Int. Res. J. of Science & Engineering, 2016; Vol. 4 (1): 39-42 ISSN: 2322-0015

RESEARCH ARTICLE

Synthesis of Cycloruthenated complexes (II) and its characterization

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Manuscript Details

Received : 27.02.2016
Accepted: 16.03.2016
Published: 10.05.2016

ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

Cite this article as:
Khandekar SR,Suradkar KP and Hande DV. Synthesis of Cycloruthenated complexes (II) and its characterization . *Int. Res. Journal of Science & Engineering*, 4(1): 39-42.

ABSTRACT

Cycloruthenated (II) complexes offer several favorable properties suited for anticancer drug design, which provide a new class of compounds for clinical uses as an alternative to platinum antitumor drugs for the treatment of cancer. In the present work various precursors and ligand were synthesized such as $[Ru(bpy)_2Cl_2].2H_2O$, $[Ru(phen)_2Cl_2].2H_2O$ and 2-phenyl imidazoline respectively for the production of Cycloruthenated (II) complexes like $[Ru(bpy)_2(2PZ\text{-}L)]PF_6$ and $[Ru(phen)_2(2PZ\text{-}L)]PF_6$. During the study different physical methods have been used ie. Nuclear magnetic resonance (NMR); Infrared spectroscopy (IR); UV-Visible spectroscopy for characterization. These complexes have anticancerous as well as great antimicrobial properties.

Keywords: $[Ru(phen)_2(2PZ\text{-}L)]PF_6$, Cycloruthenated (II) complexes

INTRODUCTION

Reaction of a series of nitrogen donar ligands with metals salts gave complexes where ortho Metalation had occurred resulting in bidentate binding to the metal centers through N and C atoms are the cyclometalated complex (Kiyoshi et al., 2011).

Cyclometalation was discovered in the early 1960s providing a straightforward entry to organometallic compounds that feature a metal-carbon σ-bond. Cyclometalation generally supports highly susceptible M-C bond and forms highly stable organo-metallic compounds (Jiang-Yang et al., 2012). Cyclometalation reaction represents probably the mildest route for activating strong C-H and C-R bonds. Because of these capability they have been employed in various application, for example as active units in sensors, in anticancer agents ,as photophysical in organometallic light emitting diodes, for light harvesting and energy transfer such as in photovoltaic cells, as gelators and birefringents in liquid crystalline materials and as molecular or crystalline switches.

Imidazoles and benzimidazoles are present in various bioactive compounds possessing antiviral and anticanceral properties (Takashi et al 2012).The invention of Cisplatin – $[Pt[NH_3]_2Cl_2]$ has motivated us to search for alternative transition metal complexes with improved pharmacological properties. During this cycloruthenated complexes are coming out as an better option as it possesses several favorable properties suited to reasonable anticancer drug design. In the present study we synthesized and characterized the cycloruthenated complexes which having anticancerous and antiviral properties.

Chemicals :

All chemicals used in this work were of analytical grade. $RuCl_3.3H_2O$, 2,2'-bipyridine(bpy),1,10-phenanthrolinemonohydrate,benzaldehyde, ethylene diamine, KI (potassium iodide), potassium carbonate, iodine , potassium hexafluoro phosphate, methanol, ethanol, acetonitrile, DMF, DMSO, chloroform, DCM, acetone, ethyl acetate, hexane and diethyl ether.

Preparation of of ligand

2-phenyl imidazole :-

In a typical procedure,aldehyde (1.0 mmol) and diamine (1.2 mmol) in water (10 ml), were stirred for 20 min, potassium carbonate (1.5 mmol), iodine (1 mmol) and potassium iodide (25 mol %) were then added consecutively and the mixture kept at 90°C with stirring for 30–50 min. After work-up, the corresponding imidazoline or benzimidazole was obtained in good to excellent yield. The condensation of aldehydes with diamines occurs without any catalyst, and the addition of molecular iodine as an oxidant in the presence of potassium iodide and base, smoothly oxidized the condensed products of aldehydes and diamines to imidazolines / benzimidazole.

