

Conventional and green synthesis, characterization and antimicrobial potency of complex of Ru (III) with 2(*E*)[(2,4-dichlorophenyl) imino] methyl} -6- methoxy phenol [DCPIMMP]

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Abstract

Both conventional and microwave approaches are used to synthesize the Schiff base ligand and its complex with Ruthenium (III). Elemental analyses, IR and ESR spectroscopy, electronic spectra, magnetic susceptibility, and molar conductance were used to characterize the ligand and Ru (III) complex. The Ru (III) complex is non-hygroscopic, solid, and colored. Phenolic anionic (O) functions as a bidentate ligand as a result of the ligand's coordination to the metal ion via azomethine (C=N). By taking into account electronic spectral analysis and magnetic susceptibility values, octahedral geometry has been proposed. Based on its molar conductivity statistics, it is non-electrolytic in nature. Both the ligand and metal complexes have been examined to understand their microbiological activity.

Keywords: Schiff base (DCPIMMP), octahedral geometry, spectra, bidentate and Microbiological activity

I. Introduction

Schiff base and its metal complex play key roles in the coordination chemistry ^[1]. Metal complexes of Schiff's base contain donor atoms like nitrogen and oxygen ^[2,3].

Chelating ligands with donor atoms like N, S, and O are catalytically and biologically active ^[4]. Metal cations at the microscopic level can be detected using Schiff base.

Green chemistry's microwave-assisted synthesis has advantages including less pollution, less cost, quicker reaction times, and ease of processing and handling. The microwave synthesis of metal complexes is shown in the research papers below ^[5,6,7,8].

In this paper, complex of Ru (III), with Schiff base 2-{(*E*)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP] have been synthesized by conventional & micro wave method. The ligand & Complex are characterized by electronic spectra, elemental analysis, molar conductance and IR spectroscopy to determine the mode of bonding and geometry. The microbiological activities of the ligand and its metal complex are also studied

II. Materials and methods

Analytical grade chemicals were employed in the present study and were procured from Loba Chemical. Borosil glassware was used.

ELICO-SL 159 spectrophotometer was available to take absorbance.

For measuring pH, an ELICO-LI 127 pH meter was used.

CHNO model element analyzer The Flash EA 1112 series was utilized to determine the percentage compositions of the ligand's constituents (CHNO) and its Ru(III) complex.

The metal was analyzed using ICPAES (Inductive coupled plasma atomic emission spectroscopy) in an Iris Intrepid II XSP type apparatus.

Perkin Elmer Spectrophotometer 8400 FTIR UV-Vis Spectrophotometer captured the vibration spectra (IR) of Schiff's base and Ruthenium complexes (KBr discs).

The electronic Spectrum of complexes was recorded using the ELICO SL -159.

The Electron spin resonance spectra were recorded using the E - 112 ESR Spectrometer. ELICO SL - 303 model conductometer was used to measure the molar conductivity.

A. CONVENTIONAL METHOD OF SYNTHESIS OF LIGAND 2-{(E)-[(2,4-DICHLOROPHENYL)IMINO] METHYL}-6-METHOXYPHENOL

2-Hydroxy-3-methoxybenzaldehyde (0.002 mole) and 2,4-Dichloroaniline (0.002 mole) were dissolved in absolute alcohol and were refluxed for 3 hours. Then the mixture was poured into a beaker and kept in the fridge overnight. The product was filtered, dried & crystallized^[10]. Orange colour crystals of Schiff's base, 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP] obtained. In the entire paper it is represented as L (Fig. 1)

