# Spectral characterization and antifungal studies of Ruthenium(II) macrocyclic complexes derived from 2,7-Diaminophenanthrene and Diethyl benzene-1,2-dicarboxylate

**K.V. Gautam, S.S.V. College, Kahalgaon, Tilka Manjhi Bhagalpur University, Bhagalpur**
**Email: drkvgautam@gmail.com**

**Abstract:** A novel complex of Ruthenium(II) macrocyclic ligand derived by the condensation of 2,7-Diaminophenanthrene and Diethyl benzene-1,2-dicarboxylate have been designed, synthesized and characterized by Elemental analyses, IR and UV-Vis. data in order to find out their antifungal activities. The stoichiometry of the complex has been found to be 1 : 1 (Metal : Ligand). The analytical data indicate that the complex exhibit octahedral geometry. The antifungal activity of the macrocyclic ligand and its metal complex has been screened in vitro against fungi such as A. flavus, Trichoderma harizanum, T. viridae and Rhizoctonia solani.

**Keywords:** Antifungal activity, Metal complexes, Macrocyclic ligands, Square planar.

## Introduction:

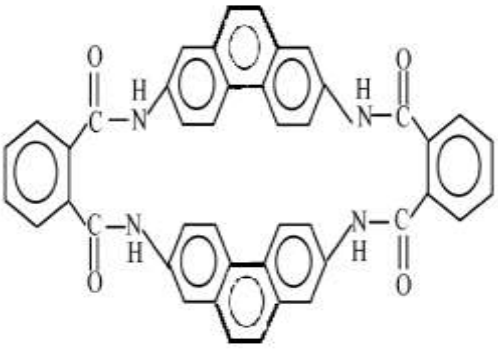
Researches on macrocyclic complexes have gained momentum during recent years[1-11]. Antique macrocyclic metalloenzymes like hemoglobin, chlorophyll and phthalocyanins have profoundly influenced the course of evolution of biological species in natural environments. Only during the past few decades synthetic macrocyclic complexes, encompassing a range of structural forms have come out. It is exhilarating to observe the ensemble of information, covering various aspects including synthesis, structure determination, thermodynamic equilibrium and application of macrocyclic complexes in a variety of fields such as commercial dyes, optical and electrical materials, sensors, potential medicinal application and catalysts.. It is well known that various organic ligands possess strong fungicidal, insecticidal, herbicidal and antibacterial properties It has been reported that the activity of biometals is very often altered through the formation of chelates with different bioligands.

In recent years, an extensive literature has been published in the field of chelate compounds with antimicrobial activities. Metal coordination complexes have been widely studied for their antimicrobial, and anticancer properties. Many drugs demonstrated modified pharmacological and toxicological properties when administered in the form of metallic complexes. Transition metals form some specific and important drugs. These drugs showed antiserothenine, antihistaminic, anticonvulsant and antifungal activities. It has been well established that certain platinum and palladium complexes demonstrated carcinostatic activity. It is suggested that the compounds exert antimicrobial activity either by killing the microbe or by inhibiting the growth of the microbe. The antimicrobial activity of these compounds depends upon the nature of the microorganisms. This prompted us to design and synthesize antifungal active macrocylic complexes formed by the condensation of 2,7-Diaminophenanthrene and Diethylbenzene-1,2-dicarboxylate using metal salts. The in vitro antifungal activities of the investigated compounds were tested against fungi such as A. flavus, Trichoderma harizanum, T. viridae and Rhizoctonia solani.

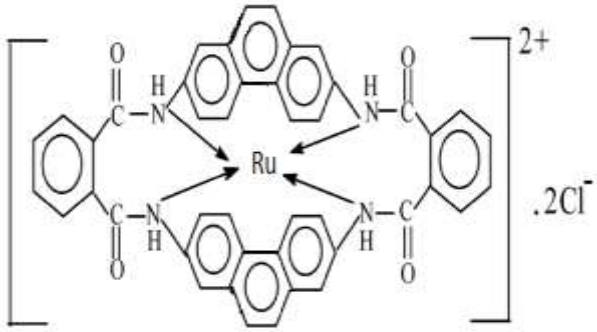
## Experimental :

All chemicals used were CP grade and AR grade. Lithium perchlorate ($LiClO_4$) was purchased from Nice. Anhydrous grade ethanol and DMSO were obtained from Fisher Scientific Company.

Synthesis of macrocyclic ligands: An ethanolic solution of Diethylbenzene-1,2-dicarboxylate (10 mmol) was added to the ethanolic solution of 2,7-Diaminophenanthrene (10 mmol) and refluxed for 8h.Then the solution was reduced to one-third on a water bath. The solid complex precipitated was filtered and washed thoroughly with ethanol and dried in vacuo.



Synthesis of metal complexes: A solution of macrocyclic ligand (5 mmol) in ethanol (20 ml) was added to a solution of $RuCl_2$ (5 mmol) in ethanol (10 ml) and the mixture was refluxed for 8 h and concentrated to one-third volume on a water bath after cooling. The solid product formed was filtered, washed with ethanol and dried in vacuo.




