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Synthesis, Spectral Characterisation and MIC Evaluation of Schiff Base Ligands Derived from o-Vanillin

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ABSTRACT

The synthesis, characterization and Antimicrobial screening of Schiff base ligands 2-methoxy -6-((p-tolylimino) methyl phenol (L1), 2-((2- hydroxyl-3- methoxybenzylidene) amino) benzoic acid (L2) and 3-methoxy-4-((3-hydroxyphenylimino) methyl) phenol(L3) were discussed in this paper. The ligands were synthesized and it was characterized by Analytical data, melting point, IR, UV and 1H-NMR. The MIC evaluations of antimicrobial activity of the Schiff bases have been investigated and were recorded.

Keywords: Schiff base ligands, synthesis, IR, UV, MIC evaluation.

INTRODUCTION

In coordination chemistry a ligand is an ion or molecule that binds to a central metal atom to form a coordination complex [1,2]. Coordination compounds are having great impact and importance in biological system [3].

Schiff bases are aldehyde or ketone like compounds in which the carbonyl group is replaced by an imine or azomethine group. They are widely used for industrial purposes and also exhibit a broad range of biological activities [4].

Schiff base ligands have wide range of biological properties [5,6] and they are used in the fields of antitumor [7], antiviral [8], antifungal [9], antibacterial [10] and anti-inflammatory [11]. As biological models, they help in understanding the structure of biomolecules and biological processes occurring in living organisms. They are involved in the treatment of cancer drug resistance, and often tested as antimalarial [12].

Schiff base ligands may contain variety of substituents with different electron-donating or electron-withdrawing groups, and therefore may have interesting chemical properties. They have attracted the scientists due to the particular interest due to their biological activities [13-16].

(Figures 1-3) In this study we have synthesized the ligands L1: 2-methoxy -6-((p-tolylimino) methyl phenol from o-vanillin and p-toluidine, L2: 2-((2- hydroxyl-3- methoxybenzylidene) amino) benzoic acid from o-vanillin and 2-amino benzoic acid, and L3: 3-methoxy-4-((3-hydroxyphenylimino) methyl) phenol from o-vanillin and 3-aminophenol. The ligands were synthesized and it was characterized by Analytical data, IR, UV and1H-NMR. The MIC evaluation of antimicrobial activity of the Schiff bases has been investigated.

EXPERIMENTAL

Materials and methods

The synthesisof ligand L^1 is done by, Equimolar quantity of o-vanillin (0.002 mol, 2.1342 g) and p-toluidine (0.002 mol, 3.0430 g) dissolved separately in ethanol and were mixed in RB flask and refluxed for 3 hours over a water bath. The mixture was cooled and orange coloured compound is separated, filtered, washed with small amount of alcohol and then with distilled water and dried. Melting point was noted. (M.P=91°C; Yield=80%)

Similarly the ligand L^2 has been synthesized by mixing the equimolarquantity of o-vanillin (0.01 mole, 1.52 g) and 2-aminobenzoic acid (0.01 moles, 1.367 g) were dissolved separately in ethanol. The o-vanillin solution was added

drop wise. The above solution was magnetically stirred for about 1 h. The solvent was evaporated and cooled at room temperature, when brick red colored compound was separated out. It was washed with ether and recrystallized from ethanol. (M.P=99°C; yield=75%).

The synthesis of ligand L^3 is done by mixing of the equimolar quantity of o-vanillin (0.002 mole) and 3-aminophenol (0.002 mole) dissolved separately in ethanol are mixed in RB flask and heated under refluxed for 4 hours over a bath. The mixture is cooled and orange coloured compound is separated, filtered and washed with small amount of methanol and dried. Melting point was noted and purity was ascertained by TLC method (M.P=140°C; yield=84%)

The purity of the ligands checked by TLC method.

RESULTS AND DISCUSSION

The characteristic and analytical data of Schiff base ligands were given in the (**Table 1**). The ligands are soluble in DMSO and DMF whereas insoluble in ether.

Vibrational spectra

The vibrational spectra of the ligand (L^1) **(Figure 4)** shows a band at 1585 cm^{-1} corresponds to ν (>C=N-) [14] and another broad band at 3403 cm^{-1} which is the characteristic frequency of hydrogen bonded ν (O-H).