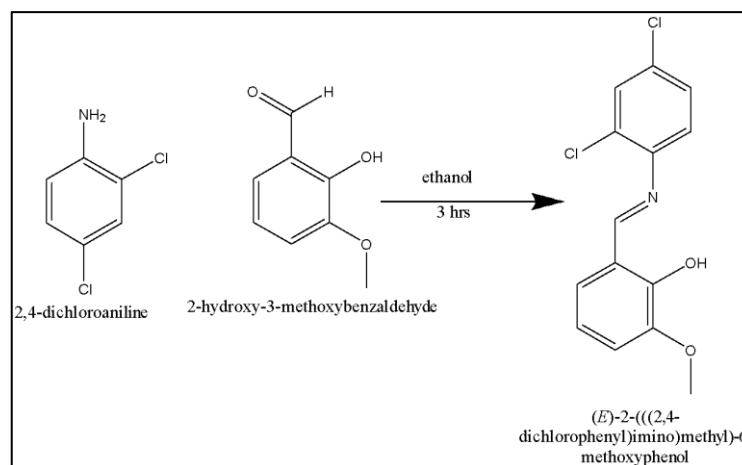


Figure 1: Preparation of Schiff's base

B. Green synthesis: preparation of schiff's base by microwave method.

A beaker containing 0.002 moles each of 2,4-Dichloroaniline and 2-Hydroxy-3-methoxybenzaldehyde was then microwave-irradiated at 180 °C for 0.40 minutes. Higher yields were produced in less time during the reaction. Schiff's base, 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol, was produced as brown crystals.

C. Preparation of Ruthenium complex by conventional method.

At pH 4.0 - 5.1, Ruthenium chloride and ligand (dissolved in ethanol) in a molar ratio of 1:3 was refluxed on a water bath for 3.5 hours. When cooled at room temperature dark brown colored complex separated which was filtered, washed with water and then with ethanol & recrystallized^[10].

D. Green synthesis: preparation of Ruthenium complex by microwave method.

In a 50-ml borosil beaker, the reaction mixture contained a 1:3 ratio of Ruthenium chloride and ligand, as well as 3–4 ml of dry ethanol. For 1.2 minutes, the reaction mixture was irradiated at 700 watts. The reaction was finished with better yields in two minutes. The resultant product was then recrystallized. Using silica gel G, TLC was used to monitor the reaction's development and the product's purity.

E. Biological Studies

Antibacterial screening aims to determine the susceptibility of the pathogenic microorganism to test whether the complex can be used as a therapeutic agent.

The stock solution of 2000 ppm of ligand and Ru(III) complex was prepared on active ingredient basis. It was kept at room temperature till it was used. Antimicrobial potency of ligand and its Ru(III) complex was investigated by Rup plate method. Sterile Sabourauds agar plates for fungus *Candida albican* and Sterile Mueller Hinton agar plates for bacterial test cultures were seeded with 1.0 ml of 24 hour old, 0.1 O.D. Rultures. Wells

were punched in the above media and compounds 50 μ l were added. Depending on their culture plates are incubated for 48 hours at 37°C / R.T. inhibited area around the wells were measured in millimeters.

III. Result & Discussion.

Ruthenium complex is colored, solid stable and non-hygroscopic at room temperature. The Analytical and physical data of ligand and their metal complexes are recorded in Table - I.

Compounds (Colour)	Molecular Weight	Reaction period & yield		M.P.	% Elemental Analysis Found (Calculated)						Λ_m Ohm-1 $\text{cm}^2\text{mol}^{-1}$
		Conventional methods	Micro synthesis		C	H	O	Cl	N	M	
DCPIMMP (orange)	296.15	3 hours 79%	0.4 Minutes 92%	138	56.70 (56.78)	3.79 (3.74)	10.76 (10.80)	23.96 (23.94)	4.78 (4.73)	-----	----
[DCPIMMP] ₃ Ru.H ₂ O (dark brown)	1004.50	3.5 hours 83%	3.1 Minutes 92%	127	50.10 (50.22)	3.23 (3.21)	11.08 (11.15)	21.25 (21.18)	4.25 (4.18)	10.09 (10.06)	6.00

Table - I The Analytical and physical data of ligand and Metal complexes

A. Infrared Spectral Analysis

IR was recorded with a Perkin Elmer FTIR -8400S Spectrometer (4000-400 cm^{-1}).

The most important conclusions based on infrared spectra bands of the Ligand DCPIMMP and complex [DCPIMMP]₃Ru.H₂O are tabulated in Table II, (figure 2 & figure 3)

Compound	ν phenolic (-OH) cm^{-1}	$\nu(\text{C-O})$ stretching cm^{-1}	$\nu(\text{C=N})$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	$\nu(\text{M-O})$ cm^{-1}
Ligand (Orange)	3312	1250	1612	----	-----
Ru L ₃ . H ₂ O Brown	3422 lattice water	1330	1600	470	430

Table-II: The Important IR bands of Ligand and Their Metal Complexes

A sharp band around 3312 cm^{-1} in IR of ligand reveals intramolecular hydrogen bonded -OH group^[11,12,13,] which is not seen in the spectra of Ru complexes inferring the dissociation of the phenolic proton on complexation and involvement of phenolic anionic oxygen in coordination.

