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A Comparative Study of Green and Conventional Synthesis of Schiff Base And its Metal Complexes from 3, 5-Dichloro Aniline And 3-Chloro-4 Fluroaniline

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Abstract

The new Schiff base ligand (E)-N-(3, 5-dichlorophenyl)-1-(3, 4-dimethoxyphenyl) methanimine (L1) was prepared through condensation reaction of 3,5-Dichloroaniline and 3-Chloro-4- Fluroaniline in 1:1 molar ratio using conventional and green method. The new ligand was characterised by elemental analysis and spectral techniques. The coordination behavior of a transition metal ions Ni(II) with the newly prepared schiff base is reported . The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analysis, FTIR, , 1H NMR, 13C NMR. Comparison between the two methods and the yield results prove that green method is more efficient and requires less reaction time than conventional method. The synthesized ligand and its complexes were screened for antimicrobial activities. The complexes were found to possess high biological activities against different organisms.

Keywords: *3-Chloro-4- Fluroaniline, 3,5-Dichloroaniline; In vitro antibacterial activity; Metal complexes*

1. Introduction

Schiff bases are indeed fascinating organic compounds with a Carbon – nitrogen double bond(imine functional group), where the nitrogen is typically attached to an aryl or alkyl group. They were first reported by Hugo Schiff in 1864, marking an important discovery in organic chemistry. Since then a variety of techniques for the synthesis of imines have been described. In common Schiff bases are products of condensation reactions between primary amines with ketones or aldehydes synthesized under specific condition.[1] Over the previous few decades, great research has been directed in the direction of the improvement of new applied sciences for environmentally benign procedures (green chemistry). A attainable approach beneath free-solvent is one of the modern green synthetic and environment friendly methodologies for Schiff bases that avoids the use of any kind of unsafe solution, waste of time and tiresome build-up processes. Adopting solvent -free, solvent minimized methodologies for the synthesis of Schiff bases aligns with the principles of green chemistry by reducing waste, improving efficiency and offering economic benefits. This approach is poised to become a cornerstone in modern synthetic chemistry, contributing to sustainable development and innovation in chemical processes.[2-4] Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (C=O) has been changed by using an

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imine or azomethine group. [3] A Schiff base or Schiff's base is a kind of chemical compounds containing a carbon-nitrogen double bond as functional group, the place the nitrogen atom related to aryl group or alkyl group (R) however no longer hydrogen. The Schiff base is synonymous with an azomethine.[5] The Schiff base complexes have been used in catalytic reactions and as models for biological systems. Chiral Schiff bases are derived from the condensation of salcylaldehyde with 2-amino alcohols have found widespread use as ligands in asymmetric synthesis. These compounds act as tridentate ligands, and a great number of metallic complexes derived from them have been described in the literature. Depending upon the nature of the metal centre, these chrial complexes are able to promote a variety of enantiomer selective transformations. [6]

2. Method

2.1.Conventional Method

Schiff bases are prepared by condensation of respective aldehyde and aromatic amine in equimolar concentrations (0.01 M). Ethanolic solution of aldehyde(10 ml) were added to an ethanolic solution of amine (10 ml). To this catalytic amounts of glacial acetic acid were added. The reaction mixture was refluxed for 6 hours. The progress of the reaction was monitored by TLC using n- hexane and ethyil aetate in ratio (3:2). After the refluxing obtained precipitate dried, weighed and recrystallized in ethanol. The melting point of the ligands were determined by open capillary method. The ligands were subjected to IR, ^{1}H NMR, ^{13}C NMR.[8]

2.2. Green synthesis

Schiff bases are prepared by condensation of respective aldehyde and aromatic amine in equimolar concentrations(0.01M).Ethanolic solution of aldehyde (10 ml) were added to an ethanolic solution of amine (10 ml). To this catalytic amounts of lemon juice were added.[6&7] The reaction mixture was refluxed for 4 hours. The progress of the reaction was monitored by TLC using n- hexane and ethyil aetate in ratio (3:2). After the refluxing obtained precipitate dried, weighed and recrystallized in ethanol. The melting point of the ligand were determined by open capillary method. The ligands were subjected to IR, ^{1}H NMR, ^{13}C NMR.[9]

