

Proceeding Paper

Synthesis, Characterization, and Catalytic Applications of Schiff-Base Metal Complexes [†]

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Abstract: The ligand named 1-(3-chlorophenyl)-N-(pyridine-2-yl)methanimine Schiff base was obtained with the method of mixing 2-amino pyridine with 3-chloro benzaldehyde in methanol as an initial material. Transition metals, like Cu(II), were added to the prepared ligand as a dopant. The molecular structure was characterized by elemental analysis, electronic methods (UV-Visible), Vibrational methods (FT-IR), and ¹H NMR spectroscopy. The catalytic activities of the complex were studied using Claisen–Schmidt condensation for the synthesis of chalcone derivatives employed using three different catalysts by an ultrasonication method. The results reveal that the Cu(II) complex showed remarkable catalytic activity and good yield compared to the other catalysts.

Keywords: catalysis; condensation; Schiff-base complexes; transition metals



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1. Introduction

Ligands are of great importance, and Schiff bases in particular have a significant role to play in coordination chemistry and coordinate with metal ions through azomethine nitrogen [1]. Metal complexes are prepared by the condensation reaction between aldehydes and amines with various transition metals. Despite extensive research in this area, these compounds remain highly relevant and interesting in the field of inorganic chemistry [2–4]. These compounds have been studied in a comprehensive way due to their remarkable chemical characteristics and their potential applications in diverse fields. Their relatively easy synthesis also adds to their appeal as research leads [5–10].

Schiff-base ligands have gained substantial attention in the coordination chemistry field owing to their simple synthesis, accessibility, and electrical characteristics. They have also been the focus of recent attention due to their importance in various fields [11]. They find extensive use in the catalysis and pharmaceutical industries [12,13].

This study intended to prepare metal complexes of Cu(II) with the Schiff bases obtained from 2-amino pyridine and 3-Chloro benzaldehyde. The prepared ligands and their metal complexes were evaluated using various analytical techniques like elemental analysis, electronic spectra, IR, and ¹H NMR spectroscopic studies. Finally, we observed the synthesized complexes to be promising candidates to catalyze Claisen–Schmidt condensation for the synthesis of chalcone derivatives (bioactive substances) with good yield.

2. Experimental Methods

2.1. Materials and Methods

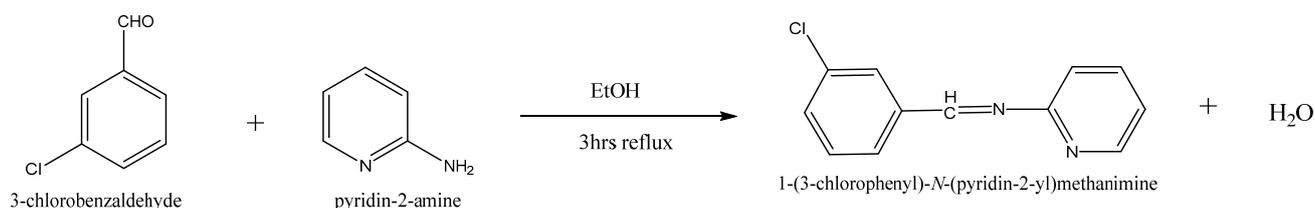
Highly pure chemicals of analytical reagent grade (AR) were utilized. They included 2-amino pyridine (Sigma-Aldrich, Chennai, India), 3-Chloro benzaldehyde (Sigma-Aldrich, Chennai, India), and $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, Chennai, India). Throughout the experiment, double-distilled water was utilized.

2.2. Instruments

An Elementar Vario EL III analyzer was utilized to conduct chemical analyses on carbon, hydrogen, nitrogen, and chlorine elements. KBr discs were used to record FT-IR spectra on a Perkin-Elmer 1650 spectrometer, New York, NY, USA within the range of $4000\text{--}400\text{ cm}^{-1}$. The ^1H NMR spectra were obtained using TMS as an internal standard and recorded using a 300 MHz Varian-Oxford Mercury instrument Palo Alto, CA, USA as a solution in DMSO-d_6 . The UV-Visible spectra were recorded in the range of $200\text{--}1000\text{ nm}$ on a JASCO V770 spectrometer, Easton, PA, USA.