In the IR spectrum of the ligand a band at 1612 cm^{-1} is due to C=N stretching of azomethine group^[12,14,15] has shifted to lower regions in IR of Ru (III) complexes at 1600 cm^{-1} which indicates the coordination of azomethine nitrogen to metal atom in complexes^[12,14]. The shifting suggests the donation of electron density from Nitrogen to metal.

The strong band at 1250 cm^{-1} due to C - O (phenolic) in the ligand has been shifted to the 1330 cm^{-1} in the spectra of Ru complex which reveals that the oxygen atom of this phenolic (C-O) group is bridged to the metal ions^[15].

No peak is depicted at region $400\text{-}500\text{ cm}^{-1}$ in the vibration spectra of ligands.

However, the complex reveals new peaks that arise at $400\text{-}500\text{ cm}^{-1}$. The band at 470 cm^{-1} is caused by stretching frequencies of (M-O) while the band at 430 cm^{-1} is caused by (M-N)^[12,14]. which suggests that the atoms of oxygen and nitrogen are engaged in coordination.

The IR spectrum of Ru(III) metal complexes exhibit a broad and strong absorption band in the region 3422 cm^{-1} confirms the presence of $\nu(\text{OH})$ absorption for lattice water^[12,15,16 esmada]

The strong absorption band due to methoxy group occurring at $1048\text{-}1049\text{ cm}^{-1}$ has remained at the same position in the complex showing no participation of oxygen atom of methoxy group in the complexation^[15].

Thus IR spectra proves that ligand behaves as {negatively} bidentate & coordinated to metal ion via azomethine (N) & phenolic, anionic(O).

