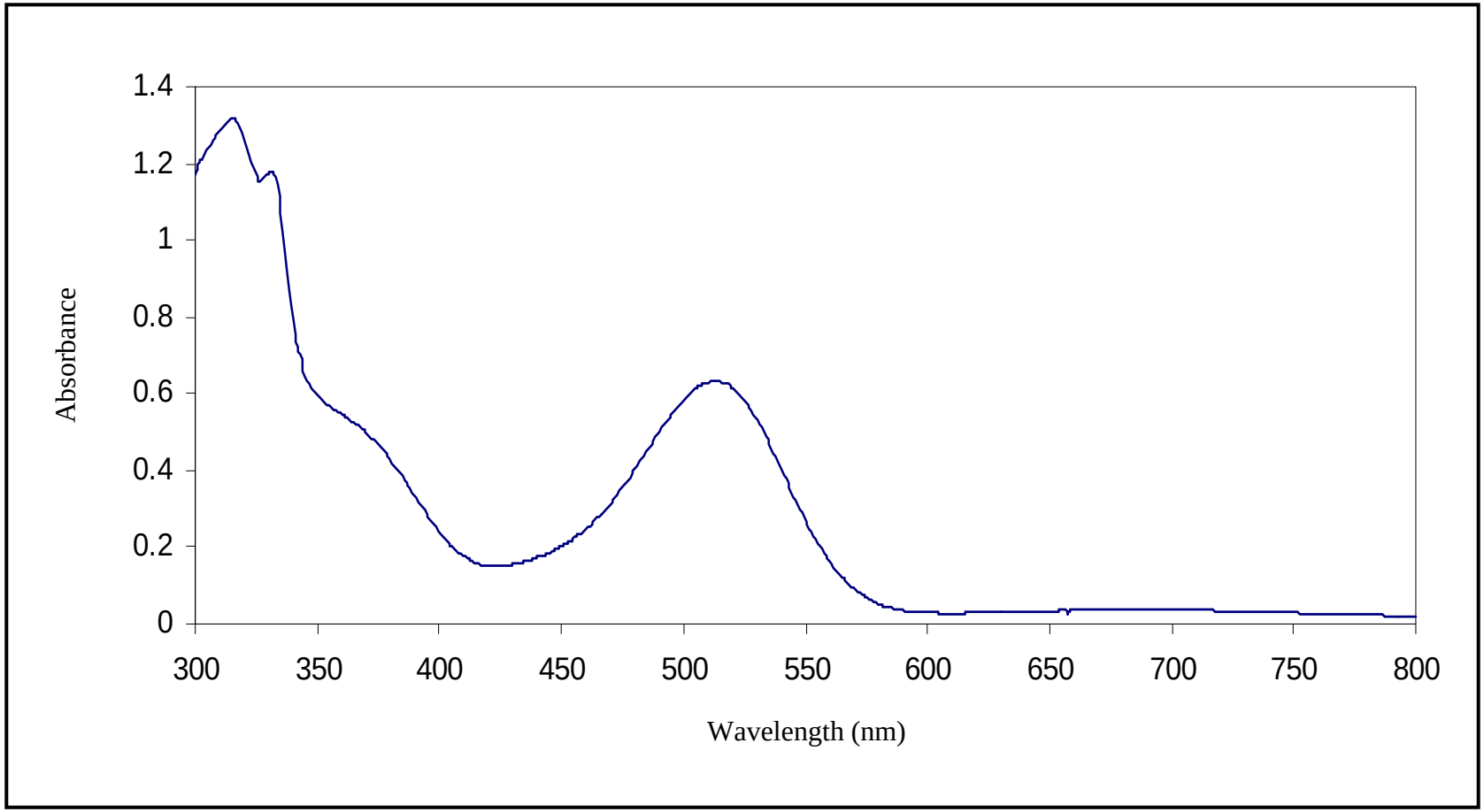


Figure 16. UV-Visible absorption spectrum of [Ru(tpy)(Clazpy)NCS]PF_6 in CH_3CN.

3.2.2.4 Nuclear Magnetic Resonance spectroscopy (1D and 2D)

Nuclear Magnetic Resonance (NMR) spectroscopy is an important technique to determine the molecular structure of the compounds. The structure of complexes were investigated by using 1D and 2D NMR spectroscopic techniques (^{1}H NMR, ^{1}H-^{1}H COSY NMR, ^{13}C NMR, DEPT NMR and ^{1}H-^{13}C HMQC NMR). The NMR spectra of all complexes were recorded in DMSO-d_6 on UNITY INOVA 500 MHz. The tetramethylsilane ($Si(CH_3)_4$) was used as an internal reference.

Nuclear Magnetic Resonance spectroscopy of the [Ru(tpy)(Clazpy)(Cl)]PF_6 complex

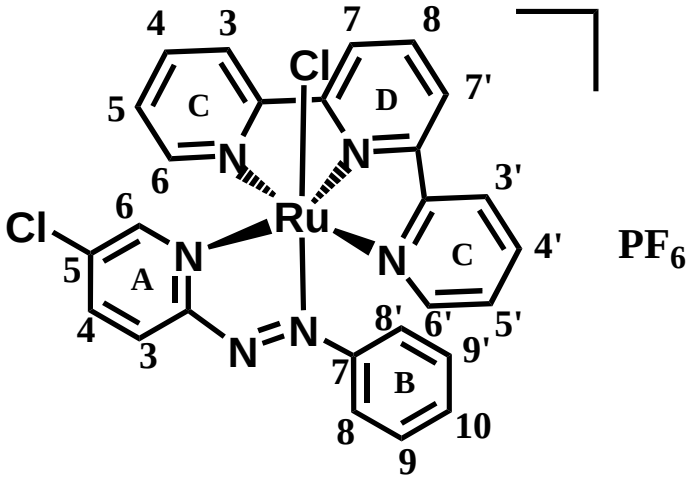


Table 11 showed the chemical shift and *J*-coupling constant data of the [Ru(tpy)(Clazpy)(Cl)]PF_6 complex and NMR spectra are shown in Figure 17 to Figure 22.

Table 11 ^{1}H and ^{13}C NMR spectroscopic data of the $[Ru(tpy)(Clazpy)(Cl)]PF_6$ complex

Position (complex)	δ_H (ppm), Multiplicity, *J* in Hz	δ_C (ppm)
6A	9.64, 1H, d, 2.5 Hz	147.8
3A	8.90, 1H, d, 9.0 Hz	126.4
6C, 6′C	8.63, 4H, d, 8.0 Hz	124.5
7D, 7′D		123.6
4A	8.57, 1H, dd, 9.0, 2.5 Hz	138.6
8D	8.23, 1H, t, 8.0 Hz	137.3
5C, 5′C	8.16, 2H, m	139.8
3C, 3′C	7.48, 4H, d, 4.5 Hz	153.2
4C, 4′C		128.4
10B	7.23, 1H, t, 7.5 Hz	129.6
9B, 9′B	7.04, 2H, t, 7.5 Hz	129.0
8B, 8′B	6.23, 2H, d, 7.5 Hz	120.6
Quaternary carbons	C 2A	164.6
	C 2C, 2′C	157.2
	C 6D, 6′D	155.0
	C 5A	154.9
	C 7B	132.4

s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet

The ^{1}H NMR spectrum of the [Ru(tpy)(Clazpy)(Cl)]PF_6 complex recorded in DMSO-d_6, shows many sharp resonances (Figure 17). The NMR spectroscopic data of **[**Ru(tpy)(Clazpy)(Cl)]PF_6 ($RuC_{26}H_{19}N_6Cl_2PF_6$) are summarized in Table 11. Ten resonances are expected for nineteen hydrogens in the **[**Ru(tpy)(Clazpy)(Cl)]PF_6 complex, six signals for eight hydrogens of Clazpy ligand and four signals for eleven hydrogens of tpy ligand. Integration of the signals corresponds to nineteen hydrogens present in complex. Major differences are expected in the chemical shifts to the proton of the Clazpy ligand. The proton H6 of the ring A of Clazpy ligand in the **[**Ru(tpy)(Clazpy)(Cl)]PF_6 complex shows the most downfield signal. This is due to the influence of the nitrogen and the chlorine atoms on the pyridine ring which was located close to them. The proton H6 resonance appeared at 9.64 ppm as doublet (d) due to the coupling with the proton H4 (J = 2.5 Hz). In addition, the peak assignments was confirmed using ^{1}H-^{1}H COSY NMR spectrum, which showed the correlation of ^{1}H-^{1}H coupling and the spectrum is shown in Figure 18.

The ^{13}C NMR of **[**Ru(tpy)(Clazpy)(Cl)]PF_6 is shown in Figure 19. The result of spectrum corresponded to the DEPT NMR spectrum (Figure 20, 21). The ^{13}C NMR spectrum of **[**Ru(tpy)(Clazpy)(Cl)]PF_6 showed 17 signals of 26 carbons, 12 signals from 19 methine carbons and 5 signals from 7 quaternary carbons. The quaternary carbons of C2A, C2C, 2′C, C6D, 6′D, C5A and C7B were assigned to the signals at 164.6, 157.2, 155.0, 154.9 and 132.4 ppm, respectively. The signals of carbon C2A occurred at a lowest field because it located between the nitrogen atoms on pyridine ring. The ^{13}C NMR signal assignments were based on the ^{1}H-^{13}C HMQC spectrum (Figure 22).