2.3. Synthesis of Schiff-Base Ligand—1-(3-Chlorophenyl)-N-(pyridine-2-yl)methanimine [CPPM]

Equimolar concentrations of 2-amino pyridine (0.05 mol, 4.70 g) with 3-Chloro benzaldehyde (0.05 mol, 5.66 mL) in ethanol were used as a solvent. Glacial acetic acid (2 drops) was introduced to the content. The same was warmed up to room temperature and then agitated for approximately 4 h under reflux. A pale yellowish solid compound was isolated after cooling. After filtering the precipitate and washing it with ice-cold water, the residue was recondensed from methanol. The new compound was synthesized by the method summarized in Scheme 1.



Scheme 1. Synthesis of Schiff-base ligand (CPPM).

2.4. Synthesis of Schiff-Base Metal Complexes

The preparation of the metal complexes was performed through the addition of the appropriate metal sulphate, CuSO_4 (0.5 g, 0.002 mol), in water to the solution of the ligand (1 g, 0.004 mol) in a mixture of ethanol and a drop of glacial acetic acid was introduced to the content. The resultant mixture was agitated under reflux for five hours. A bluish-green metal complex was obtained after filtering and subsequent washing, followed by drying.

3. Results and Discussion

3.1. Elemental Analysis

Table 1 contains information regarding the ligand and its metal complexes, including information obtained from analysis and specific physical characteristics. The metal complexes had distinct colors and were not prone to absorbing moisture. Based on the analysis, the metal complexes exhibited a 2:1 ratio of ligand to metal. The observed percentages of carbon, hydrogen, nitrogen, and metal ion aligned well with the values expected, confirming the proposed structural formula, $[\text{M}(\text{CPPM})_2]$, where CPPM is 1-(3-chlorophenyl)-N-(pyridine-2-yl)methanimine.

3.2. Electronic Spectral Study

Figure 1 shows the absorption spectra of the ligand 1-(3-chlorophenyl)-N-(pyridine-2-yl)methanimine and exhibits characteristic bands at 212.63, 231.27, and 311.67 nm. The absorption bands at 212.63 and 231.27 nm correspond to the $\pi\text{--}\pi^*$ transition, while the peak

at 311.67 nm indicates the appearance of the $n-\pi^*$ transition. The changes in electronic energy levels suggest that the ligand contains an azomethine group [14,15]. Figure 2 shows the absorption spectra of the complex and it is noted that the copper complexes exhibit a distinct absorption band between 276.68 and 313.77 nm, which indicates the formation of a complex ion. Data pertaining to the spectral properties are given in Table 2.

Table 1. Elemental analysis data of the ligand (CPPM) and its corresponding metal complexes.

Compound	Empirical Formula	Color and Yield	M.Wt.	Analytical Data (%)				
				C	H	N	Cl	M
CPPM	C ₁₂ H ₉ ClN ₂	Pale yellow (72%)	216	66.5	4.2	12.9	16.4	—
Cu(CPPM) ₂ ·H ₂ O	C ₂₅ H ₂₃ Cl ₂ CuN ₄	Bluish-green (78%)	510.55	58.4	4.5	10.9	13.8	12.36