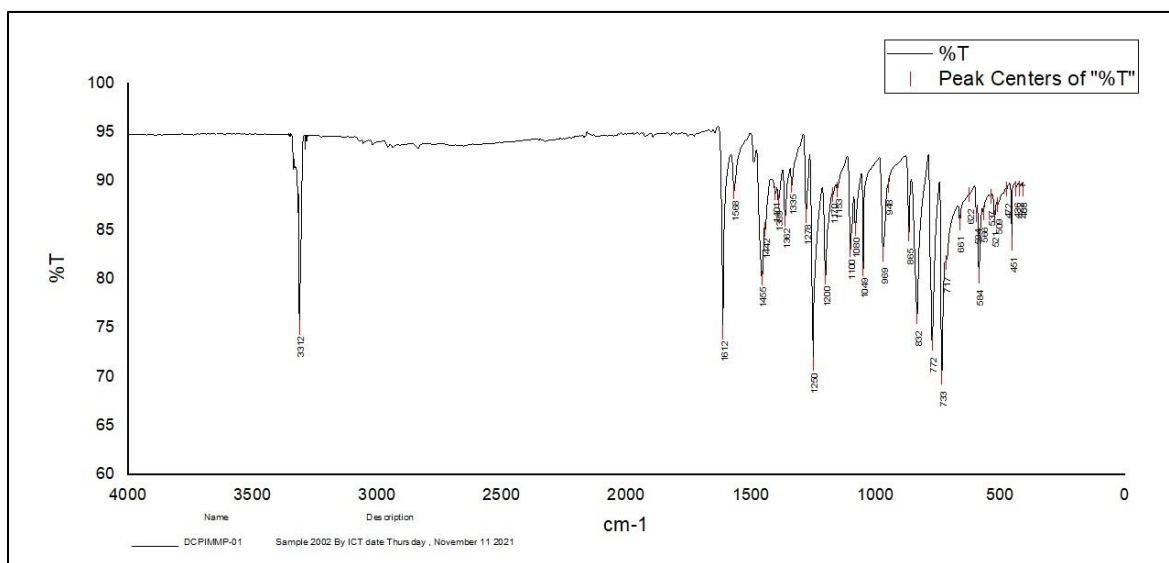


Figure 2: IR Spectra of ligand

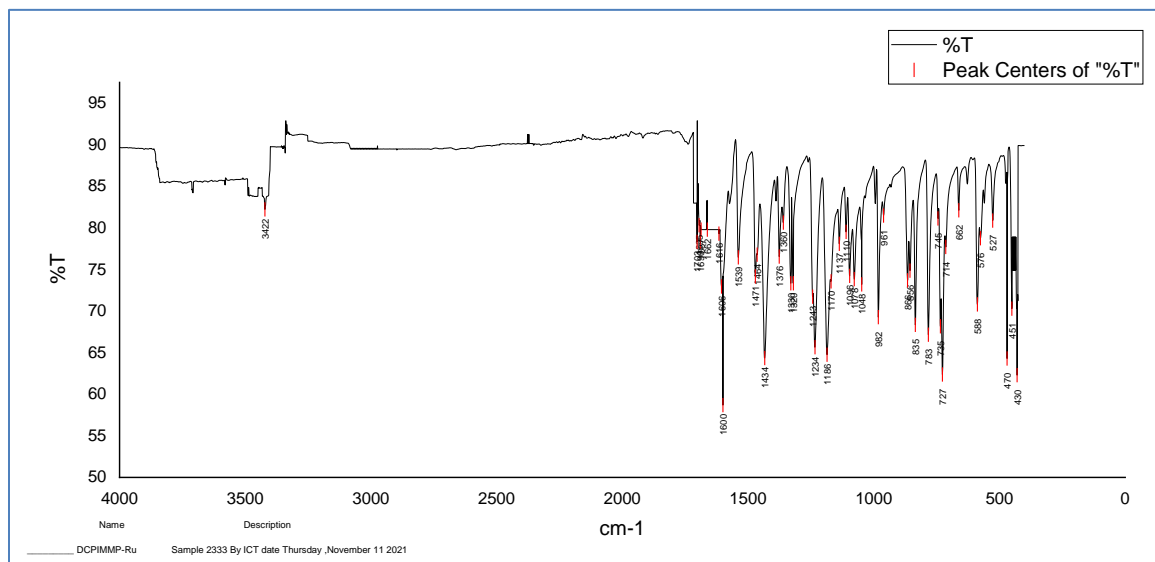


Figure 3: IR Spectra of Ru complex

B. Molar Conductance.

Ruthenium complex (1×10^{-3} M) in chloroform has molar conductance of (Λ_m) is $6.0 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. at room temperature. which inferred non - electrolytic nature. ^[15,17].

C. Electronic Spectra and Magnetic Susceptibility Measurements of Complexes

LABMAN-Visible Spectrophotometer is used to record electronic spectra as shown in Table III

Compound	Band, λ max (nm)	Band, λ max (cm^{-1})	Assignments	ν_2/ν_1	10 Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})
Ru L ₃ .H ₂ O (brown)	710	14084 $\nu \text{ cm}^{-1}$	${}^2T_{2g} \rightarrow {}^4T_{1g} (\nu_1)$	1.29	27227	512.25	5290
	550	18182 cm^{-1}	${}^2T_{2g} \rightarrow {}^4T_{2g} (\nu_2)$				
	440	22727 cm^{-1}	${}^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g} (\nu_3)$				

Table III: Electronic Spectra and Magnetic Moment of the Ru (III) Complex

The magnetic moments of Ru complexes fall in the range 1.97-2.08 , corresponding to a single unpaired electron in low-spin $4d^5$ configuration.

The magnetic moment value is 1.77 B.M which proves the octahedral Ru (III) complex ^[12,14,15] .

The electronic transition takes place in the UV-Visible electromagnetic region.