**Results and Discussion:**

All the complexes are stable at room temperature, insoluble in water and partially soluble in acetonitrile but soluble in DMF and DMSO. The physical properties and analytical data of the complexes are enlisted in Table 1.

The elemental analysis data of the complexes are in good agreement with theoretical values. These complexes showed high conductance values (145~166 $ohm^{-1}$ $cm^2$ $mol^{-1}$) indicating their electrolytic nature. High molar conductance values of all the complexes in DMSO indicate that the chloride ions are present outside of the coordination sphere which is confirmed by silver nitrate test. In the present study Ru(II) complex was 0 B.M, i.e. diamagnetic in nature, at room temperature suggesting a octahedral geometry around the Ruthenium ion.

Table-1

| S.No. | Compound | Found (Calculated)% | | | | $\Lambda_m$ hmo $cm^2$ $mol^{-1}$ |
|---|---|---|---|---|---|---|
| | | M | H | C | N | |
| 1. | L | - | 4.0(4.14) | 77.4(78.10) | 8.0(8.28) | - |
| 2. | $[RuL]Cl_2$ | 12.7(13) | 3.3((3.60) | 67.66(68.04) | 7.0(7.21) | 90 |

**Antifungal activity:**

NCCLS approved standard potato dextrose agar medium was used for antifungal activity by well diffusion method. DMSO was used as the solvent and fluconazole (antifungal agent) as control. The PDA medium was prepared and inoculation was done inside the Laminar Air Flow. A well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution, covered with petri plates and they were incubated at 35 $^oC$ for 72 h. During the incubation period, the solution was diffused and affected the growth of the inoculated microorganisms. The inhibition zone was developed, at which the concentration was noted. The minimum inhibitory concentration (MIC) values of the compounds against the growth of microorganisms are summarized in Table 3.

**Isolation and identification:**

The organisms (A. flavus, T. harizanum, T. viridae and Rhizoctonia solani) were isolated by primary selection from a sample of naturally contaminated cassava waste by serial dilution and courplate technique. The pure cultures were identified by their pharmacology and colony characteristics. The organisms were maintained on PDA slant (potato dextrose agar) stored at 4 $^{o}$C.

**IR spectra**:

The infrared spectra gave some important information regarding to the skeleton of the complexes.

The IR spectra of the macrocyclic ligand show characteristic band for $\nu_{(N-H)}$ at 3237 $cm^{-1}$ and amide (C = O) at 1609 $cm^{-1}$. In the complexes, $\nu_{(N-H)}$ bands were shifted to lower frequencies (104 $cm^{-1}$), due to coordination of the NH groups. On the other hand, the stretching vibration of $\nu_{(C=O)}$ was not affected, which indicates that the carbonyl groups are not involved in coordination to the metal cation. The coordination of nitrogen to the metal atom is supported by the appearance of a new band in the region 433 $cm^{-1}$ assignable to $\nu_{(Ru-N)}$ vibration.

**Electronic spectra:**

The electronic absorption spectra of ligand and its complex was recorded at 300 K using suitable solvent. The solvent, absorption region, assignment of the absorption bands and the proposed geometry of the complex are given in Table 2. From the table, we concluded that the complex was having octahedral geometry geometry.

Based on the above spectral data, the proposed structure of the macrocyclic ligand and its metal complex is shown in Fig. 1 and 2.

Table-2

| S.No. | Compound | Solvent | Absorption($cm^{-1}$) | Geometry |
|---|---|---|---|---|
| 1. | L | | 30498 | - |
| 2. | $[RuL]Cl_2$ | DMSO | 36590 | Octahedral geometry |

**Antifungal activity**:

Disc diffusion method: The in vitro antifungal activity of the compounds was tested against filamentous fungi such as A. flavus, Trichoderma harizanum, T. viridae and Rhizoctonia solani by serial Dilution method. The minimum inhibitory concentration (MIC) values of the compounds against the growth of microorganisms are summarized in Table 3.

Table-3

Antifungal activity of the synthesized compound MIC (minimum inhibitory concentration$\times 10^{-4}$ M)

| S.No. | Compound | A. flavus | T. Viridae | T. Harizanum | R. Solani |
|---|---|---|---|---|---|
| 1. | L | 1.2 | 1.3 | 1.3 | 1.2 |
| 2. | $[RuL]Cl_2$ | 2.1 | 2.4 | 2.4 | 2.1 |

A comparative study of the ligand and its complex (MIC values) indicate that metal chelate show higher antibacterial activity than the free ligand.

**Acknowledgments**: The author Dr. Kirti Vardhan Gautam is thankful to University Department of Chemistry, Tilka Manjhi Bhagalpur University, Bhagalpur and S.S.V.College, Kahalgoan for providing essential lab facilities and support to the research work.

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