The vibrational spectra of the ligand (L^2) **(Figure 5)** shows a strong band at 1602 cm^{-1} is assigned to the overlap of ν (C=O) and ν (>C=N-) stretching frequencies. The ν_{C-O} (phenolic) stretching frequency of ligand is seen at 1450 cm^{-1} [15].

The vibrational spectra of the ligand (L^3) **(Figure 6)** shows a band at 1603 cm^{-1} corresponds to ν (>C=N-) and ν (>C=O) (phenolic) displayed at 1460 cm^{-1}. The broad band ranges from 3403- 3474 cm^{-1} which is the characteristic frequency of hydrogen bonded ν (O-H).

Electronic spectra

The electronic spectra of the ligands (L^1) (**Figure 7**), (L^2) (**Figure 8**) and (L^3) (**Figure 9**) were recorded in DMSO. The

Table 1: Physical characteristics and analytical data of Schiff bases.

S. No	Schiff base	Molecular Formula	Colour	% yield	Elemental analysis (%) found (Calculated)			Melting Point °C (Decomposition temperature)
					C	H	N	
1	Ligand(L^1)	$C_{15}H_{15}O_2N$	Orange	80	73.92 (74.68)	5.96 (6.22)	5.21 (5.80)	91
2	Ligand(L^2)	$C_{15}H_{13}O_4N$	Brick red	75	55.83 (56.07)	3.96 (4.07)	3.99 (4.36)	99
3	Ligand(L^3)	$C_{14}H_{13}O_3N$	Orange	84	68.89 (69.13)	5.17 (5.34)	5.63 (5.76)	140

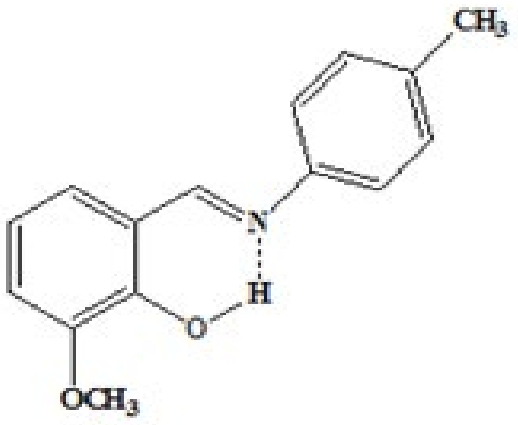

Figure 1: Structure of 2-methoxy-6-((p-tolylimino)methyl) phenol (L^1) .

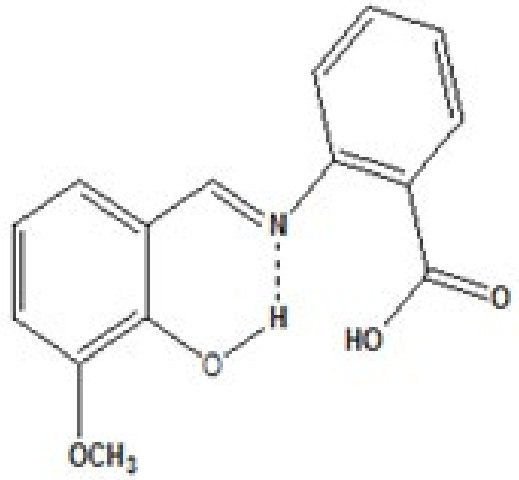

Figure 2: Structure of 2-((2-hydroxy-3-methoxybenzylidene) amino)benzoic acid (L^2).

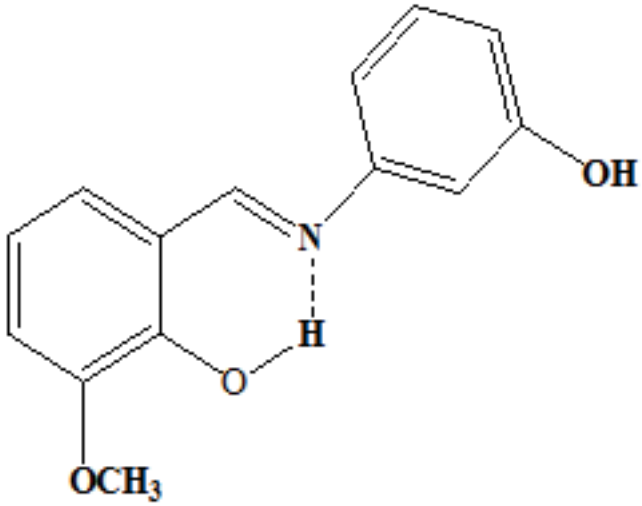

Figure 3: Structure of 3-methoxy-4-((3-hydroxyphenylimino) methyl) phenol (L^3).