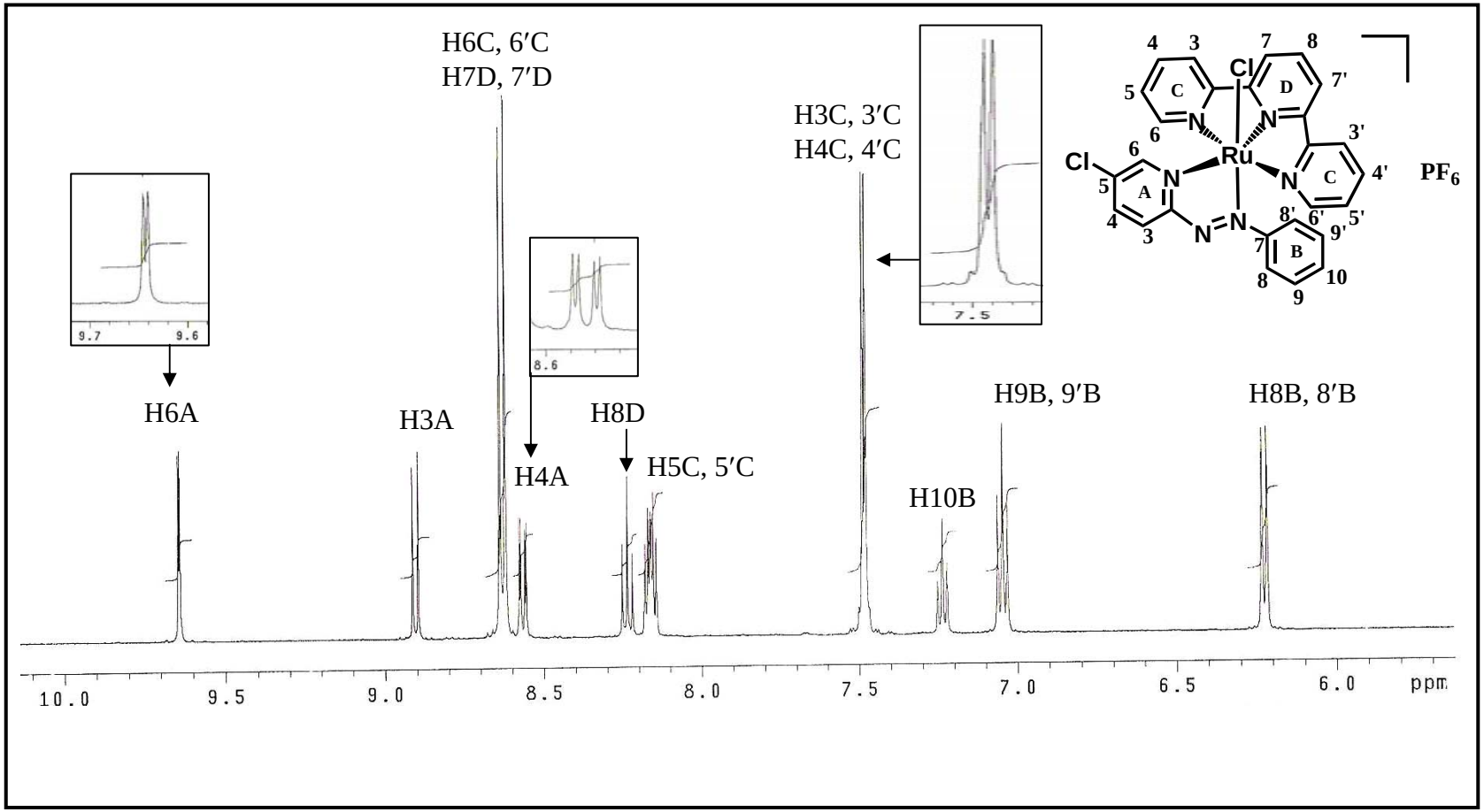


Figure 17. ^{1}H NMR spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in DMSO-d_6.

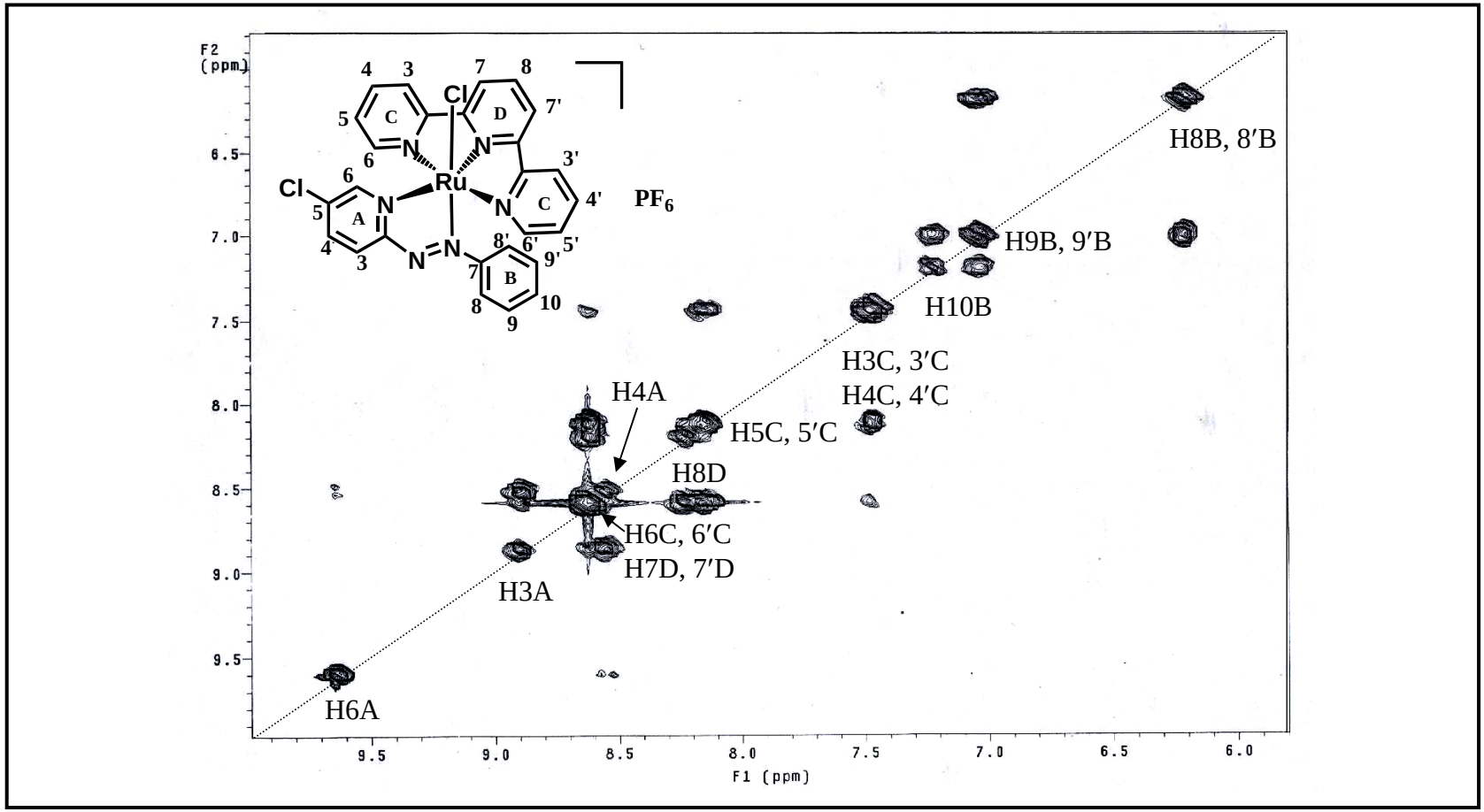


Figure 18. ^{1}H-^{1}H COSY NMR spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in DMSO-d_6.

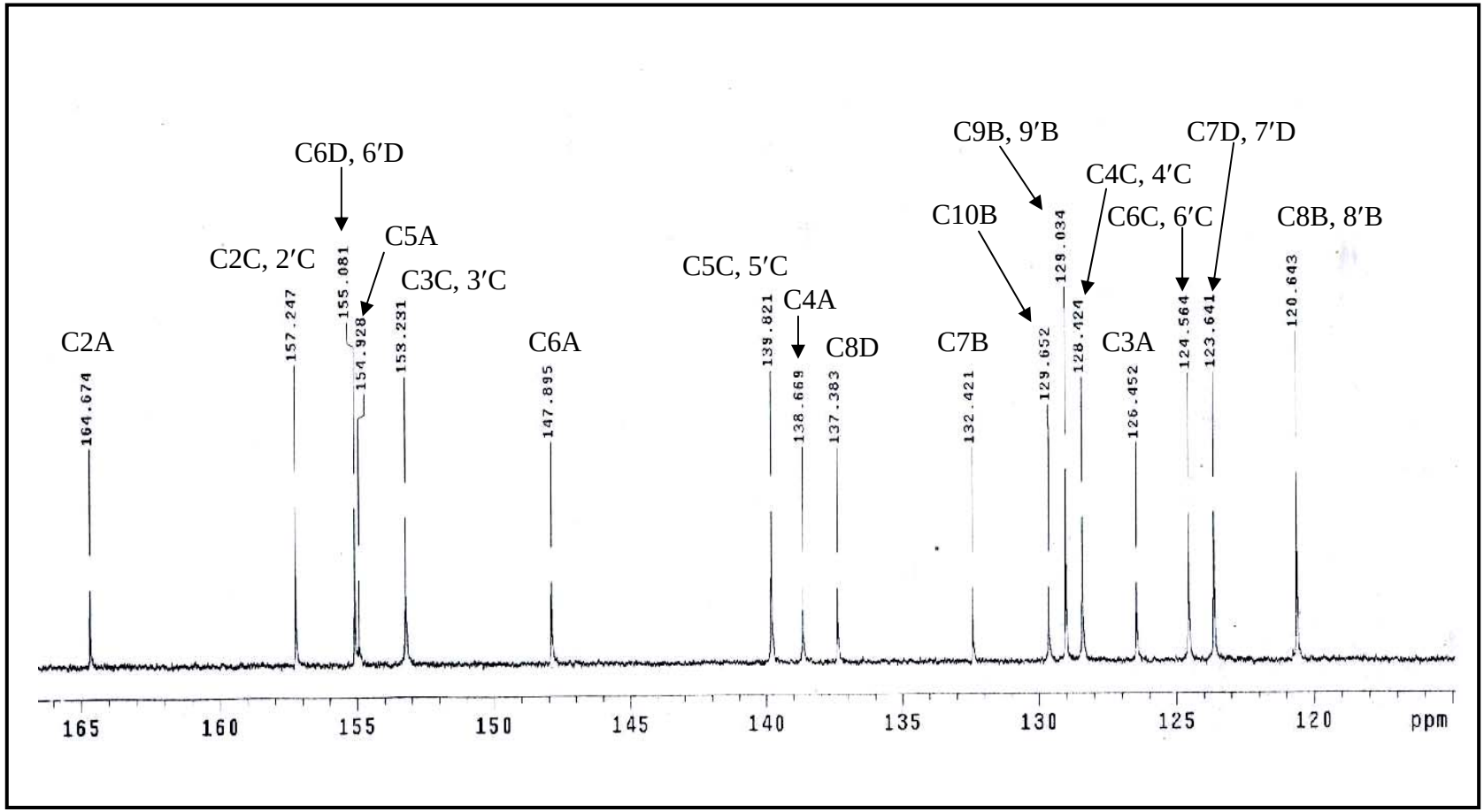


Figure 19. ^{13}C NMR spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in DMSO-d_6.