Octahedral geometry was suggested by the electronic spectra of the Ruthenium complex recorded in chloroform. The ground state of Ruthenium(III) is ${}^2T_{2g}$ and the first excited doublet levels in order of increasing energy are ${}^2A_{2g}$ and ${}^2T_{1g}$ which are known to arise from $t_{2g}^4 e_g$ configuration . The Ruthenium (III) complexes display electronic spectra with transition at 14084 cm^{-1} , 18182 cm^{-1} , and 22727 cm^{-1} which may be assigned to ${}^2T_{2g} \rightarrow {}^4T_{1g}$, ${}^2T_{2g} \rightarrow {}^4T_{2g}$, and ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$ in increasing order of energy. The B, C, and 10 Dq parameters were calculated using the following equations ^[12,14,17]

The B, C, and 10 Dq parameters were calculated using the following equations:

$${}^2T_{2g} (t^5) = 0,$$

$${}^4T_{1g} (t^4 e) = 10 Dq - 5B - 4C,$$

$${}^4T_{2g} (t^4 e) = 10 Dq + 3B - 4C,$$

$${}^2A_{2g}, {}^2T_{1g} (t^4 e) = 10 Dq - 2B - C.$$

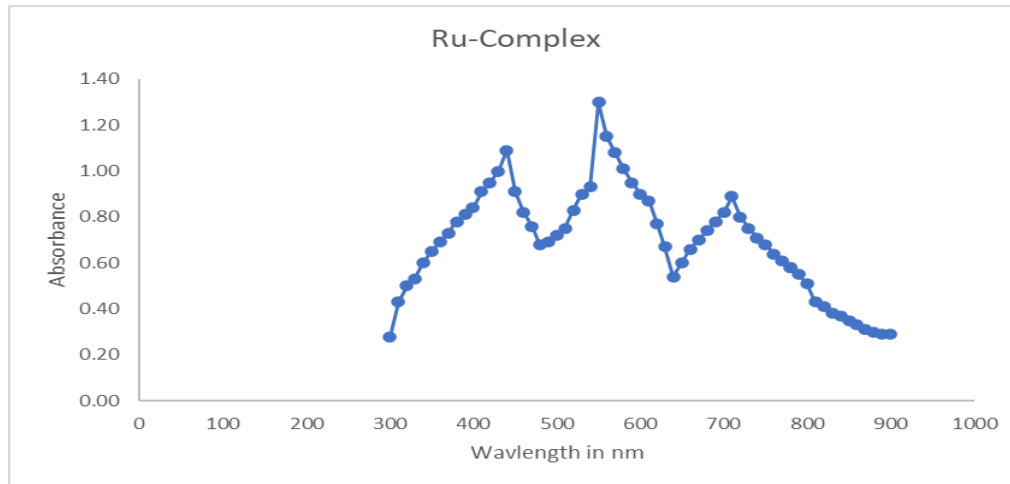


Figure 4 : Electronic Spectra of the Ru (III) Complex Figure

E Determination of Composition of the Extracted Species

Mole Ratio Method and Job's Continuous Variation Method prove the composition of the complex to be 1:3 (Ru: ligand)^[18]

Graph of Ru: DCPIMMP Job's Continuous Variation method is shown in Fig. 5.

Graph of Ru: DCPIMMP mole ratio method is shown in Fig. 6.