spectrum of the ligand (L^1) shows two absorption maxima at 321.22 nm (35587 cm^{-1}) and 281.25 (31153 cm^{-1}) which may be assigned to π-π* and n-σ* transition respectively. The spectrum of the ligand (L^2) (**Figure 5**) shows three bands at 276 nm (36232 cm^{-1}), 315 nm (31746 cm^{-1}) and 356 nm (28090 cm^{-1}). The band at 36232 cm^{-1} suggesting the presence of π-π* transition [16]. The spectrum of the ligand (L^3) (**Figure 6**) is dark orange in colour shows 3 absorption bands at 210.38 nm, 228.48 nm, 310.22 nm at the frequency of 47431 cm^{-1}, 43767 cm^{-1} and 32235 cm^{-1} could be assigned to π-π* and n-σ* transitions are due aromatic part of ligands of azomethine linkage in the Schiff Bases.

^{1}H-NMR spectra

The 1H-NMR spectrum of the ligand (L^1) (**Figure 10**) shows a signal at δ 8.9 ppm suggesting the presence of –CH=N- linkage. The multiplet in the proton NMR spectrum which extends from δ 6.8 to 7.3 ppm corresponds to the seven protons of the aromatic ring [17].

The 1H-NMR spectrum of the ligand, (L^2) (**Figure 11**), shows a signal at δ 3.95 ppm and a strong signal at δ 11.13 ppm corresponding to $–OCH_3$ and hydroxyl group of –COOH group respectively, the peak at δ 9.92 ppm is attributed to phenolic –OH group present in the ligand, the signal at δ 8.85 ppm is assigned to (-CH=N-) proton and the signals

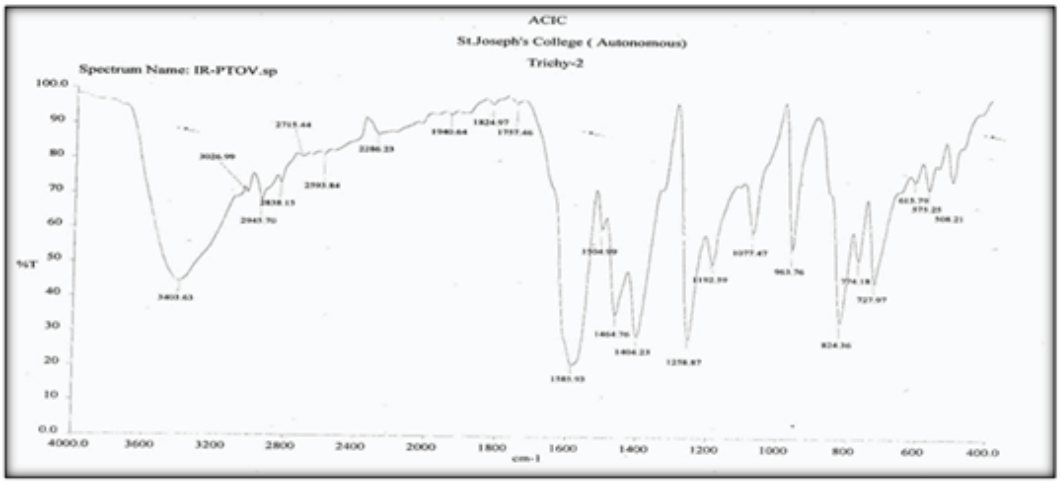

Figure 4: IR spectrum of L^1-2-methoxy-6-((p-tolylimino) methyl)phenol.