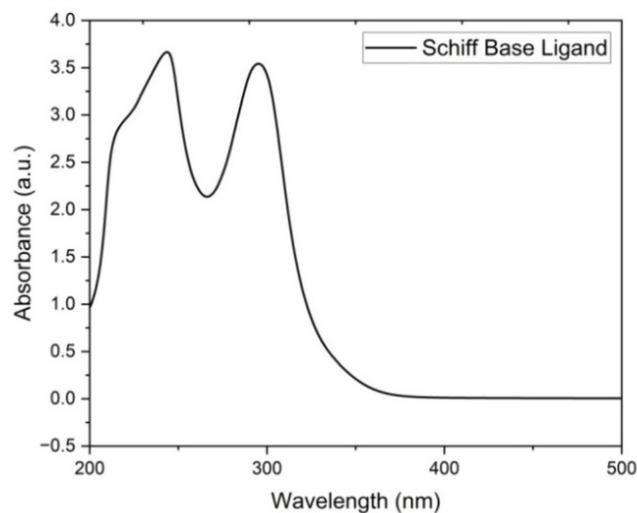


Figure 1. Electronic spectrum of Schiff-base ligand 1-(3-chlorophenyl)-N-(pyridine-2-yl)methanimine.

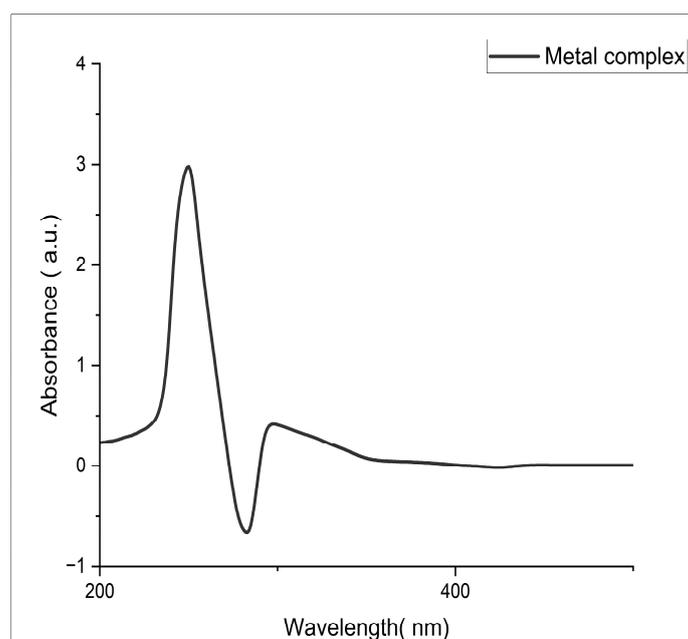


Figure 2. Electronic spectrum of Schiff-base Cu(II) complex.

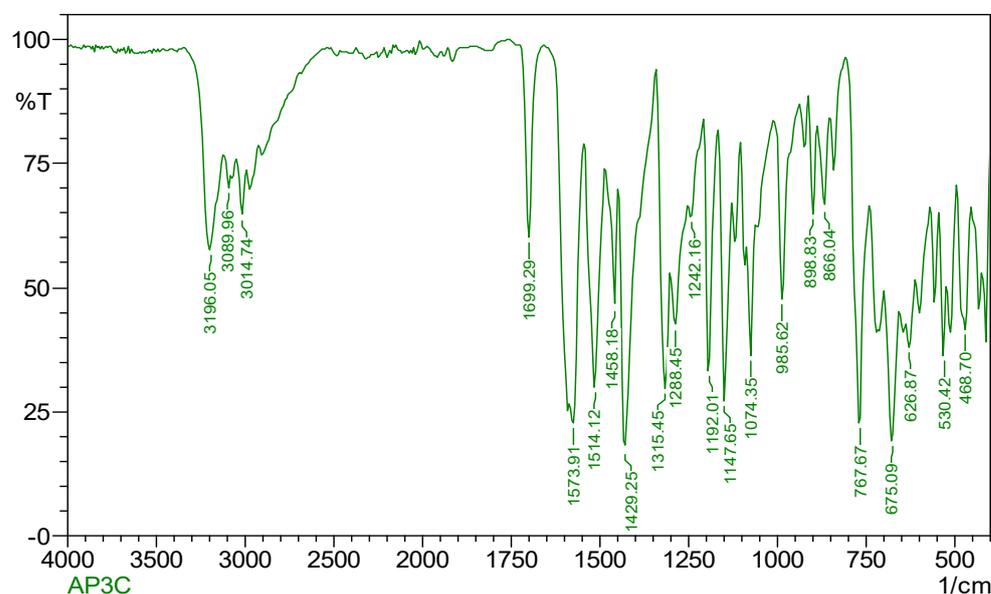
Table 2. Electronic spectral data of Schiff-base ligand (CPPM) and its corresponding metal complexes.

