



SYNTHESIS, PHYSICO-CHEMICAL AND CATALYTIC ACTIVITY OF COPPER (II)
MIXED LIGAND SCHIFFS BASE COMPLEX SYNTHESIZED BY
2-ACETYL PYRIDINE AND 2-ABA

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Abstract:

The Cu (II) mixed ligand compound was synthesized by using [2-Acetyl Pyridine-2-Amino Benzoic Acid] as primary ligand Schiff's base & 1,10-Phenanthroline as secondary mixed ligand with Copper(II) Chloride. [Cu [2-Ac.Py+2-ABA] [1, 10-Phen] Cl] catalyses the selective and very mild aerobic oxidation of Primary Alcohols to aldehydes in acetonitrile: water (2:1) in the presence of 2, 2, 2, 6-tetra-methylpiperidiny-1-oxyl (TEMPO) and H₂O₂ as co catalysts.

Keywords: Mixed ligand; Schiff's Base; Catalytic nature.

Introduction:

Mixed ligand Schiff base and its Copper(II) Catalytic active complexes have been studied extensively over the past decade. Copper (II) with d⁹ configuration permits a wide range of symmetries and coordination numbers and it has significant use in bioinorganic chemistry. Hence, this field has attracted the attention of several chemists to investigate further in view of the growing interest to make the reactions very fast.[1] In the present research paper, we report catalytic study of Copper (II) complex of mixed ligands Schiff base, 4-H(2-carboxyphenyl)-pyridine-2-yl, ethyleneamine and 1,10-phenanthroline. The synthesized Mixed Ligand Cu (II) complex catalyzed more efficiently the aerobic oxidation of benzyl alcohol into benzaldehyde than the corresponding homoligated Cu (II) complexes. [2] Green Chemistry demands Microwave reactions under solvent free and less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling. The azomethine linkage and hetero aromatic moiety in the synthesized complexes exhibit extensive catalytic activity.[3] In this study, we report the synthesis, physicochemical characterization and catalytic significances of Mixed ligand Cu (II) complexes with ligands derived from (2-carboxyphenyl)-pyridine-2-ylethyleneamine and 1, 10-Phenanthroline, (Fig.1). The reaction was carried out by microwave methods. The metal complexes formed with new ligands may be used as precursors for the synthesis of new compounds, exhibit interesting physical, chemical and catalytic properties.[4]

Materials and Methods:

Purification of solvents: Chemicals were reagent grade and purchased from Aldrich. Solvents were reagent grade and used with no other purification, other than drying over the

specified molecular sieves when required. Microwave assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800 W and microwave frequency 2450 MHz. The microwave reactions were performed using on/off cycling to control the temperature. Sulphuric acid, nitric acid from SD-ine. DMSO, Dimethylformamide, DCM, Acetonitrile from SD-fine. n-Bu₄NClO₄.

Synthesis of Ligands (L₁): Scheme: [(L₁):

Microwave method for the synthesis of Schiff bases: The equimolar (1:1) ratio of 2-(1-Pyridine-2-yl-ethyleneamino)-benzoic acid (L), were synthesized by mixing of a solution 2-Acetylpyridine (0.121 g, 1 mmol) in 10 ml of ethanol with solution of 2-aminobenzoic acid (0.137g, 1mmol) dissolved in 10 ml of absolute ethanol while stirring. The reaction mixture was then irradiated by the microwave oven by taking 5 ml of dry ethanol as a solvent. The reaction was completed in a short time (6 min) with higher yields. The resulting product was then recrystallized with ethanol and finally dried under reduced pressure over anhydrous CaCl₂ in desiccators. The shiny brown needle crystalline product was obtained, washed with ether and dried. This was then characterized by infrared and ¹H NMR spectra. Satisfactory results were obtained. [Yield: (78%) (L₁).]

Microwave method for the synthesis of metal

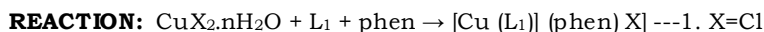
complexes: The ligand, phen and the metal salts were mixed in 1:1:1 (metal: ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-5 mL of dry ethanol as a solvent. The reaction was completed in a short time (6 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous CaCl₂ in a

desiccators. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 81%).

[L₁]: Yield 81 (80%); M.P.- 148°C; Colour: Golden brown; Anal. Calc. for C₁₄H₁₂N₂O₂: C, 66.99,(67%); H, 5.03,(5.5%); N, 11.18,(11.80%); Found: C, 66.99,(66.9%); H, 5.03,(5.04%); N, 11.18,(11.20%); IR (KBR) (cm⁻¹) 1617 ν(C=N); 1672 ν(C=O); Uv-Vis: 250nm, 270nm, 330nm λ_{max}(nm); ¹H NMR: (CDCl₃) (400 MHz) δ CH₃: 2.48 ppm and Ar-H:6.5 -8.3 ppm; Azomethine (C=N):8.5 ppm.

Results and Discussion:

The metal complexes are coloured, solid and stable towards air and moisture at room temperature. Reaction was completed within 4-8 min by the microwave irradiation technique and yields have been improved from 78% to 81%. All the metal chelates have 1:1 (metal:ligand) stoichiometry. The observed molar conductance



Physico-chemical methods: **1] ¹H NMR:** The proton NMR spectra of the Schiff base ligands were recorded in DMSO-d₆ solution using TMS as internal standard. The ¹H-NMR spectra of the L₁ ligands showed multiplet at δ 7.127-7.652 due to aromatic protons while the azomethine proton resonates as singlet at δ 8.5. The phenol -OH groups have signals at δ 12.243 ppm which is disappeared on deprotonation.