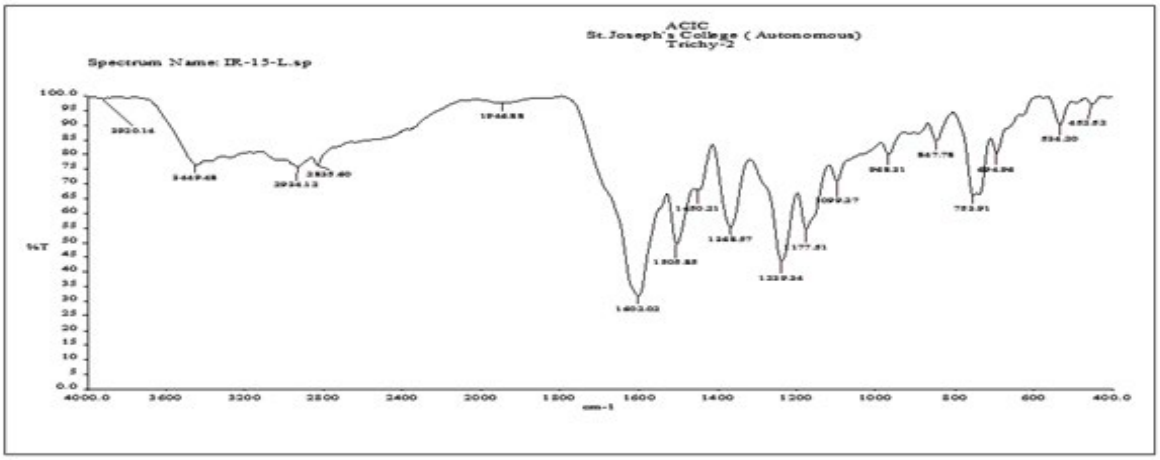

Figure 5: IR spectrum of L^2- 2-((2-hydroxy-3-methoxybenzilidene)amino)benzoic acid.

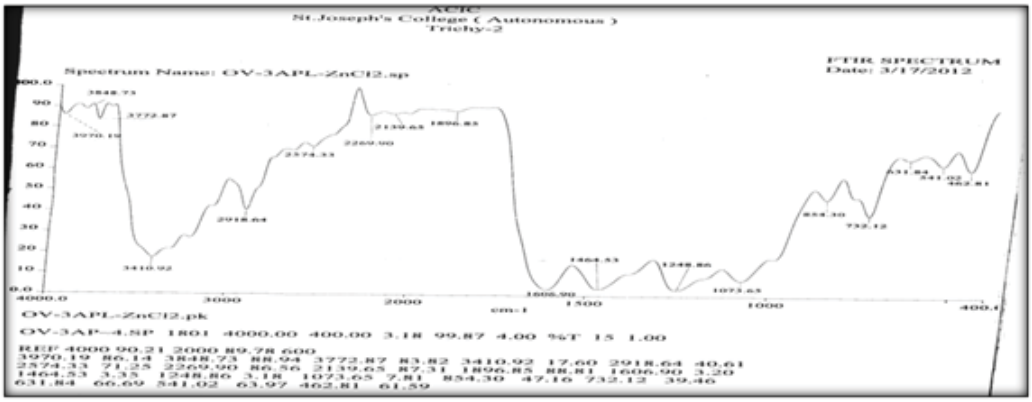

Figure 6: IR spectrum of L^3-3-methoxy4-((3-hydroxyphenylimino)methyl)phenol.

for the protons of the phenyl group attached to the ligand are observed in the range δ=6.67-7.94 corresponds to seven protons [18].

The spectrum of the ligand (L^3) (**Figure 12**) shows a signal at δ8.8 ppm a single peak suggesting the presence of –