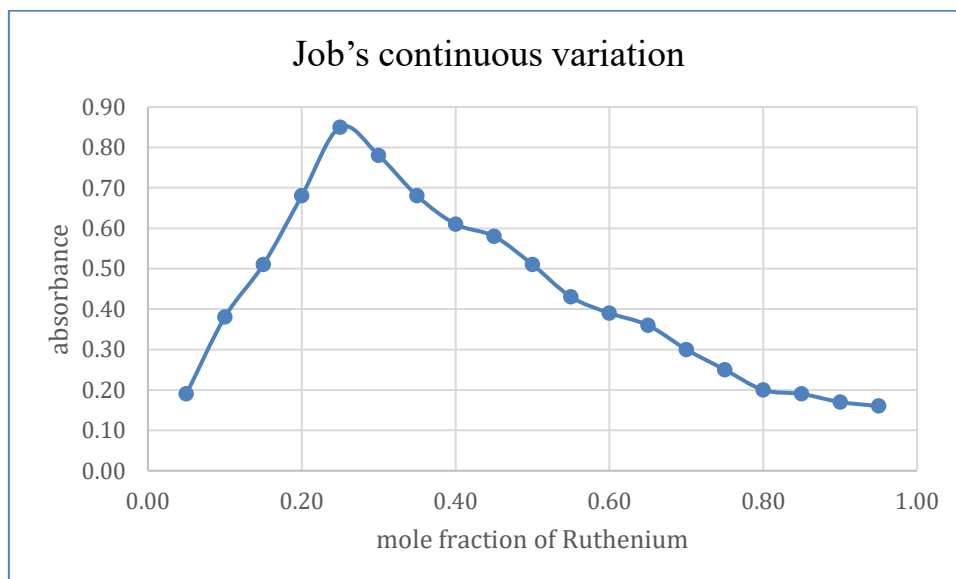


Figure 5: Ru: DCPIMMP Job's Continuous Variation method

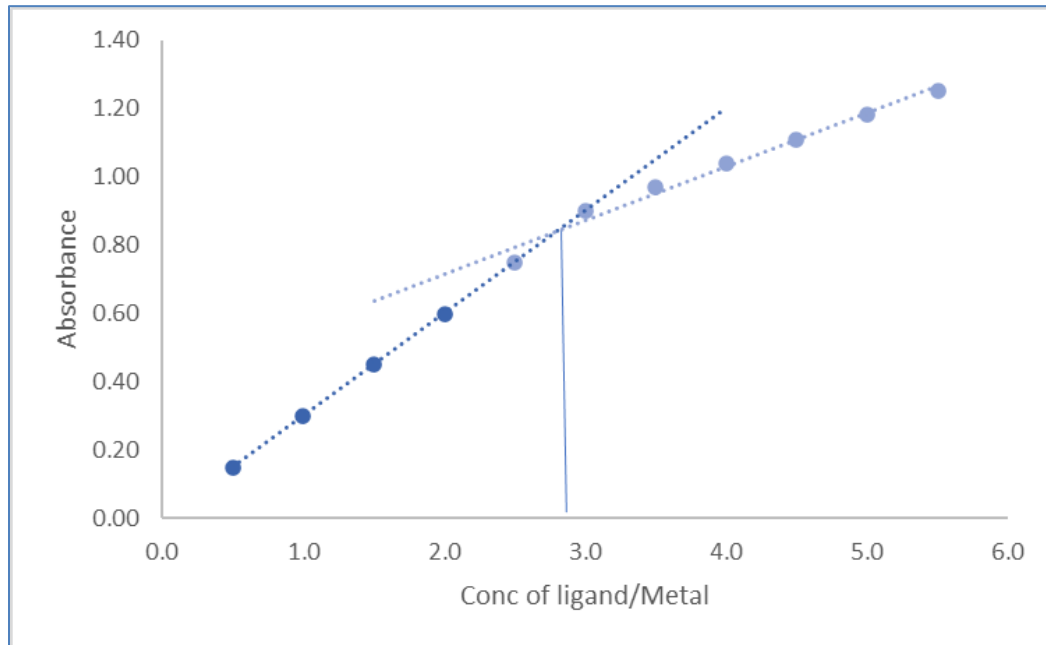


Figure 6: Ru: DCPIMMP by mole ratio method

F. Proposed Structure of Complex

Spectroscopic, magnetic, and analytical results suggested that the ligand forms stable complexes with Ru (III). According to experimental data, the complexes' likely structures can be demonstrated as (Fig.7)

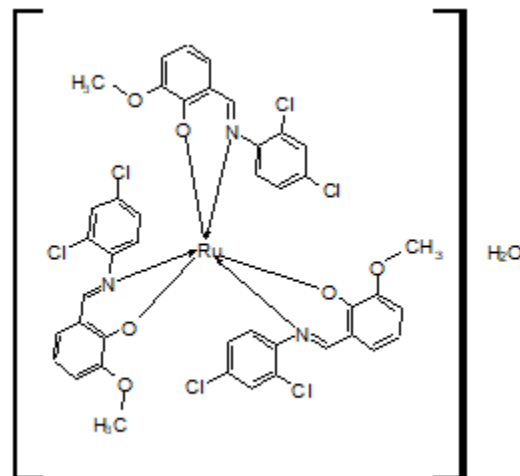


Fig : 7 Proposed Structure of Complexes

G. Biological Activity

Schiff base ligand DCPIMMP and its Ru complex were assessed for antibacterial potency by Cup plate method^[14,19,20,21] against “gram positive bacteria (staphylococcus aureus and corynebacterium diphtheria), gram negative bacteria (Escherichia coli and Klebsiella pneumonia)” and “antifungal activity against Candila albicans and aspergillus species”^[14].