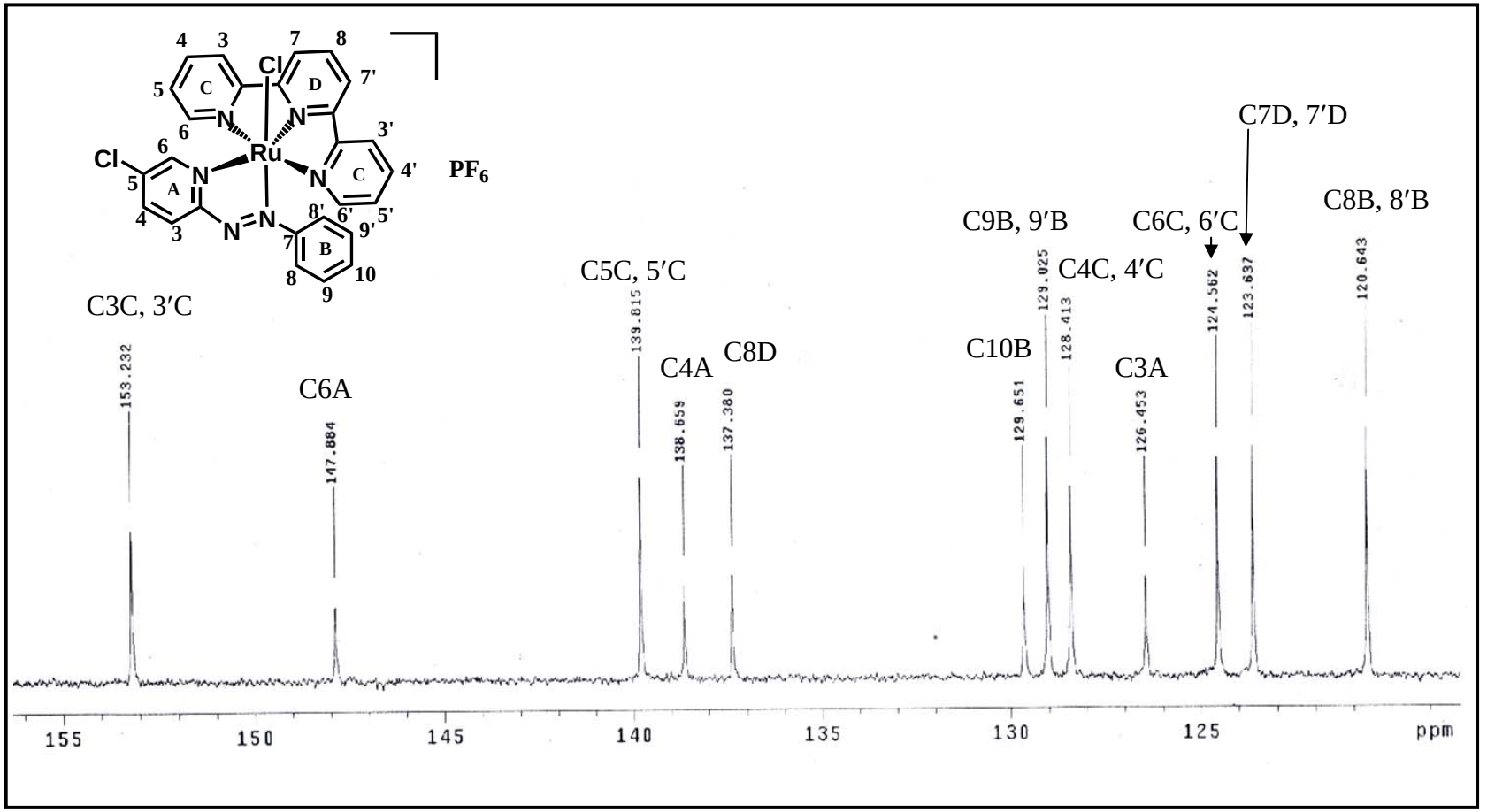


Figure 20. DEPT90 NMR spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in DMSO-d_6.

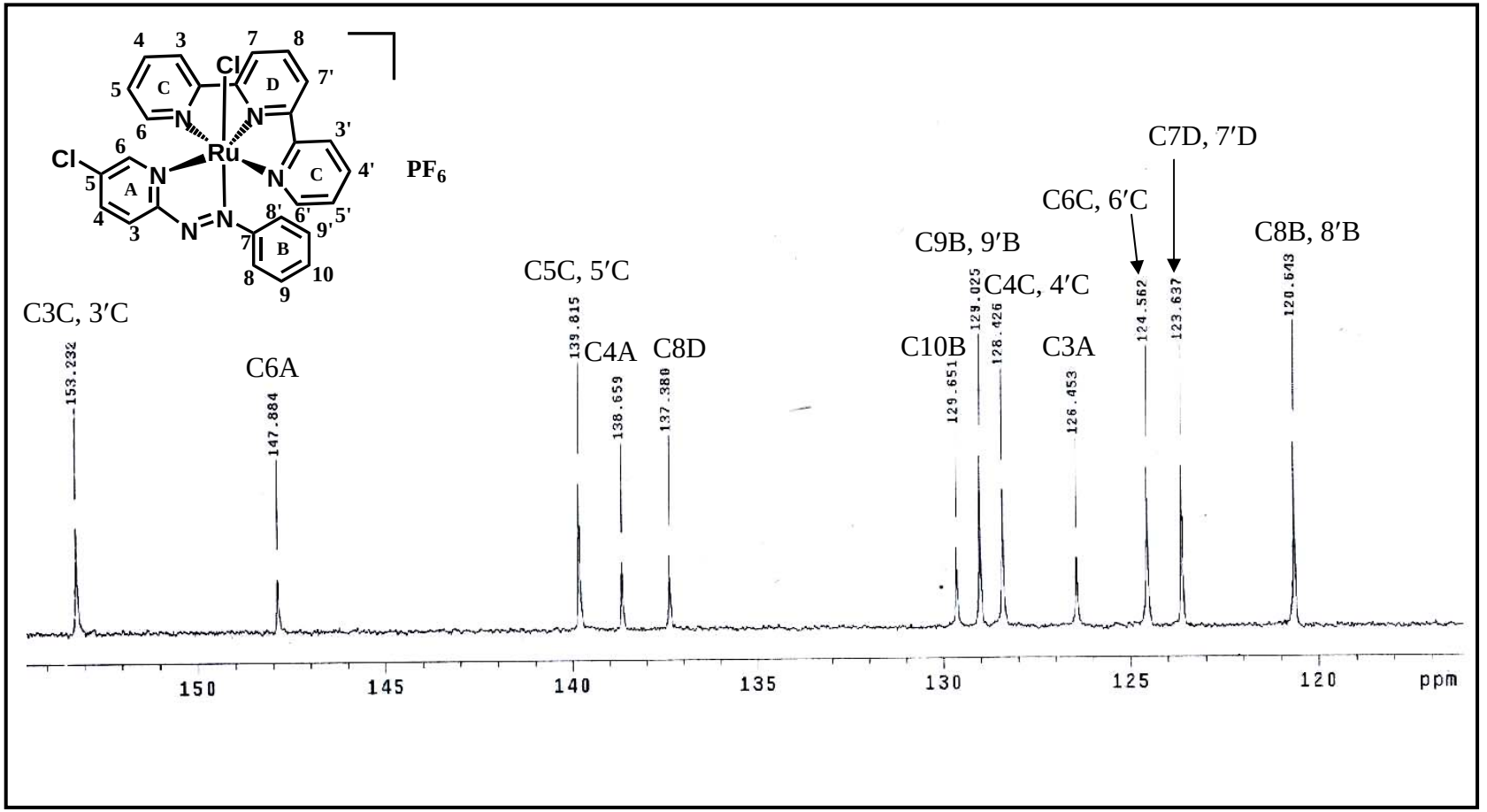


Figure 21. DEPT135 NMR spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in DMSO-d_6.