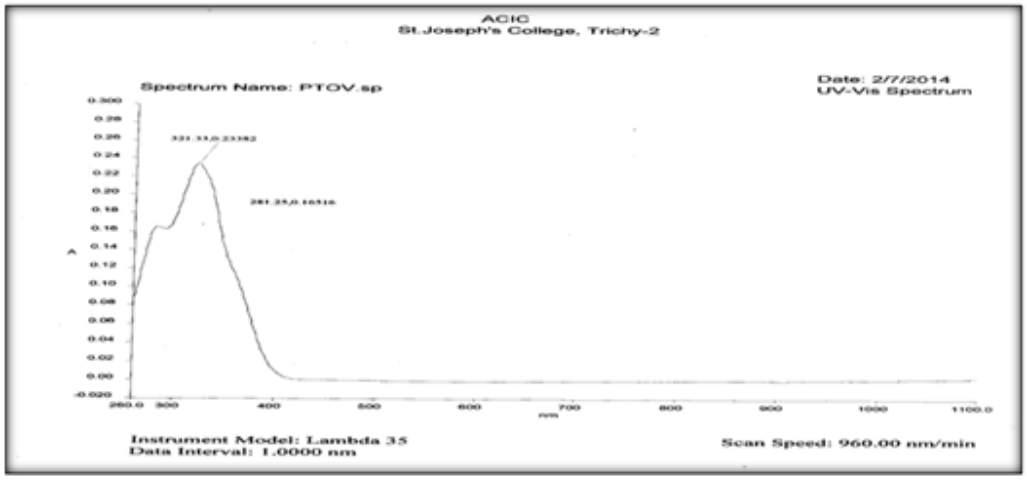

Figure 7: UV spectrum of L^1- 2-methoxy-6-((p-tolylimino) methyl)phenol.

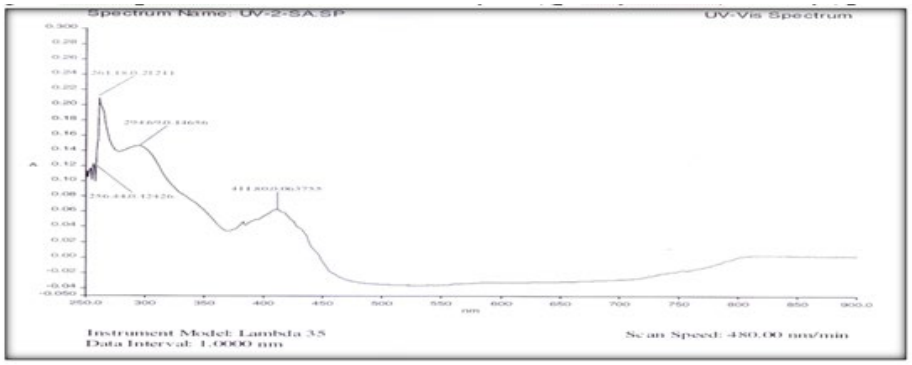

Figure 8: UV spectrum of L^2-2-((2-hydroxy-3-methoxybenzilidene)amino)benzoic acid.

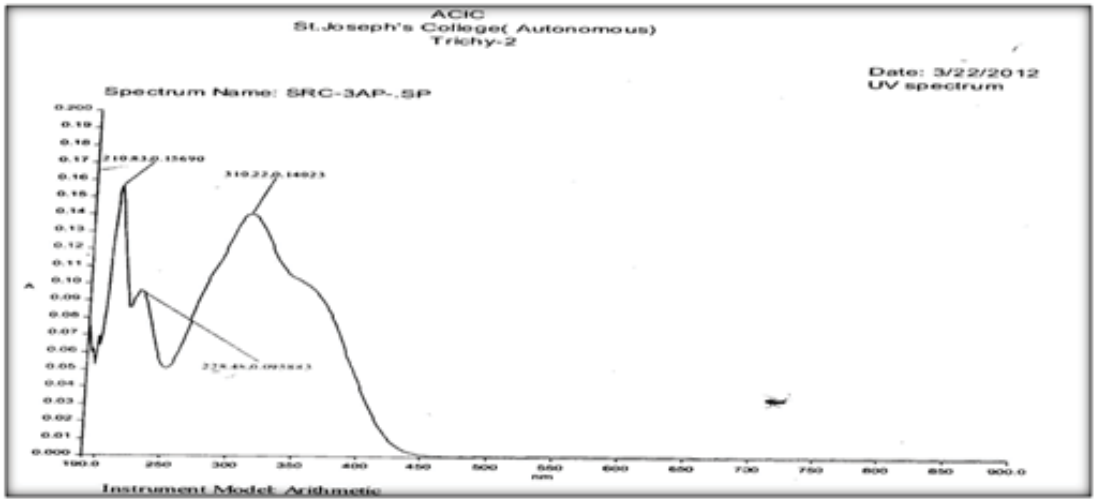

Figure 9: UVspectrum of L^3-3-methoxy4-((3-hydroxyphenylimino) methyl)phenol.