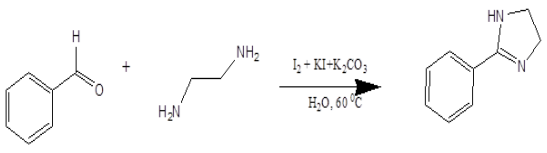

Figure 1 : Synthetic scheme of ligand

Preparation of the Precursor Complexes:

a) $[Ru(bpy)_2Cl_2].2H_2O$ (P1):

The mixture of $RuCl_3.H_2O$(250 mg,0.9 mmol), LiCl (405 mg, 9.5mmol), 2,2'-bipyridyl (298 mg, 1.9mmol) were heated at reflux in grade dimethyl formamide (15 mL) for 8 hour. After the reaction mixture was cooled to room temperature, 50 mL of reagent grade acetone was added and the resultant solution cooled at 0°C overnight. Filtering yielded a red to red-violet solution and a dark-green-black microcrystalline product .The solid was washed three times with 25 mL portions of water followed by three 25 mL portions of diethyl ether, and then it was dried by suction. Finally the black colour product was obtained by filtering it. IR was taken in KBr, which gives the different values as 3066 cm^{-1} (=C-H); 1672 cm^{-1}(-C=N) ; 1460 cm^{-1}, 1417 cm^{-1} (-C=C-) ; and 3497 cm^{-1}.

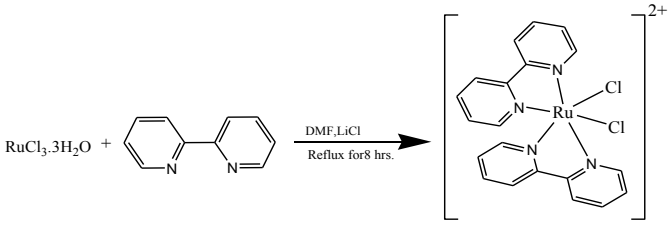

Figure 2: Synthetic scheme of P1.

b) $[Ru(phen)_2Cl_2].2H_2O$ (P2):-

The mixture of $RuCl_3.H_2O$ (250 mg,0.9 mmol), LiCl (405 mg, 9.5 mmol), 1,10-phenanthroline monohydrate (379 mg, 1.9 mmol) were heated at reflux in grade dimethyl formamide (15 mL) for 8 hour. After the reaction mixture was cooled to room temperature, 50 mL of reagent grade acetone was added and the resultant solution cooled at 0°C overnight. Filtering yielded a red to red-violet solution and a dark-green-black microcrystalline product. The solid was washed three times with 25 mL portions of water followed by three 25 mL portions of diethyl ether, and then it was dried by suction. Finally the dark brownish product was obtained by filtering it. IR was taken in KBr, which gives the different values as 3047 cm^{-1}(=C-H);1672 cm^{-1}.

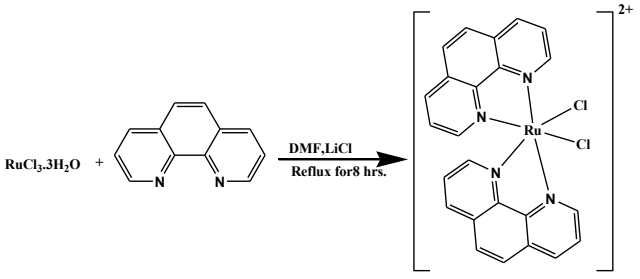

Figure 3: Synthetic scheme of P2

Physical methods

The ligands and complexes synthesized during the study have beencharacterized by Nuclear magnetic resonance(NMR); Infrared spectroscopy(IR); UV-Visible spectroscopy. These methods are briefly outlined as follows:

1. Infrared spectroscopy (IR):

The spectra of solid samples were recorded by using KBr pellets as in theso called Shimadzu FTIR-8400

spectrophotometer at department of thechemistry, University of Pune.

2.UV-Visible spectroscopy:-

UV-visible absorption measurements were carried on JASCO V-630 Spectrophotometer using matched pair of 1 cm quartz cells at Department of chemistry, University of Pune.

3. NMR spectroscopy :

^{1}H NMR spectra of the ligands and the complexes were measured on a Varian-Mercury 300 MHz spectrometer with $CDCl_3$,DMSO-d_6 as solvent at room temperature and all the chemical shifts are given relative to tetramethylsilane (TMS) as the internal standard at Department of chemistry, University of Pune and National Chemical Laboratory (NCL).

RESULTS AND DISCUSSION

Synthesis Of Complexes:

a) [Ru(bpy)$_2$(2PZ-L)]PF$_6$(1):-

The ligand 2-phenylimidazoline (28.0958 mg ,0.1921 mmol) cis-[Ru(bpy)$_2$Cl$_2$].2H$_2$O (100 mg, 0.1921 mmol)and triethylamine 5mL was added to ethanol-water (20 mL,$V_{ethanol}$:V_{water}=2:1) solvent . The reaction mixture was magnetically stirred and refluxed for 12 hours under nitrogen atmosphere. The reaction mixture was concentrated by rotary evaporator and a saturated KPF_6 aqueous solution was added to give precipitate. The precipitate was filtered and was with water and dried. After drying the precipitate was collected by using acetonitrile.