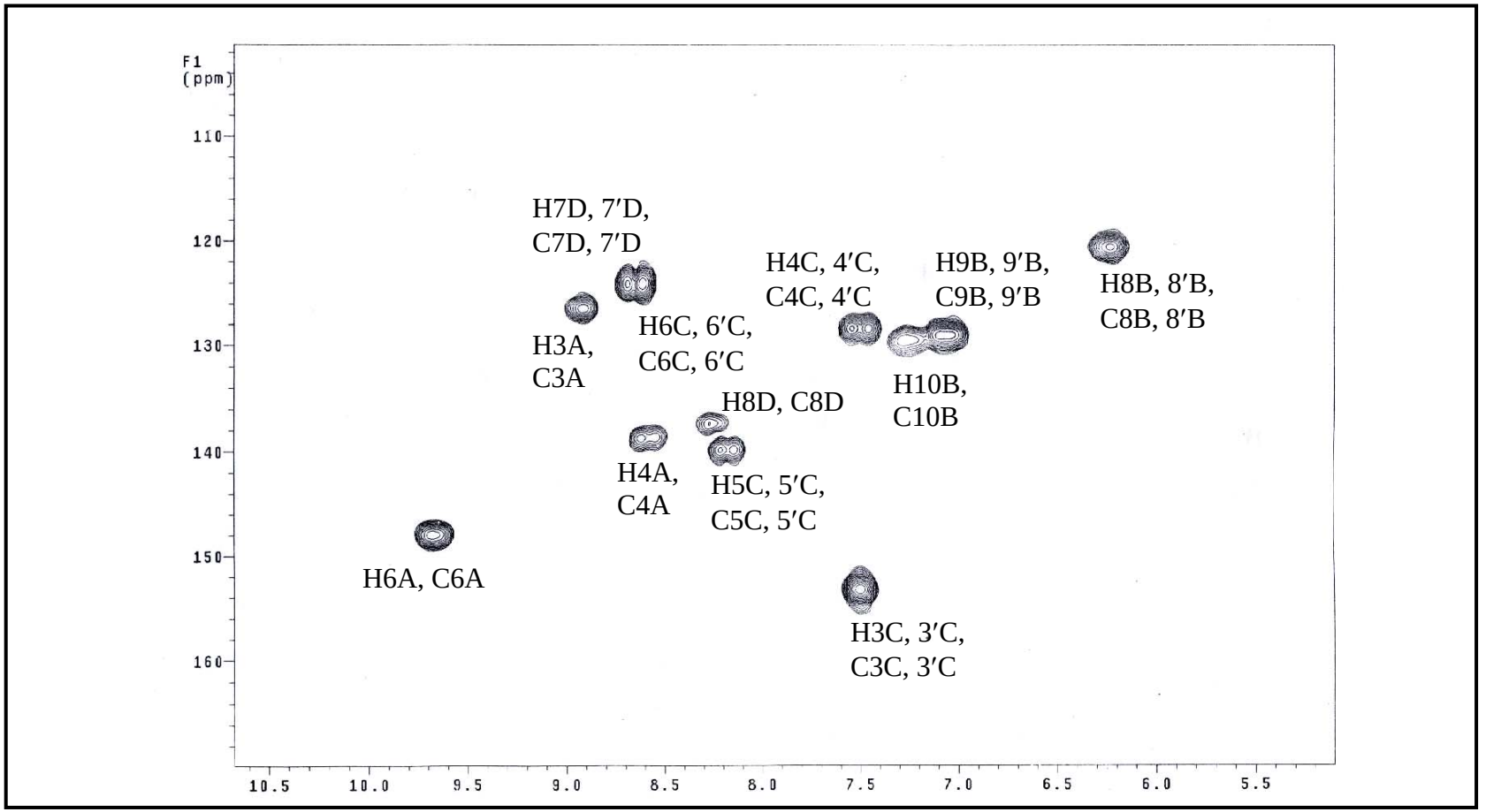


Figure 22. ^{1}H-^{13}C HMQC NMR spectrum of [Ru(tpy)(Clazpy)Cl]PF_6 in DMSO-d_6.

Nuclear Magnetic Resonance spectroscopy of
the [Ru(tpy)(Clazpy)(NCS)]PF_6 complex

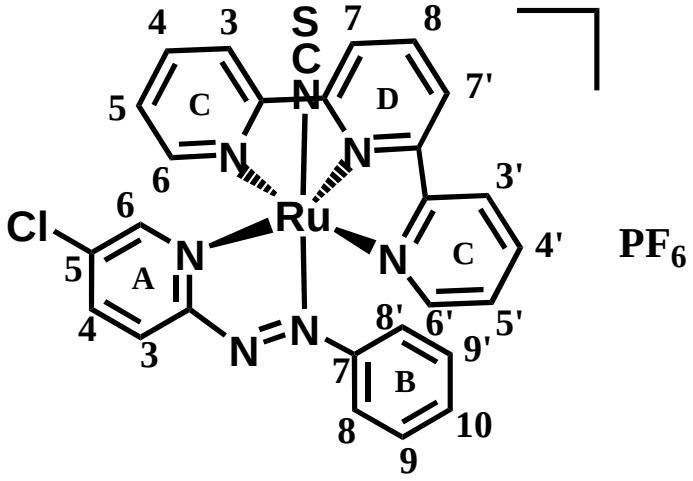


Table 12 showed the chemical shift and *J*-coupling constant data of the [Ru(tpy)(Clazpy)(NCS)]PF_6 complex and NMR spectra are shown in Figure 23 to Figure 28.

The ^{1}H NMR spectrum of **[**Ru(tpy)(Clazpy)(NCS)]PF_6 was carried out in DMSO-d_6. The NMR spectroscopic data of **[**Ru(tpy)(Clazpy)(NCS)]PF_6 ($RuC_{27}H_{19}N_7SClPF_6$) are summarized in Table 12. The ^{1}H NMR spectrum of **[**Ru(tpy)(Clazpy)(NCS)]PF_6 is shown in Figure. 23. The total eleven resonances are expected for nineteen hydrogens in the **[**Ru(tpy)(Clazpy)(NCS)]PF_6 complex, six signals for eight hydrogens of the Clazpy ligand and five signals for eleven hydrogens of the tpy ligand. Integration of the signals corresponds to nineteen hydrogens present in complex. The peak assignment was supported by using simple correlation ^{1}H-^{1}H COSY NMR spectroscopy (Figure. 24). In addition, the protons H3A, H4A and H6A appear at lower downfield than protons H8B, 8′B, H9B, 9′B and H10B because the pyridine protons have less electron density than the phenyl protons. Since the greater π-backbonding interaction to azo group increases the electron density in the phenyl ring, this provides higher field phenyl protons.

Table 12. ^{1}H and ^{13}C NMR assignments of **[**Ru(tpy)(Clazpy)(NCS)]PF_6

H-Position	δ_H (ppm), Multiplicity, *J* in Hz	δ_C (ppm)
6A	9.29, 1H, d, 2.0 Hz	147.8
3A	8.96, 1H, d, 9.0 Hz	127.6
6C, 6′C	8.69, 4H, d, 8.0 Hz	124.9
7D, 7′D		124.0
4A	8.65, 1H, dd, 9.0, 2.0 Hz	139.0
8D	8.32, 1H, t, 8.0 Hz	138.2
5C, 5′C	8.24, 2H, dt, 8.0, 1.5 Hz	140.2
3C, 3′C	7.64, 2H, dd, 8.0, 1.5 Hz	153.6
4C, 4′C	7.56, 2H, dt, 8.0, 1.5 Hz	128.7
10B	7.26, 1H, t, 8.0 Hz	129.9
9B, 9′B	7.06, 2H, t, 8.0 Hz	129.0
8B, 8′B	6.20, 2H, dd, 8.0, 1.0 Hz	120.4
Quaternary carbons	C 2A	163.6
	C 2C, 2′C	156.9
	C 6D, 6′D	155.0
	C 5A	154.1
	C NCS	141.4
	C 7B	134.0

s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet

The ^{13}C NMR signal assignments (Figure. 25) were based on the HMQC spectrum (Figure. 28). The result of spectrum corresponded to the DEPT NMR spectrum (Figure 26, 27). The ^{13}C NMR spectrum of **[**Ru(tpy)(Clazpy)(NCS)]PF_6 showed 18 signals of 27 carbons, 12 signals from 19 methine carbons and 6 signals from 8 quaternary carbons. The quaternary carbons of C2A, C2C, 2′C, C6D, 6′D, C5A, C- NCS and C7B were assigned to the signals at 163.6, 156.9, 155.0, 154.1, 141.4 and 134.0 ppm, respectively. The signals of carbon C2A occurred at the lowest field because it located between the nitrogen atoms on the pyridine ring.

3.2.2.5 Cyclic Voltammetry

Electrochemical properties of all the complexes were studied by cyclic voltammetry at a glassy carbon as a working electrode and were examined in acetonitrile using tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte at the scan rate of 50 mV/s. Voltammetric data are given in Table 13 and selected voltammograms are shown in Figure 29 to 30. The voltammograms displayed $Ru^{III/II}$ couple at the positive potential and ligand reductions at the negative potential. The ferrocene as internal standard.

In this experiment, different scan rates were used to check the ΔEp is of the redox couple. The couple having an equal anodic current (i_{pa}) and cathodic current (i_{pc}) was referred to as a reversible couple. On the other hand, the unequal currents were referred unequally transfer of reduction and oxidation peaks. This led to an irreversible couple. When different scan rates were applied, these currents gave equal anodic and cathodic currents at higher scan rates, which led to quasi-reversible couple.

Table 13. Cyclic voltammetric[a] data for **[**Ru(tpy)(Clazpy)Cl)]PF_6 and **[**Ru(tpy)(Clazpy)(NCS)]PF_6 complexes in 0.1 M TBAH acetonitrile at scan rate of 50 mV/s. (ferrocene as an internal standard)

Compound	$E_{1/2}$ (V) (ΔE_p (mV))	
	Oxidation	Reduction
Clazpy	-	-1.05 (120)
[Ru(tpy)(Clazpy)Cl)]PF_6	1.35 (60)	-0.58 (70), -1.24 (85)
[Ru(tpy)(Clazpy)(NCS)]PF_6	1.40[b]	-0.50 (75), -1.20 (80)

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa}-E_{pc}$

[b] anodic peak potential, V

Oxidation range

The cyclic voltammograms of the **[**Ru(tpy)(Clazpy)Cl]PF_6 and **[**Ru(tpy)(Clazpy)(NCS)]PF_6 complexes are shown in Figure 29 and 30, respectively. In the potential range 0.0 to +1.5 V at a scan rate of 50 mV/s in acetonitrile, one electron oxidation response was observed corresponding to the Ru(II) ⟶ Ru(III) couple. The **[**Ru(tpy)(Clazpy)Cl]PF_6 exhibits one electron quasi-reversible oxidation for the Ru(II)/Ru(III) couple, with $E_{1/2}$ = 1.35 V. The **[**Ru(tpy)(Clazpy)(NCS)]PF_6 exhibit a one electron irreversible oxidation peak for the Ru(II)/Ru(III) couple, giving the $E_{1/2}$ = 1.40 V. The **[**Ru(tpy)(Clazpy)(NCS)]PF_6 complex is oxidized at a more positive potential than the **[**Ru(tpy)(Clazpy)Cl]PF_6 complex. The Ru(II)/Ru(III) oxidation potential in these complexes is observed to be sensitive to the nature of X ligand (X = Cl or NCS). The X ligand can be either *trans* to N-azo or to the pyridine of the Clazpy ligand, but the X ligand is cis to the terpyridine.