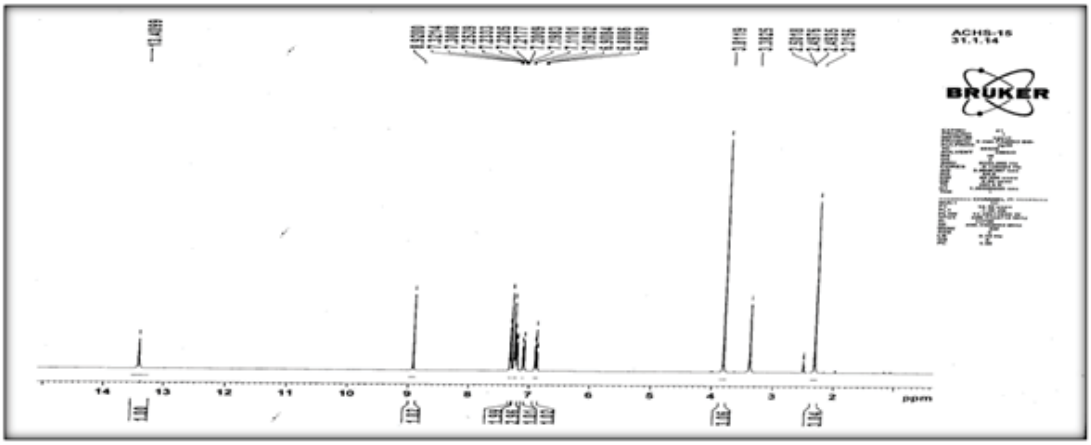

Figure 10: NMR spectrum of L^1- 2-methoxy-6-((p-tolylimino) methyl)phenol.

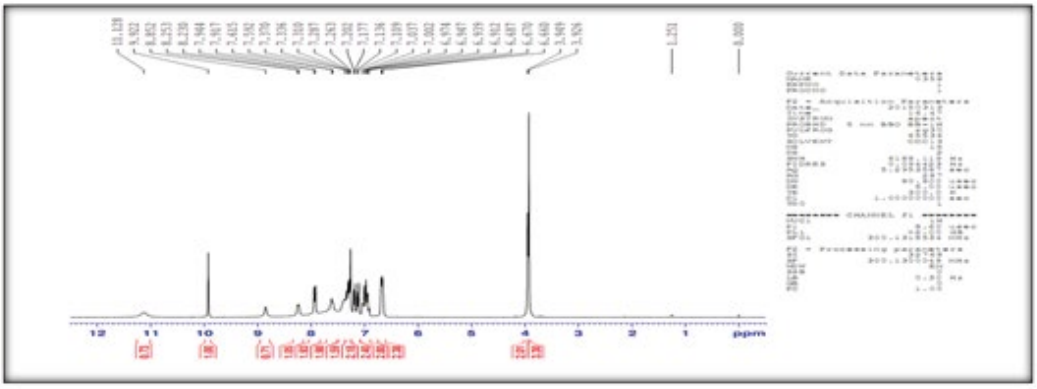

Figure 11: NMR spectrum of L^2- 2-((2-hydroxy-3-methoxybenzilidene)amino)benzoic acid.

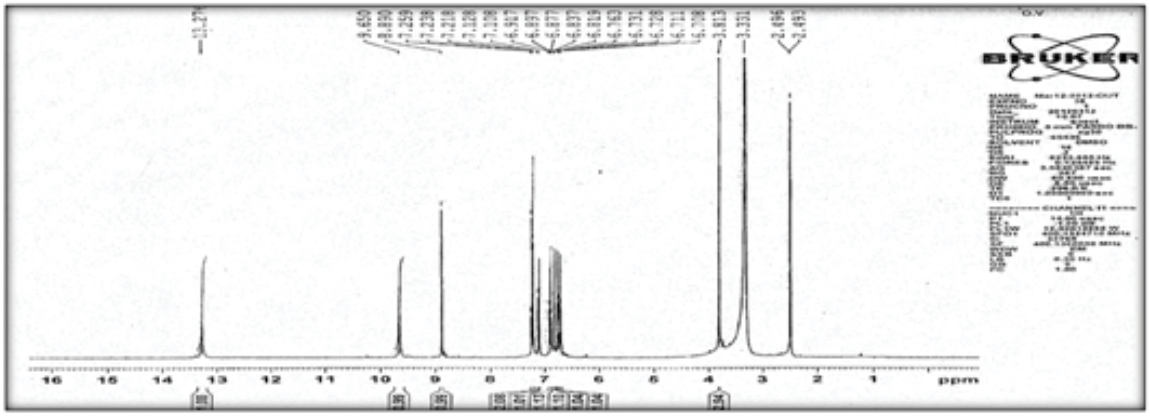

Figure 12: NMR spectrum of L^3-3-methoxy 4-((3-hydroxyphenylimino) methyl)phenol.