Compound	Absorption, λ_{\max}	Band Assignments
Schiff-base ligand—CPPM	212.63, 231.27, 311.67	$\pi-\pi^*$, $n-\pi^*$
$\text{Cu}(\text{CPPM})_2\text{H}_2\text{O}$	311.67	$n-\pi^*$

Where, CPPM is 1-(3-chlorophenyl)-N-(pyridine-2-yl)methanimine.

3.3. IR Spectroscopic Study

Figure 3 indicates the IR spectra of the ligand (CPPM) which shows a moderately intense band at 1699 cm^{-1} and it is ascribed to the $\nu(\text{C}=\text{N})$ vibration of the azomethine group [16]. A band in the 1434 cm^{-1} region shows the occurrence of an aromatic ring, while in Schiff-base complexes, its presence is confirmed by a band appearing in the 1667 cm^{-1} region, which corresponds to the $\nu(\text{C}=\text{N})$ band. IR spectral data of Cu(II) complex of the ligand CPPM are given in Table 3.

**Figure 3.** IR spectrum of Schiff--base ligand.**Table 3.** IR spectral data of ligand (CPPM) and its corresponding complexes (cm^{-1}).

Compound	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{Cl})$	$\nu_{\text{Ar}}(\text{C}-\text{H})$	$\nu(\text{N}-\text{C})$	$\nu(\text{M}-\text{N})$
Schiff-base ligand CPPM	1514.12	1699	767.67	3089	866.04	-
$\text{Cu}(\text{CPPM})_2\text{H}_2\text{O}$	1523.31	1667	760.14	3011.72	852.67	530.42

3.4. ^1H NMR Spectral Analysis

The presence of the azomethine proton was indicated by two peaks in the 8.2–8.8 ppm range. A series of multiplets between 6.58 and 7.7 ppm was attributed to the aromatic protons. The results align with conclusions derived from the analysis of the IR spectrum (Figure 4).