Table 1 Physical Data of Schiff Base Through Green Synthesis

Compound	Melting Point (^{0}C)	Yield %	Time (hours)
L_1-$C_{15}H_{13}Cl_2NO_2$	90	92	6
L_3-$C_{13}H_8ClFN_2O_2$	128	80	6

Table 2 Physical Data of Schiff Base Through Conventional Method

Compound	Melting Point (^{0}C)	Yield %	Time (hours)
L_2-$C_{15}H_{13}Cl_2NO_2$	90	86	4
L_4-$C_{13}H_8ClFN_2O_2$	128	69	4

Table 3 Study of Antimicrobial Activity

Concentration	*Staphylococcus aureus*	
	Schiff base	Metal complex
10^{-1}	Inhibits Bacterial Growth	Inhibits Bacterial Growth
10^{-2}	ModerateBacterial growth	Inhibits Bacterial Growth
10^{-3}	Bacterial growth	Moderate Bacterial Growth
10^{-4}	Bacterial growth	Bacterial growth

2.3.Tables

Melting point of the Schiff base and metal complexes were noted and it was found that melting point of metal complexes were high compare to their ligands. The yied of the compound through green method is more efficient than the conventional method (Table 1 & Table 2).The antimicrobial activity Compared with the Schiff base its metal complex showed better antimicrobial activity at a concentration of 10^{-1}, 10^{-2} and 10^{-3} for *staphylococcus aureus*(Table 3).

2.4.Figures

The structures of synthesized Schiff base and metal complex compounds were confirmed on the basis of

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FTIR spectra, **^{1}H NMR** and **^{13}C NMR**. co-ordintion, shown in Figure 3 & Figure 4 [10].

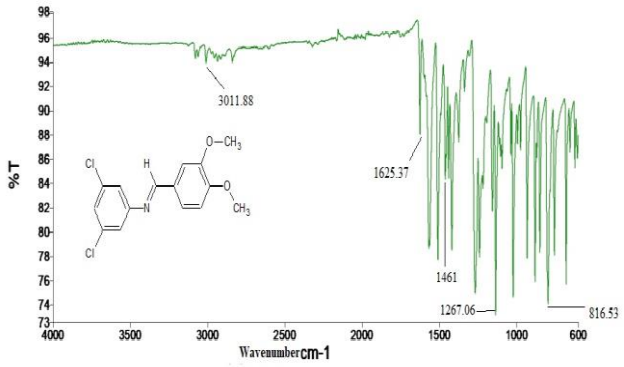

Figure 1 IR spectrum of (*E*)-*N*-(3, 5-dichlorophenyl)-1-(3, 4-dimethoxyphenyl) methanimine (L_1)

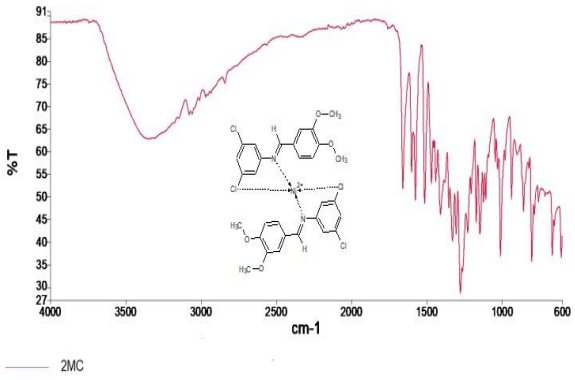

Figure 2 IR Spectra of [NiL_1] Cl.6H_2O

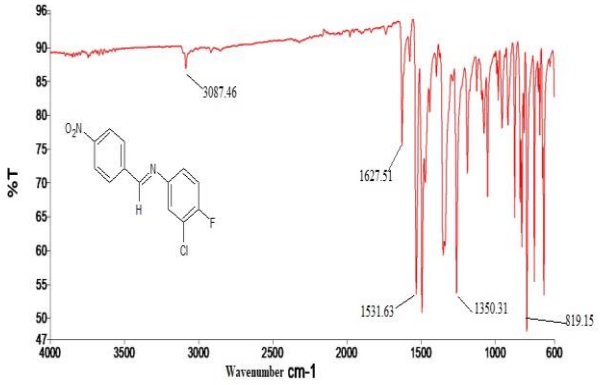

Figure 3 IR spectrum of (*E*)-*N*-(3, 5-dichlorophenyl)-1-(3,4-dimethoxyphenyl) methanimine (L_2)