Hence the Clazpy should have any electronic variations due to the changing the X ligand to a greater extent than tpy ligand. It was due to the π-back bonding occurring from the t_{2g} orbitals of metal to the π* orbitals of azo where the X ligand is *trans* to N-azo of the Clazpy ligand.

Reduction range

Two couple appeared in this range. In the **[**Ru(tpy)(Clazpy)X]PF_6 complexes (X = Cl or NCS) have a quasi-reversible couple when higher scan rates were applied. The first reduction couple of the **[**Ru(tpy)(Clazpy)NCS]PF_6 complex (-0.50 V) occurred at more potential than that in the **[**Ru(tpy)(Clazpy)Cl]PF_6 (-0.58 V). These results showed that the **[**Ru(tpy)(Clazpy)NCS]PF_6 accepted electron better than the **[**Ru(tpy)(Clazpy)Cl]PF_6. The expected reduction processes are displayed in equation 7 to 8.

$$[Ru^{II}(tpy)(Clazpy)X]^{+} + e^{-} \rightleftharpoons [Ru^{II}(tpy)(Clazpy^{\cdot-})X]^{0} \quad 7$$

$$[Ru^{II}(tpy)(Clazpy^{\cdot-})X]^{0} + e^{-} \rightleftharpoons [Ru^{II}(tpy)(Clazpy^{\cdot-})X]^{-} \quad 8$$

The cyclic voltammogram shows that the NCS^- group is a better ligand than the chloride to stabilize the ruthenium(II) center.

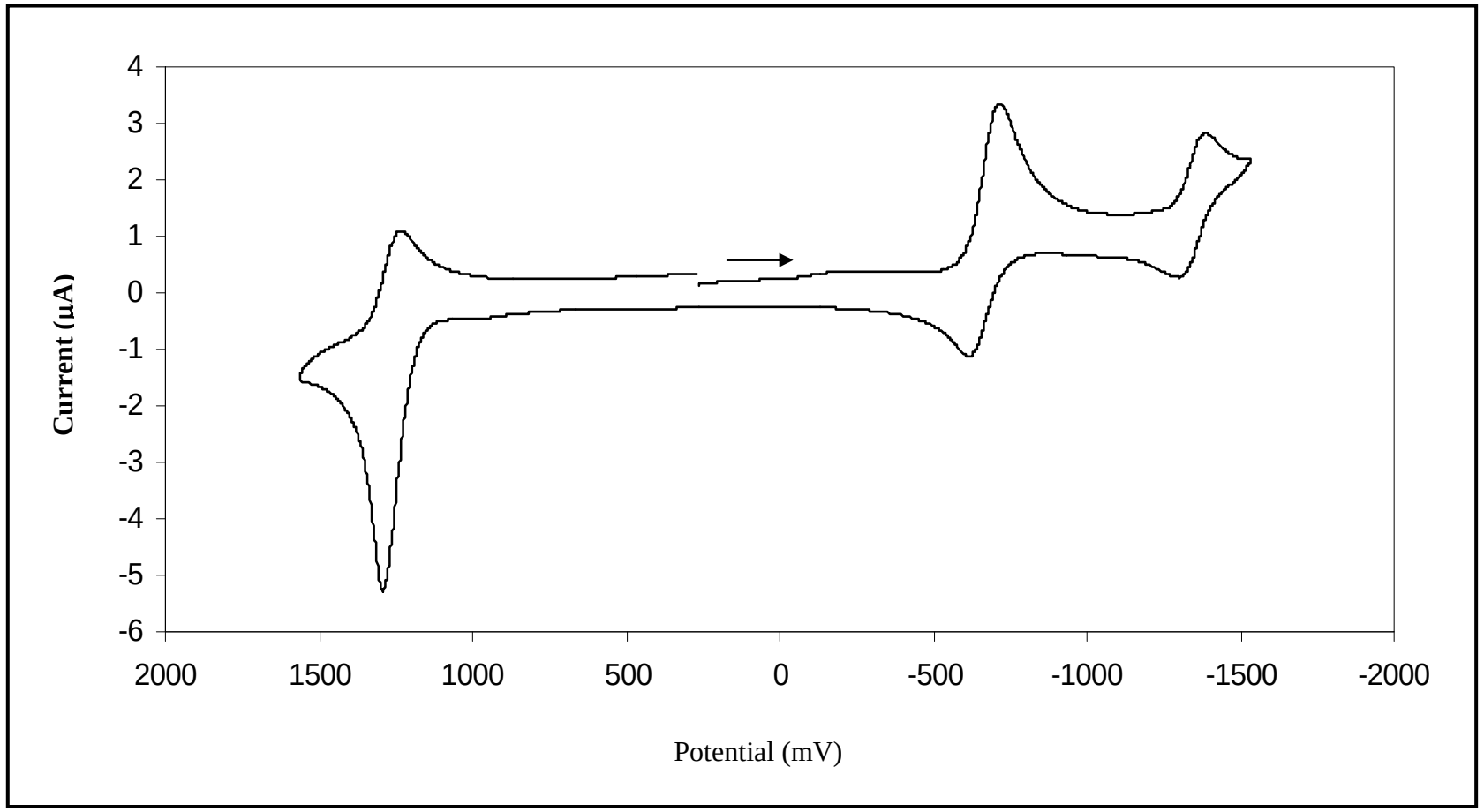


Figure 29. Cyclic voltammogram of [Ru(tpy)(Clazpy)Cl]PF_6 in 0.1 M TBAH CH_3CN at scan rate 50 mV/s.

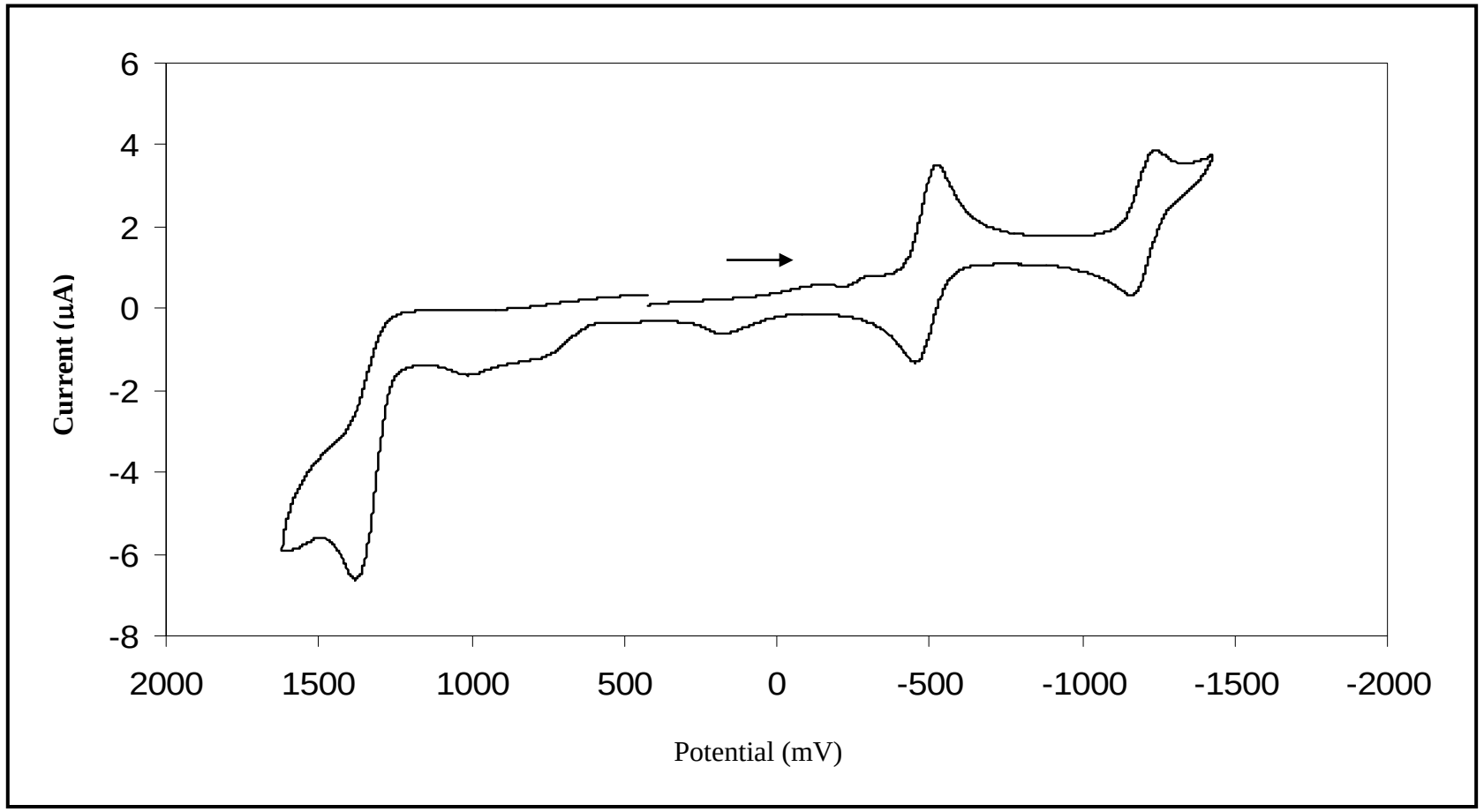


Figure 30. Cyclic voltammogram of [Ru(tpy)(Clazpy)NCS]PF_6 in 0.1 M TBAH CH_3CN at scan rate 50 mV/s.