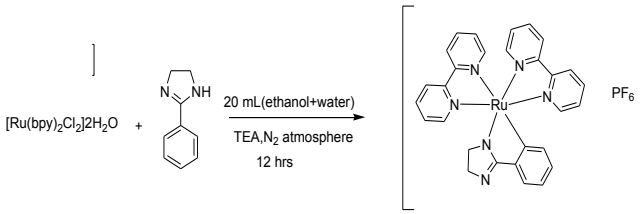

Figure 12: Synthetic scheme of complex **1**

b) [Ru(phen)$_2$(2PZ-L)]PF$_6$(2) :-

The ligand 2-phenylimidazoline (25.72 mg ,0.1759 mmol), cis-[Ru(phen)$_2$Cl$_2$].2H$_2$O (100 mg, 0.1759 mmol) and triethylamine 5mL was added to ethanol-water (20 mL ,$V_{ethanol}$:V_{water}=2:1) solvent . Then reaction mixture was magnetically stirred and refluxed for 12 hours under nitrogen atmosphere. The reaction mixture was concentrated by rotary evaporator and a saturated KPF_6 aqueous solution was added to give precipitate. The precipitate was filtered and was with water and dried. Product was purified by column chromatography using acetonitrile as an eluent.

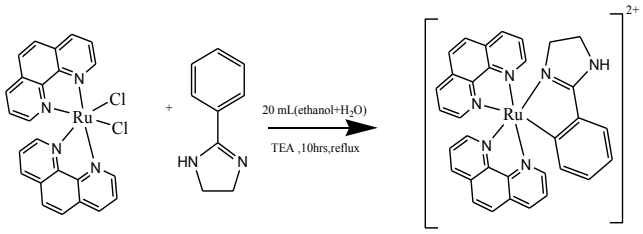

Figure 13: Synthetic scheme of complex **2**

Characterization:

UV-Visible Spectroscopy:-

The complexes [Ru(bpy)$_2$(2PZL)]PF$_6$, [Ru(phen)$_2$ (2PZL)] PF$_6$ exhibits the absorption bands at 500-800 nm in visible region due to d-d transition and ligand based π-π* transition occurs in the UV region of 210-350 nm. The molar extinction coefficient (ε_{max}) value for the complexes were 10^3-10^4 mol^{-1}cm^{-1}in visible region.

Fluorescence Spectroscopy:-

The fluorescence spectroscopic data for the complexes [Ru(bpy)$_2$(2PZ-L)]PF$_6$ and [Ru(phen)$_2$(2PZ-L)]PF$_6$ in Acetonitrile and Dimethylformamide solvent are as follows.

Table 1: **Photophysical data of UV-Visible Spectroscopy.**

COMPLEXES	**ABSORBANCE λ_{max}/ε(M^{-1}cm^{-1})**			
	Acetonitrile		**Dimethylformamide**	
	Ligand transition	**MLCT**	**Ligand transition**	**MLCT**
[Ru(bpy)$_2$(2PZ-L)]PF$_6$	**4410**/5855.05 **18292**/24627.65 **9245**/10514.85	**3486**/4067.5	**7350**/8456.3 **28094**/36958.25	**6492**/7189.2
[Ru(phen)$_2$(2PZ-L)]PF$_6$	**36264**/41800.45 **33223**/41880	**8469**/9742.7	_	**7490**/8240

Table 2: Fluorescence data : Intensity and λ_{em} in different solvent

Sr. No.	Complexes	Acetonitrile	Dimethylformamide
1	**$[Ru(bpy)_2(2PZ\text{-}L)]PF_6$**	355/485	260/492
2	**$[Ru(phen)_2(2PZ\text{-}L)]PF_6$**	389/469	320/490

Table 3: IR spectral data:

Complexes/ligand	-C=C-	-C=N	-C-H	-N-H	-S-CH_3	-S=O
$[Ru(bpy)_2(2PZ\text{-}L)]PF_6$	1453	1633	3076	-	-	-
$[Ru(phen)_2(2PZ\text{-}L)]PF_6$	1417	1621	3067	-	-	-

IR Spectroscopy:

The solid IR spectrum of the ligand and their complexes have corresponding stretching frequency as given below

CONCLUSION

In the present investigation Cycloruthenated (II) complexes were synthesized and characterized by spectroscopic analysis. Spectroscopical and theoretical data of these complexes were compared. On the basis of this comparison it is concluded that the Cycloruthenated (II) complexes possesses anticancerous and enormous antimicrobial properties.

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