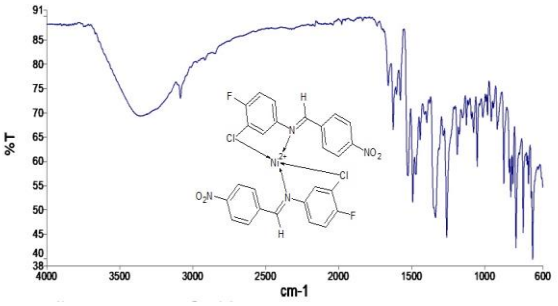

Figure 4 IR Spectra of [NiL_2] Cl.6H_2O

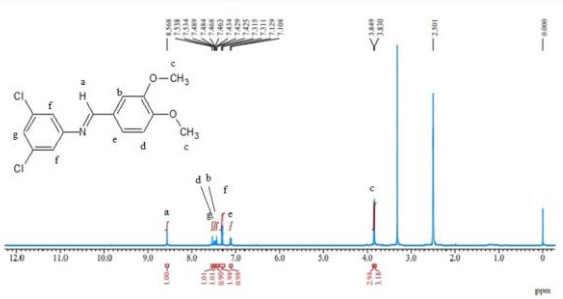

Figure 5 ^{1}H NMR spectrum of (*E*)-*N*-(3, 5-dichlorophenyl)-1-(3,4-dimethoxyphenyl) methanimine (L_1)

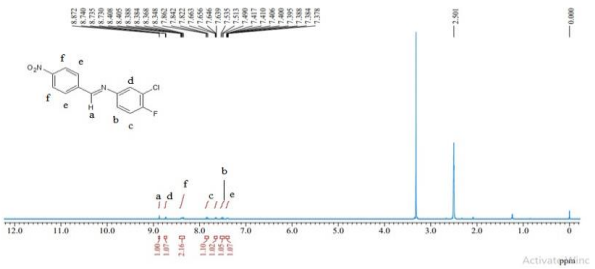

Figure 6 ^{1}H NMR spectrum of (*E*)-*N*-(3,5-dichlorophenyl)-1-(3,4-dimethoxyphenyl) methanimine (L_2)

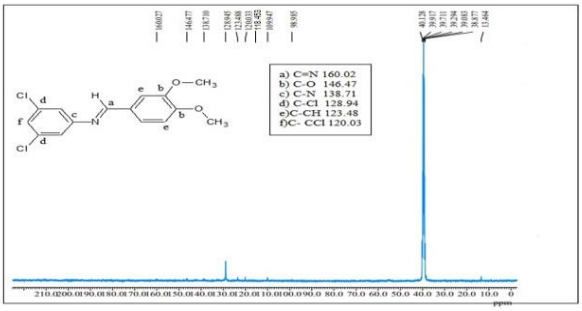

Figure 7 ^{13}C NMR Spectrum of (E)-N-(3, 5-dichlorophenyl)-1-(3,4-dimethoxyphenyl) methanimine (L1)

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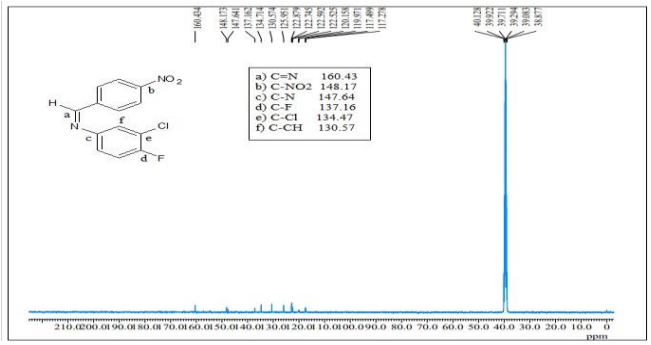

Figure 8 ^{13}C NMR spectrum of (*E*)-*N*-(3, 5-dichlorophenyl)-1-(3,4-dimethoxyphenyl) methanimine (L_3)