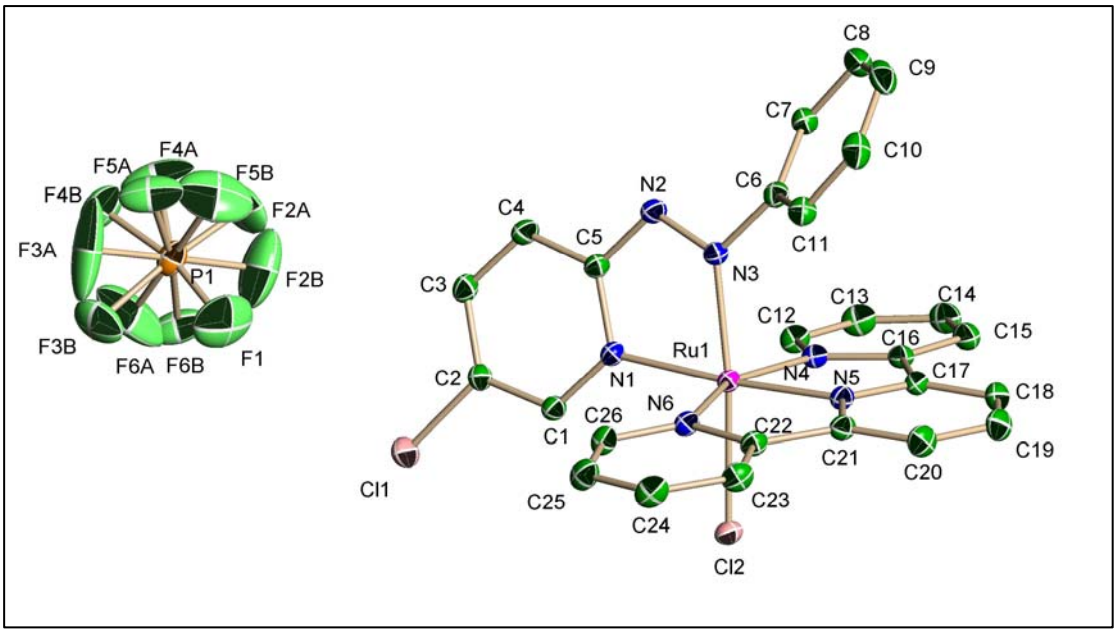
3.2.2.6 X-ray Crystallography

X-ray crystallography is the most important technique to identify the geometry of compounds. The single crystals of the $[Ru(tpy)(Clazpy)Cl]PF_6$ was grown to obtain the suitable X-ray quality crystals for structure determination. X-ray diffraction data were collected on the APEX CCD diffractometer with the Xtal 3.7.1 program system and equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073) at 293 K.

Single crystal of the $[Ru^{II}(tpy)(Clazpy)Cl]PF_6$ was obtained by slow recrystallisation from a EtOH/acetone solution at room temperature, in the dark. In case EtOH/acetone molecule was crystallized with one ruthenium complex in the $P\bar{1}$ space group. Details of X-ray structure determination of the complex is given in the Table 14-16. Figure 31 shows molecular structure of cation of $[Ru(tpy)(Clazpy)Cl]^+$ with atom numbering scheme. The ruthenium(II) is in distorted octahedral environment bound to three nitrogen atoms of the tpy ligand (N4, N5, N6), two nitrogen atoms (N1, N3) of the Clazpy ligand and one of the chlorine atom. The three nitrogen atoms of the tpy ligand (N4, N5, N6) and one nitrogen (N1, N_{py}) atom of the Clazpy ligand define in the equatorial plane. In addition, the trans axial positions are occupied by one nitrogen (N3, N_{azo}) atom of the Clazpy and the chlorine atom. This result is consistent with the literature observations for the $[Ru(tpy)(azpy)L]^+$ (Pramanik, N. C., *et al*., 1998).

The tpy ligand is coordinated to the ruthenium center in the common way, which the central nitrogen is closest to ruthenium (Corral, E., *et al*., 2006). The N(1)-Ru-N(6) angle is 102.13(7)°, greater than that 99.28(13)°, in the $[Ru(tpy)(azpy)Br]BF_4$ (Hansongnern, K., *et al*., 2003) and 100.25(14)° in the $[Ru(tpy)(apy)Cl](ClO_4)$ (Corral, E., *et al*., 2006). The bite angle of the Clazpy ligand, N(3)-Ru(1)-N(1) is 76.54(7)°. The bond distance of Ru-N1 (pyridine) and Ru-N3 (azo) are the 2.0485, 1.9721 Å, respectively. It is noticeable that the bond distance of

the Ru-N3 (azo) is shorter than the Ru-N1 (pyridine), because of the stronger π-back bonding, dπ(Ru) ⟶ π*(azo). The bond distance of Ru-N3 (azo) (1.9721 Å) is shorter than those in the [Ru(tpy)(apy)Cl](ClO$_4$) (1.981 Å) (Corral, E., *et al*., 2006) and in the [Ru(tpy)(azpy)Cl]Cl (1.999 Å) (Hansongnern, K., *et al*., 2001), respectively. Since the Clazpy ligand is a stronger π-acceptor than the apy and the azpy ligands. In this case the Clazpy ligand is a stronger π-acceptor than the azpy ligand consistent with literature review (Sahavisit, L., *et al*, 2005). In addition the Ru-Cl(2) bond length in the [Ru(tpy)(Clazpy)Cl]PF$_6$ complex (2.4044(6) Å) is slightly longer than the Ru-Cl bond length of [Ru(tpy)(apy)Cl](ClO$_4$) (2.3962(9)). The result is consistent with the above. Moreover, the N=N bond distance (1.300(2) Å), which is sensitive to extent of π-back bonding in the Clazpy ligand. Finally, during refinement, the F(2), F(3), F(4), F(5) and F(6) atoms of hexafluorophosphate anion were found to be distributed over two positions, F(2A), F(3A), F(4A), F(5A), F(6A) and F(2B), F(3B), F(4B), F(5B), F(6B), the figure is shown below.



[Ru(tpy)(Clazpy)Cl]PF$_6$

Table 14. Crystal data and structure refinement for $[Ru(tpy)(Clazpy)Cl]PF_6$.

Empirical formula	$C_{26}\ H_{19}\ Cl_2\ F_6\ N_6\ P\ Ru$	
Formula weight	732.41	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.5073(10) Å	α= 64.9970(10)°.
	b = 12.3239(10) Å	β= 66.6340(10)°.
	c = 12.6434(11) Å	γ = 62.5440(10)°.
Volume	1395.9(2) $Å^3$	
Z	2	
Density (calculated)	1.743 mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	728	
Crystal size	0.208 x 0.150 x 0.108 mm^3	
Theta range for data collection	1.84 to 28.02°.	
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=16	
Reflections collected	18849	
Independent reflections	6724 [R(int) = 0.0225]	
Completeness to theta = 28.02°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6724 / 0 / 425	
Goodness-of-fit on F^2	1.039	
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0303, $wR2$ = 0.0760	
R indices (all data)	$R1$ = 0.0339, $wR2$ = 0.0783	
Largest diff. peak and hole	0.605 and -0.451 $e.Å^{-3}$	

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6.