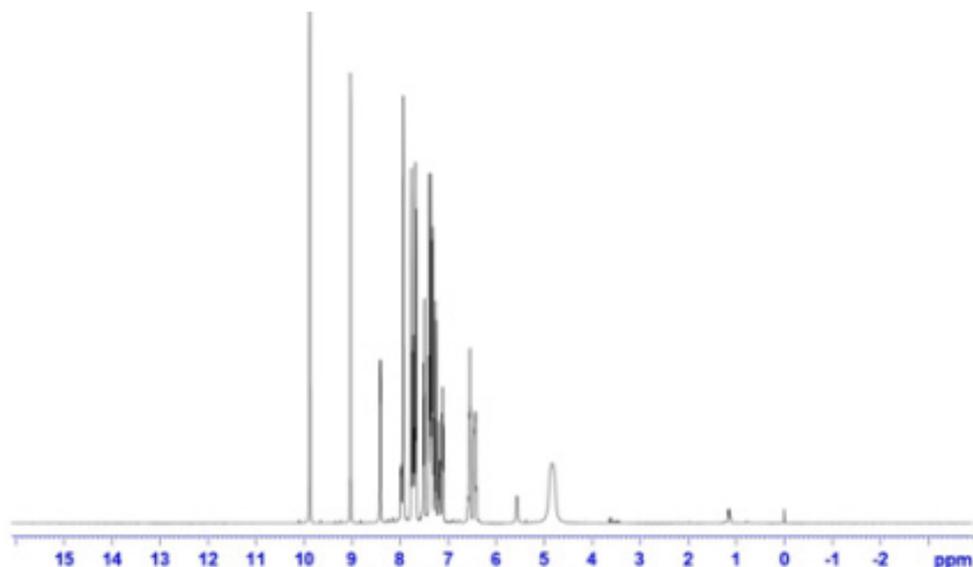


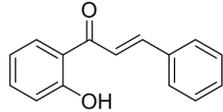
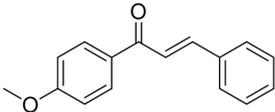
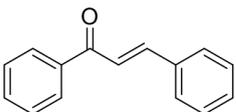
Figure 4. ^1H NMR spectrum of Schiff-base ligand.

4. Catalytic Studies

In this study, Claisen–Schmidt condensation was used for the synthesis of chalcone derivatives. The condensation of various aldehydes (Benzaldehyde (0.00942 mol), Salicylaldehyde (0.00819 mol), and Anisaldehyde (0.00734 mol)) was treated with acetophenone in the presence of three different catalysts, including KOH (0.000178 mol), *p*-Toluene sulphonic acid (PTSA) (0.00005807 mol), and the metal complex (1.959 mol). The same was sonicated for 60 min in an ultrasonic cleaner water bath at 70 °C. The contents were subsequently cooled, filtered, and dried, followed by recrystallization from alcohol to produce chalcone.

Table 4 demonstrates that chalcones were successfully synthesized with a high yield by condensing acetophenone with various types of aromatic aldehydes under ultrasound irradiation at 70 °C for 60 min, with a metal complex acting as a catalyst. The results of this method were compared to those of two other catalysts. The current method resulted in a greater product yield and shorter reaction time when compared to previously reported procedures [17–20] in the literature. From the above data, it is evident that Schiff-base metal complexes were used as efficient catalysts with an appreciable yield of >90%.

Table 4. Reaction of various aldehydes with acetophenone in the presence of different catalysts.

Compound Name	Catalyst	Product	Yield (%)
1. Salicylaldehyde	KOH		87
	PTSA		67
	Metal Complex		95
2. Anisaldehyde	KOH		56
	PTSA		78
	Metal Complex		90
3. Benzaldehyde	KOH		88
	PTSA		82
	Metal Complex		98

The physicochemical and IR data of synthesized compounds catalyzed by the Cu (II) complex are shown in Table 5.

Table 5. Physicochemical and IR data of synthesized compounds catalyzed by Cu (II) complex.

Comp. No.	Compound Name	Melting Point (K)	Yield (%)	IR
1	C ₁₅ H ₁₂ O ₂ (E)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one	467.72	95%	1647.54(C=O), 1588.76(C=C), 3034.54 (aromatic C-H), 3210.01(C=C-H), 3321.89 (OH)
2	C ₁₆ H ₁₄ O ₂ (E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one	402.02	90%	2660.90(C=C stretch), 3300(C=C-H stretch), 1767.54(C=O), 1112.10(C-O-C), 3089.96(C-H aromatic)
3	C ₁₅ H ₁₂ O (E)-Chalcone	356	98%	1576.21(C=C), 1675.32(C=O), 3056.46(aromatic C-H)

5. Conclusions

The complexation of a metal with a Schiff-base ligand was carried out and analyzed using elemental analysis, UV-Visible, IR, and ¹H NMR techniques. The prepared complex was used as a catalyst in the production of chalcone derivatives through ultrasonication. The results indicate that the prepared complex had a noteworthy ability to catalyze a reaction, with a higher yield (more than 90%) compared to other catalysts such as KOH and PTSA. Based on the above study, it can be inferred that the prepared metal complexes can be used as potential catalysts for organic synthesis.

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