According to data from table V (figure 8), metal chelates of the Ru(III) complex exhibit greater antibacterial and antifungal action than free ligands. Compared to ligands, metal chelates exhibit increased biological activity. Chelation theory and the idea of overtones can both be used to explain it.

The ligand orbitals overlap, and the metal ions' partial sharing of their positive charges with donor groups. The polarity of the metal ion is decreased by this chelation. The complex's lipophilicity was increased by the delocalization of electrons over the entire chelate ring, and as a result, the Ru complex penetrates lipid membranes more deeply and inhibits microbial enzyme activity^[14,19,20,21]. Metal complexes impair protein synthesis, which hinders the organism's ability to expand further and interferes with the respiration process of the cell. Depending on whether the microbe's cells are impermeable or whether its ribosomes differ, different complexes have varying degrees of action against various organisms^[14].

Complexes	Cultures					
	S.a	C.d.	E.c	K.p	C.a	Asp.
DCPIMMP	18	8	07	06	02	12
[DCPIMMP] ₃ Ru.H ₂ O	29	9	13	11	04	17

Table V: Inhibition zone of growth in millimeters

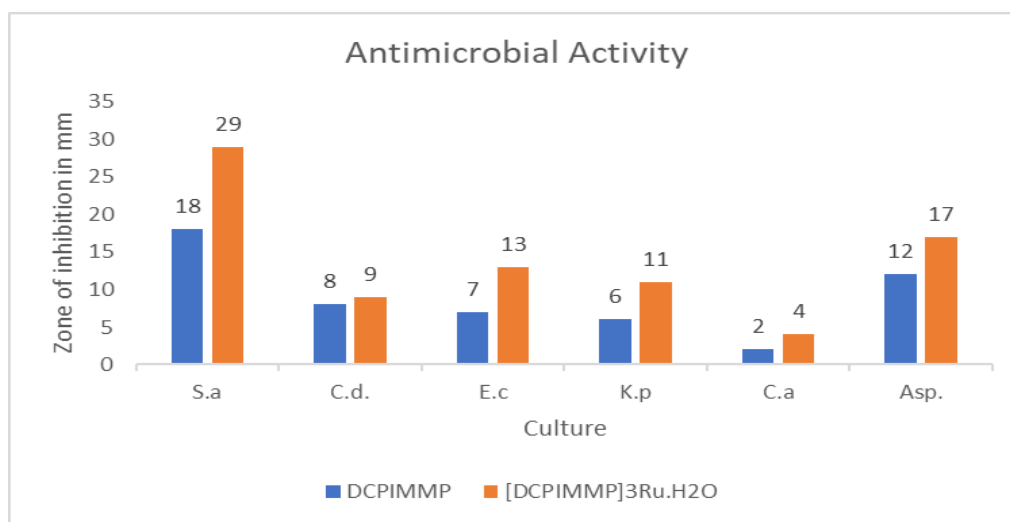


Figure 8: Graph showing zone of inhibition of growth in millimeters

IV. Conclusion.

According to the information from the study mentioned above, the Schiff base DCPIMMP 2- $\{(E)-[(2,4\text{-dichlorophenyl})\text{imino}]\text{methyl}\}$ -6-methoxyphenol exhibits bidentate complexing activity with metal Ru(III) ions. Complexes' analytical information and their molecular composition agree well. The behavior of the ligand, which is demonstrated by IR spectra, is that of a bi-negative, bidentate ligand coupled to the metal ion by azomethine (N) and phenolic anionic (O). According to elemental analysis and the job technique and mole ratio method, the

ratio of metal to ligand is 1:3. The results of the electronic spectrum and magnetic susceptibility experiments indicate that the structure of the binuclear Ru(III) complex with DCPIMMP is octahedral. Electronic spectra and its parameters reveals the covalent interaction between the metal and the ligand. The structure for the complex has been presented in light of the aforementioned evidence, and it fully accords with theoretical consideration (Fig.6). In comparison to the ligand, the metal complexes exhibit improved microbiological activity.

V. Acknowledgement

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