3. Results and Discussion

3.1.Results

A weak band at 1625cm^{-1}(Figure1) shows -CH=N region, a band at 3011.88 cm^{-1} indicating C-H stretching, a strong band at 1267.06cm^{-1} shows C-O of aryl ether and a strong band at 816cm^{-1} shows C-Cl. In the metal complex it shows at 1640cm^{-1}. The spectra of metal complex of Schiff base L_1 shows strong band at 1611 cm^{-1} region (Figure 2) and metal complex of Schiff base L_2 shows strong band at 1610 cm^{-1} which is characteristic to C=N group. ^{1}H NMR of Schiff base L_1 H_a δ 8.5684ppm (s, 1H,-CH=N), H_b δ 7.538 ppm(s, 1H), H_c δ 3.830 and 3.849 ppm(2s,6H,-OCH_3), H_d δ 7.464 ppm(d, 1H), H^e δ 7.108- 7.129(d,1H), H_f δ 7.109 and 7.129 ppm (2s,2H), H_g δ7.428(s,1H) in Figure 5. ^{1}H NMR of Schiff base L_3 H_aδ 8.872ppm (s,1H),H_bδ7.663(d,1H), H_c 7.862ppm (d,1H), H_d δ8.735ppm(s,1H), H_e δ 7.378ppm(m,2H), H_f δ 8.348ppm(m,2H) in Figure 6. The ^{13}C NMR spectrum of L_1 showed signals at δ 160.03ppm due to (C=N), at δ 146.48ppm for (C-O), at δ 138.770ppm for (C-N), at δ 128.94ppm for (C-Cl), at δ123.49ppm for aromatic carbon, at δ 120.30ppm for (C-CCl). (Figure 7). The ^{13}C NMR spectrum of L_2 showed signals at δ 160.43ppm due to (C=N), at δ 146.17ppm for (C-N), at δ 137.16ppm for (C-F) and at δ 122.59ppm for (C-CH) for aromatic carbon.(Figure 8).Antimicrobial activity studied,Sample from(*E*)-*N*-(3,5-dichlorophenyl)-1-(3,4-dimethoxy phenyl)methanimine(L_1,L_3)and its metal complex were carried out using bacteria *staphylococcus aureus.* by disc diffusion method. [11&12] The results were obtained showed in Table 3.

3.2.Discussion

A weak band at 1625cm^{-1} and shows 1627cm^{-1} (Fig 1A and Fig 1C) -CH=N region. In the metal complex it shows at 1611cm^{-1} and 1610cm^{-1} ^{1} (Fig 1B and Fig 1D) respectively. There is a shift in the band to about 14cm^{-1}which is due to nitrogen of azomethine metal coordination. A singlet peak at δ 8.5684ppm and δ 8.872 ppm in ^{1} H NMR spectrum of compound L_1 and L_2 respectively corresponds to the H_a proton attached to the azomethine carbon it is desheilded due to the presence of double bond and aromatic ring. A singlet at δ 8.735 ppm for the proton present in between chlorine and nitrogen. The signal at δ 160.03 ppm and δ 160.43 ppm in the ^{13}C NMR spectrum of compound L_1 and L_3 respectively is indicative of a carbon atom directly bonded to a nitrogen atom in a carbon-nitrogen double bond, specifically a C=N group. In organic molecules, this chemical shift typically corresponds to the carbon atom in the imine functional group, where carbon is double-bonded to nitrogen. The antimicrobial activity of the Schiff base and its metal complex was evaluated against *Staphylococcus aureus* at concentrations of 10^{-1}, 10^{-2}, and 10^{-3}. It was observed that the metal complex exhibited significantly enhanced antimicrobial activity compared to the Schiff base at all tested concentrations. This improvement suggests that the incorporation of the metal ion into the Schiff base framework enhances its ability to inhibit the growth of *Staphylococcus aureus*. Such findings highlight the potential of Schiff base metal complexes as promising antimicrobial agents.

Conclusion

In conclusion, the study demonstrated the successful synthesis of Schiff bases using both conventional and green methods. The green method was found to be more efficient based on higher yields and potentially lower environmental impact. Furthermore, the metal complexes of Schiff bases exhibited enhanced antimicrobial activity compared to the Schiff bases themselves, suggesting their potential application as antimicrobial agents. This structured approach helps

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to clearly present the experimental findings, their implications, and potential avenues for future research in the field of Schiff bases and their metal complexes.

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