Atom	Distance (Å)
Ru(1)-N(5)	1.9682(17)
Ru(1)-N(3)	1.9721(17)
Ru(1)-N(1)	2.0485(17)
Ru(1)-N(4)	2.0704(18)
Ru(1)-N(6)	2.0731(18)
Ru(1)-Cl(2)	2.4044(6)
Cl(1)-C(2)	1.719(2)
N(1)-C(1)	1.343(3)
N(1)-C(5)	1.357(3)
N(2)-N(3)	1.300(2)
N(2)-C(5)	1.374(3)
N(3)-C(6)	1.438(3)
N(4)-C(12)	1.343(3)
N(4)-C(16)	1.365(3)
N(5)-C(17)	1.348(3)
N(5)-C(21)	1.351(3)
N(6)-C(26)	1.340(3)
N(6)-C(22)	1.370(3)
C(1)-C(2)	1.377(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.381(3)
C(3)-C(4)	1.377(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.391(3)
C(4)-H(4)	0.9300
C(6)-C(7)	1.382(3)
C(6)-C(11)	1.383(3)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Distance (Å)
C(7)-C(8)	1.381(4)
C(7)-H(7)	0.9300
C(8)-C(9)	1.371(5)
C(8)-H(8)	0.9300
C(9)-C(10)	1.370(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.387(4)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(12)-C(13)	1.383(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.368(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.381(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.380(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.475(3)
C(17)-C(18)	1.388(3)
C(18)-C(19)	1.388(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.374(4)
C(19)-H(19)	0.9300
C(20)-C(21)	1.388(3)
C(20)-H(20)	0.9300
C(21)-C(22)	1.471(3)
C(22)-C(23)	1.384(3)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Distance (Å)
C(23)-C(24)	1.383(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.371(4)
C(24)-H(24)	0.9300
C(25)-C(26)	1.376(3)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
P(1)-F(3A)	1.456(7)
P(1)-F(6A)	1.465(9)
P(1)-F(2A)	1.471(5)
P(1)-F(1)	1.530(3)
P(1)-F(5B)	1.540(10)
P(1)-F(2B)	1.541(8)
P(1)-F(5A)	1.542(7)
P(1)-F(4B)	1.564(6)
P(1)-F(4A)	1.569(7)
P(1)-F(6B)	1.585(6)
P(1)-F(3B)	1.594(6)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
N(5)-Ru(1)-N(3)	99.34(7)
N(5)-Ru(1)-N(1)	175.76(7)
N(3)-Ru(1)-N(1)	76.54(7)
N(5)-Ru(1)-N(4)	79.28(7)
N(3)-Ru(1)-N(4)	88.38(7)
N(1)-Ru(1)-N(4)	99.47(7)
N(5)-Ru(1)-N(6)	79.42(7)
N(3)-Ru(1)-N(6)	99.94(7)
N(1)-Ru(1)-N(6)	102.13(7)
N(4)-Ru(1)-N(6)	158.12(7)
N(5)-Ru(1)-Cl(2)	89.79(5)
N(3)-Ru(1)-Cl(2)	169.68(5)
N(1)-Ru(1)-Cl(2)	94.23(5)
N(4)-Ru(1)-Cl(2)	88.62(5)
N(6)-Ru(1)-Cl(2)	86.38(5)
C(1)-N(1)-C(5)	118.14(18)
C(1)-N(1)-Ru(1)	129.42(14)
C(5)-N(1)-Ru(1)	112.41(14)
N(3)-N(2)-C(5)	112.08(17)
N(2)-N(3)-C(6)	111.28(17)
N(2)-N(3)-Ru(1)	120.56(14)
C(6)-N(3)-Ru(1)	127.48(14)
C(12)-N(4)-C(16)	118.8(2)
C(12)-N(4)-Ru(1)	127.59(16)
C(16)-N(4)-Ru(1)	113.65(14)
C(17)-N(5)-C(21)	122.14(19)
C(17)-N(5)-Ru(1)	118.86(15)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
C(21)-N(5)-Ru(1)	118.94(15)
C(26)-N(6)-C(22)	118.71(19)
C(26)-N(6)-Ru(1)	127.71(15)
C(22)-N(6)-Ru(1)	113.36(14)
N(1)-C(1)-C(2)	121.14(19)
N(1)-C(1)-H(1)	119.4
C(2)-C(1)-H(1)	119.4
C(1)-C(2)-C(3)	121.3(2)
C(1)-C(2)-Cl(1)	118.05(17)
C(3)-C(2)-Cl(1)	120.61(17)
C(4)-C(3)-C(2)	117.7(2)
C(4)-C(3)-H(3)	121.1
C(2)-C(3)-H(3)	121.1
C(3)-C(4)-C(5)	119.0(2)
C(3)-C(4)-H(4)	120.5
C(5)-C(4)-H(4)	120.5
N(1)-C(5)-N(2)	117.60(18)
N(1)-C(5)-C(4)	122.5(2)
N(2)-C(5)-C(4)	119.8(2)
C(7)-C(6)-C(11)	120.9(2)
C(7)-C(6)-N(3)	119.8(2)
C(11)-C(6)-N(3)	119.3(2)
C(8)-C(7)-C(6)	119.1(3)
C(8)-C(7)-H(7)	120.4
C(6)-C(7)-H(7)	120.4
C(9)-C(8)-C(7)	120.2(3)
C(9)-C(8)-H(8)	119.9

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
C(7)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	120.7(3)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	120.0(3)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(6)-C(11)-C(10)	119.0(2)
C(6)-C(11)-H(11)	120.5
C(10)-C(11)-H(11)	120.5
N(4)-C(12)-C(13)	122.0(2)
N(4)-C(12)-H(12)	119.0
C(13)-C(12)-H(12)	119.0
C(14)-C(13)-C(12)	119.3(3)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	119.3(2)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(16)-C(15)-C(14)	119.7(2)
C(16)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
N(4)-C(16)-C(15)	120.9(2)
N(4)-C(16)-C(17)	114.78(19)
C(15)-C(16)-C(17)	124.2(2)
N(5)-C(17)-C(18)	119.6(2)
N(5)-C(17)-C(16)	113.13(19)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
C(18)-C(17)-C(16)	127.2(2)
C(17)-C(18)-C(19)	118.9(2)
C(17)-C(18)-H(18)	120.5
C(19)-C(18)-H(18)	120.5
C(20)-C(19)-C(18)	120.5(2)
C(20)-C(19)-H(19)	119.7
C(18)-C(19)-H(19)	119.7
C(19)-C(20)-C(21)	119.0(2)
C(19)-C(20)-H(20)	120.5
C(21)-C(20)-H(20)	120.5
N(5)-C(21)-C(20)	119.8(2)
N(5)-C(21)-C(22)	113.05(18)
C(20)-C(21)-C(22)	127.2(2)
N(6)-C(22)-C(23)	120.9(2)
N(6)-C(22)-C(21)	115.20(19)
C(23)-C(22)-C(21)	123.9(2)
C(24)-C(23)-C(22)	119.1(2)
C(24)-C(23)-H(23)	120.4
C(22)-C(23)-H(23)	120.4
C(25)-C(24)-C(23)	119.8(2)
C(25)-C(24)-H(24)	120.1
C(23)-C(24)-H(24)	120.1
C(24)-C(25)-C(26)	119.0(2)
C(24)-C(25)-H(25)	120.5
C(26)-C(25)-H(25)	120.5
N(6)-C(26)-C(25)	122.5(2)
N(6)-C(26)-H(26)	118.8

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
C(25)-C(26)-H(26)	118.8
F(3A)-P(1)-F(6A)	89.4(9)
F(3A)-P(1)-F(2A)	142.9(14)
F(6A)-P(1)-F(2A)	110.3(8)
F(3A)-P(1)-F(1)	103.4(7)
F(6A)-P(1)-F(1)	103.7(7)
F(2A)-P(1)-F(1)	101.9(6)
F(3A)-P(1)-F(5B)	90.4(12)
F(6A)-P(1)-F(5B)	179.2(9)
F(2A)-P(1)-F(5B)	69.5(7)
F(1)-P(1)-F(5B)	77.1(6)
F(3A)-P(1)-F(2B)	178.5(11)
F(6A)-P(1)-F(2B)	89.1(10)
F(2A)-P(1)-F(2B)	37.7(6)
F(1)-P(1)-F(2B)	77.2(6)
F(5B)-P(1)-F(2B)	91.1(8)
F(3A)-P(1)-F(5A)	54.0(10)
F(6A)-P(1)-F(5A)	142.5(11)
F(2A)-P(1)-F(5A)	97.8(6)
F(1)-P(1)-F(5A)	93.8(4)
F(5B)-P(1)-F(5A)	37.1(6)
F(2B)-P(1)-F(5A)	127.4(8)
F(3A)-P(1)-F(4B)	66.0(6)
F(6A)-P(1)-F(4B)	68.9(7)
F(2A)-P(1)-F(4B)	91.4(6)
F(1)-P(1)-F(4B)	166.5(4)
F(5B)-P(1)-F(4B)	110.3(7)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
F(2B)-P(1)-F(4B)	113.2(7)
F(5A)-P(1)-F(4B)	86.6(5)
F(3A)-P(1)-F(4A)	95.5(9)
F(6A)-P(1)-F(4A)	88.7(7)
F(2A)-P(1)-F(4A)	55.6(9)
F(1)-P(1)-F(4A)	157.3(8)
F(5B)-P(1)-F(4A)	90.5(8)
F(2B)-P(1)-F(4A)	84.2(9)
F(5A)-P(1)-F(4A)	87.1(4)
F(4B)-P(1)-F(4A)	36.2(6)
F(3A)-P(1)-F(6B)	117.5(9)
F(6A)-P(1)-F(6B)	28.9(8)
F(2A)-P(1)-F(6B)	89.2(6)
F(1)-P(1)-F(6B)	89.7(3)
F(5B)-P(1)-F(6B)	151.5(9)
F(2B)-P(1)-F(6B)	61.1(8)
F(5A)-P(1)-F(6B)	171.4(7)
F(4B)-P(1)-F(6B)	88.2(5)
F(4A)-P(1)-F(6B)	92.7(4)
F(3A)-P(1)-F(3B)	42.6(10)
F(6A)-P(1)-F(3B)	66.2(7)
F(2A)-P(1)-F(3B)	174.4(7)
F(1)-P(1)-F(3B)	75.3(4)
F(5B)-P(1)-F(3B)	114.1(7)
F(2B)-P(1)-F(3B)	136.8(10)
F(5A)-P(1)-F(3B)	87.3(5)
F(4B)-P(1)-F(3B)	91.2(5)

Table 15. Bond lengths [Å] and angles [°] for [Ru(tpy)(Clazpy)Cl]PF_6. (continue)

Atom	Angle (°)
F(4A)-P(1)-F(3B)	127.4(8)
F(6B)-P(1)-F(3B)	86.0(4)