CH=N- linkage. The multiplet which extends from δ 6.7 to 7.3 ppm corresponds to the seven protons of the aromatic ring. The peak at δ 13.2 ppm indicates the hydroxyl proton.

Antifungal activities of the Schiff base ligands

Antifungal activity of the Schiff bases has been tested by disc diffusion technique [19]. The fungi *Aspergillus niger* is used to find out the antifungal activity [20]. The results were compared with standard drug Nystatin for the fungus. The new ligands showed remarkable biological activities against the fungus. The data obtained after preliminary antifungal

Figure 13: Antifungal activity of L^1 against *Aspergillus niger.*

Figure 14: Antifungal activity of L^2 against *Aspergillus niger***.**

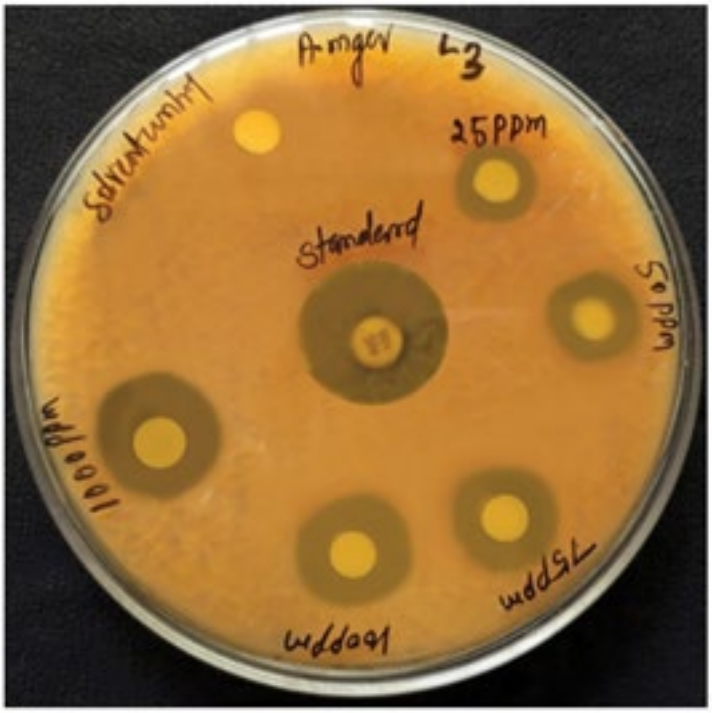

Figure 15: Antifungal activity of L^3 against *Aspergillus niger.*

Table 2: Activity of Schiff base ligands against *Aspergillus Niger*

S. No	Name of theligand	Activity against Aspergillusniger Standard=Nystatin
1	2-methoxy-6-((p-tolylimino)methyl)phenol (L^1)	++
2	2-((2-hydroxy-3-methoxybenzylidene) amino)benzoic acid (L^2)	++++
3	3-methoxy-4-((3-hydroxyphenylimino)methyl) phenol (L^3)	+++

screening showed that the following ligands were most active against *Aspergillus niger* (**Figures 13-15**).

Minimum inhibitory concentration

The three synthesized Schiff base ligands exhibited varying degree of Inhibitory effects (low to moderate) on *Aspergillus niger* and are tabulated in (**Table 2**). Even at low concentration, 75 ppm, 2-((2-hydroxy-3- methoxybenzylidene) amino) benzoic acid (L^2) and 4-((3-hydroxyphenylimino) methyl -3-Methoxyphenol (L^3) are active, whereas 2-methoxy -6-((p-tolylimino) methyl phenol (L^1) is moderately active at 100 ppm against *Aspergillus niger*.

CONCLUSION

Based on the above results the following conclusions are drawn, the ligands are acting as dibasic tridentate ligands. The melting points of the ligands are above 100°C, suggests that the three ligands are appreciably stable. After preliminary screening of synthesized ligands it is found that the three ligands are active against *Aspergillus niger*. So, Minimum Inhibitory Concentration was carried out. After the MIC evalution, it is found that the ligand L^2 has the highest activity than the other two ligands.

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