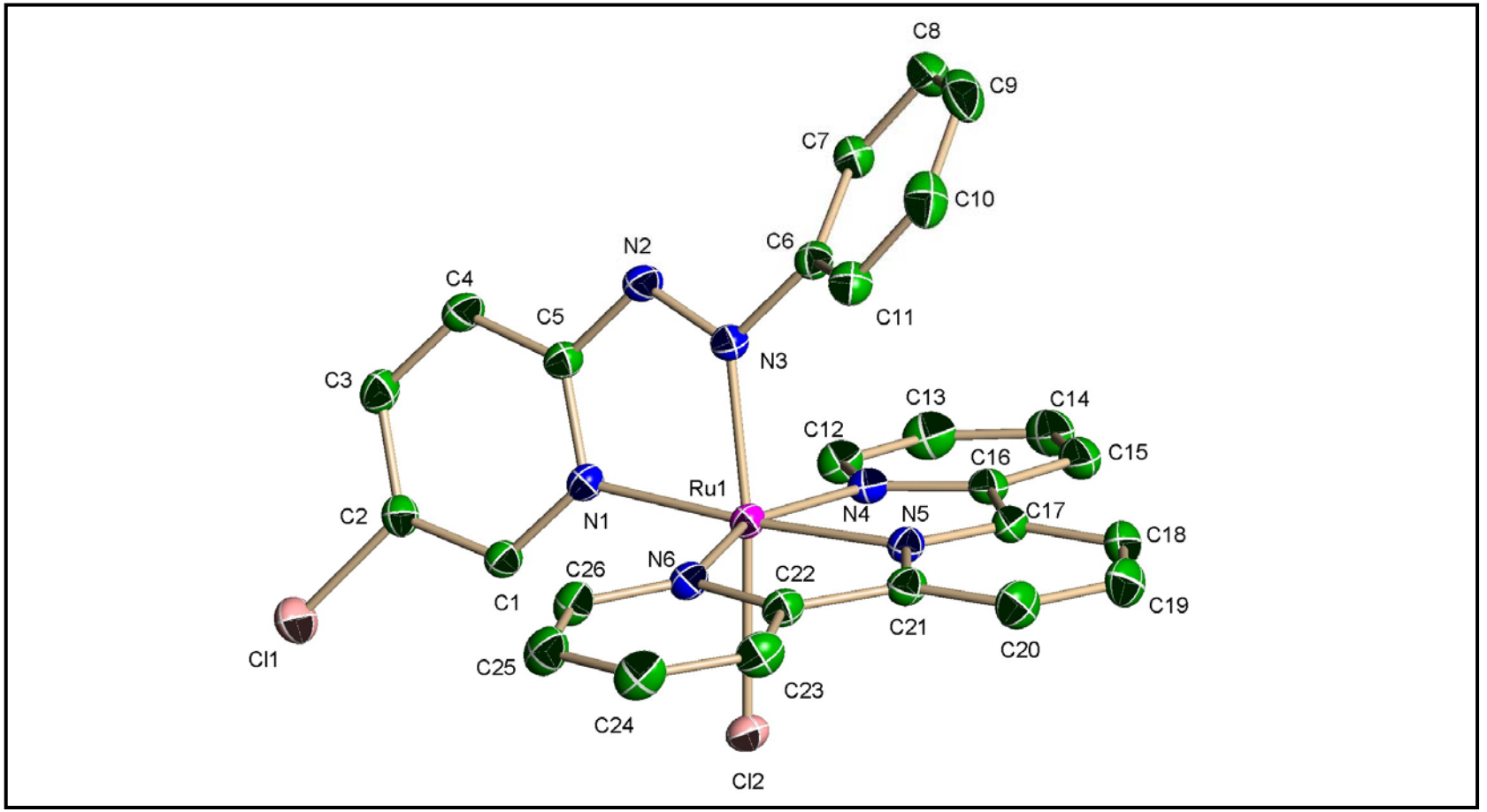


Figure 31. The structure of $[Ru(tpy)(Clazpy)Cl]^{+}$.

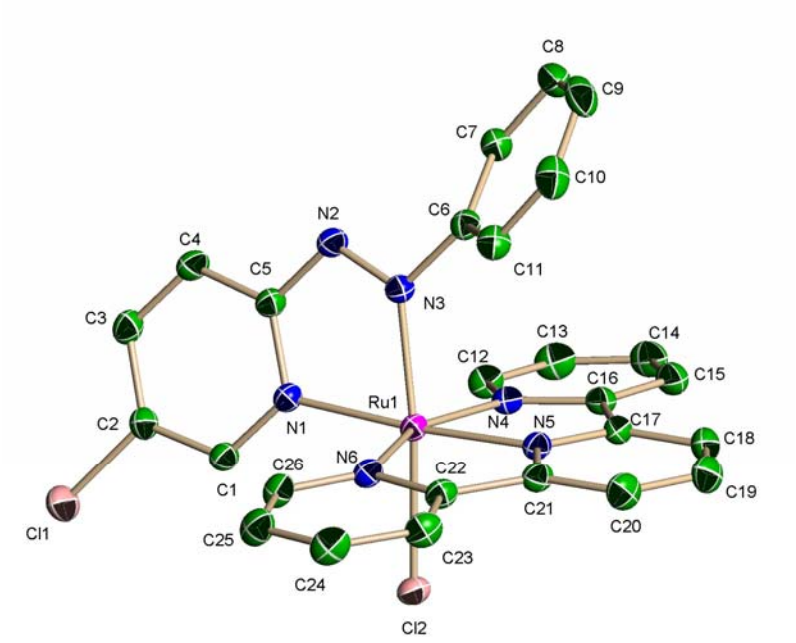
4 CONCLUSION

The ruthenium(II) complexes, $[Ru(tpy)(Clazpy)Cl]^+$ and $[Ru(tpy)(Clazpy)NCS]^+$, were prepared and characterized by using elemental analysis, Infrared spectroscopy, UV-Visible absorption spectroscopy, 1D and 2D NMR spectroscopy and their electrochemical properties were studied by cyclic voltammetry. The solid state molecular structure of the $[Ru(tpy)(Clazpy)Cl]PF_6$ was determined by X-ray crystallography.

Results from the elemental analysis, the analytical data of the complexes corresponded to the calculated values.

The ligand exhibited a sharp band at 1364 cm^{-1}, corresponding to an N=N stretching mode. In the two complexes, ν(N=N) modes were red shifted by 44-64 cm^{-1}, which was a good indication of N-coordination. Electronic spectra of the complexes exhibited highly intense MLCT transitions. The energy of the MLCT transition is an allowed transition. The ^1H, ^{13}C and DEPT NMR spectra between the ligand and complexes were compared in order to study the structures and the stereochemistry of the compounds. Results of 2D NMR experiments, ^1H-^1H COSY and ^1H-^{13}C HMQC, corresponded with the 1D NMR data. The cyclic voltammogram shows that the NCS^- ligand is a better π-acceptor than the Cl^- ligand to stabilize the ruthenium(II) center. Results from this study are consistent with the ligand field strength of ligand in the spectrochemical series. Which the NCS^- ligand is a strong field than the Cl^- ligand.

The X-ray structural studies confirmed the structure of $[Ru(tpy)(Clazpy)Cl]^{+}$.



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APPENDIX

A. Cut off solvents

Table 16. The solvents for UV-Visible spectrum and the minimum values for measurement

Solvents	λ(nm)
CH_3CN	195
Acetone	330
DMSO	265

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for [Ru(tpy)(Clazpy)Cl]PF_6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	1717(1)	1704(1)	5759(1)	31(1)
Cl(1)	6316(1)	2916(1)	2282(1)	59(1)
Cl(2)	3124(1)	-27(1)	4885(1)	42(1)
N(1)	3042(2)	2673(2)	4862(2)	34(1)
N(2)	1517(2)	3909(2)	6160(2)	41(1)
N(3)	871(2)	3160(2)	6424(2)	34(1)
N(4)	2432(2)	567(2)	7288(2)	37(1)
N(5)	381(2)	850(2)	6704(2)	35(1)
N(6)	587(2)	2381(2)	4533(2)	37(1)
C(1)	4159(2)	2460(2)	3959(2)	37(1)
C(2)	4958(2)	3193(2)	3493(2)	39(1)
C(3)	4674(2)	4138(2)	3968(2)	45(1)
C(4)	3525(3)	4365(2)	4890(2)	46(1)
C(5)	2715(2)	3637(2)	5301(2)	37(1)
C(6)	-357(2)	3431(2)	7352(2)	38(1)
C(7)	-353(3)	3635(2)	8344(2)	47(1)
C(8)	-1557(3)	3975(3)	9190(2)	61(1)
C(9)	-2737(3)	4103(3)	9045(3)	65(1)
C(10)	-2737(3)	3867(3)	8079(3)	59(1)
C(11)	-1540(2)	3528(2)	7217(2)	46(1)
C(12)	3559(2)	426(2)	7496(2)	46(1)
C(13)	3904(3)	-336(3)	8578(3)	57(1)
C(14)	3068(3)	-954(3)	9474(2)	57(1)
C(15)	1909(3)	-823(2)	9271(2)	49(1)

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for [Ru(tpy)(Clazpy)Cl]PF_6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.(Continued)

	x	y	z	U(eq)
C(16)	1616(2)	-78(2)	8168(2)	39(1)
C(17)	468(2)	50(2)	7820(2)	39(1)
C(18)	-447(3)	-583(3)	8488(2)	51(1)
C(19)	-1443(3)	-367(3)	7990(3)	58(1)
C(20)	-1500(3)	436(3)	6843(3)	53(1)
C(21)	-557(2)	1040(2)	6195(2)	39(1)
C(22)	-429(2)	1902(2)	4954(2)	39(1)
C(23)	-1244(3)	2212(3)	4231(2)	50(1)
C(24)	-1007(3)	2999(3)	3062(3)	57(1)
C(25)	37(3)	3446(3)	2632(2)	55(1)
C(26)	809(3)	3124(2)	3390(2)	45(1)
P(1)	6599(1)	6927(1)	969(1)	60(1)
F(1)	5880(4)	6194(4)	892(4)	175(2)
F(2A)	6446(12)	6533(13)	2275(5)	159(4)
F(3A)	6449(17)	8040(18)	-90(16)	269(10)
F(4A)	7089(14)	7451(10)	1588(18)	158(5)
F(5A)	5369(10)	8186(8)	883(11)	123(4)
F(6A)	8012(10)	6360(20)	354(13)	218(7)
F(2B)	6797(15)	5736(12)	2077(15)	211(6)
F(3B)	6841(9)	7210(9)	-439(6)	124(3)
F(4B)	7442(8)	7745(8)	719(9)	106(3)
F(5B)	5118(10)	7535(17)	1619(15)	201(7)
F(6B)	7971(9)	5744(6)	867(10)	110(4)

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Poster presentation

Phongarthit C. and Hansongnern K. "Synthesis and Characterization of Chloro(5-chloro-2-(phenylazo)pyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate", Pure and Applied Chemistry International Conference, Naresuan University, Phitsanulok, Thailand, January 14–16, 2009.