2] IR: The IR spectra of Schiff base ligands L₁ show bands at 1669 cm⁻¹, may be assigned to the νC=O (carboxylic group), However, the spectra of all complexes show absence of this band accompanied by the appearance of two characteristic bands at 1625 and 1409 cm⁻¹ attributed to asymmetric and symmetrical stretching of the carboxylic group respectively, indicating the involvement of the carboxylic oxygen atom in the complex formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the ν_{sy} (COO⁻) and ν_{asy} (COO⁻), the separation value (Δ) between ν_{asy}(COO⁻) in metal complexes was more than 200 cm⁻¹ (270 cm⁻¹) suggests the coordination of carboxylate group in all metal complexes in a monodentate fashion. The azomethine ν(C=N) bands in the IR spectra of the ligands appear in the range 1610 cm⁻¹, shifting of this band towards the lower frequency region by 15 cm⁻¹ in complexes indicates involvement of azomethine nitrogen in coordination with metal ion. The pyridine ring deformation mode at ν~620 cm⁻¹ in these spectra of the free ligands is shifted to

of the complexes in DMSO at room temperature is consistent with the non-electrolytic nature of the complexes. The synthesized compounds are crystalline colored, nonhygroscopic, soluble in Dimethyl formamide (DMF) and Dimethyl sulfoxide (DMSO). They were obtained with excellent yield because of the intra molecular hydrogen bond between the fairly acidic phenolic hydrogen and the azomethine nitrogen atom in 2-ACETILPYRIDINE, which catalyzes the condensation reactions. The coordination of the Ni metal of the Tridentate (ONN) ligands is realized by means of PYRIDINE nitrogen atom and AZOMETHINE of the ligands and ONE oxygen of the ligands. The Schiff base could coordinate to the metal atoms through the phenolate oxygen, imine nitrogen, and pyridyl nitrogen atoms. The Cu(II) complex adopts octahedral geometry by following synthesis procedure.

higher wave numbers in the spectra of the complexes indicating coordination of the complexes indicating coordination of the pyridine ring nitrogen atom to the copper(II). [6] The 1,10-phenanthroline bands at 717 cm⁻¹ shows their involvement in the complexes.

Magnetic Moments and Electronic Spectra; The broad band centered at 15267-13793 cm⁻¹ appearing as an envelope in the Cu(II) complexes assigned to the ²E_g and ²T_{2g} transition reveals the octahedral geometry. The ²E_g and ²T_{2g} states of the octahedral Cu (II) (d⁹) split under the influence of Tetrahedral distortion and distortion can be such as to cause three transition ²B_{1g}→²B_{2g}; ²B_{1g}→²E_g and ²B_{1g}→²A_{1g} to remained unresolved in the spectra. The octahedral geometry of Cu(II) ion in all complexes is confirmed by the measured magnetic moment value is 1.74 μ_B. It is concluded from the results that complexes are found to have molar conductance values is 16 ohm⁻¹ mol⁻¹ cm² indicating the non-electrolytic nature of these complexes. [7]

Mixed Ligand Schiff's Base Copper(II) complex-catalysed aerobic oxidation of primary alcohols to aldehydes: [CuL(1,10-phenanthroline)Cl] catalyses the selective and very mild aerobic oxidation of primary Alcohols to aldehydes in acetonitrile :water (2:1) in the presence of 2,2,2,6-tetra-methylpiperidiny1 -1-oxy(TEMPO) and H₂O₂ as cocatalysts.

Experimental: Catalytic Activity: The novel, mild oxidation procedure reported here is based on an uncomplicated [Cu L (1, 10-

phenanthroline)Cl] & TEMPO catalyst which can be easily handled. Typically, 10 mole of the alcohol where reacted with air in an acetonitrile / water (2:1) solvent mixture at room temp. The aerobic oxidation is catalyzed by the presence of 5 mol % CuCl₂, Ligand & (phen) & 5 mol% TEMPO and H₂O₂ as co-catalysts (fig.1). As shown in table 1, only 6% of benzaldehyde was produce in 1.5 h when no Phen was added (entry 1). This may be due to the poor solubility of the copper catalyst without ligand and the absence of beneficial electronic effect caused by the pyridine rings. No conversion of benzyl alcohol was observe without TEMPO present (entry2). The role of TEMPO is unclear it might act as hydrogen Acceptor during the catalytic cycle (Fig.2)¹² TEMPO most likely coordinates to the Cu(II) ion. The B-hydrogen is then transferred to TEMPO resulting in a radical -TEMPOH copper species (II). Intra molecular one-electron transfer leads to the aldehyde, TEMPOH Cu(I) species (III). The CuCl₂(L)(phen)-TEMPO catalytic system is active without base 24h are necessary for the total conversion of benzyl alcohol only 2.5h are needed with 5 mol% t-BuOK (entries 3&4).

Conclusion: In case of microwave assisted synthesis, it was observed that the reaction time decreased from hours to minutes and availability of the product with better yield, Use of solvent is

also minimized. The Schiff bases ligands act as monobasic tridentate, coordinated to the metal ions in a tri dentate manner with ONN donor sites of the carbonyl oxygen, azomethine nitrogen, and pyridine nitrogen along with anion and two Nitrogen of 1, 10-phenanthroline in the complex formation and in ligands, the coordination mode of carboxyl ate group is unidentate mode, correlating the experimental data, one can suggest the octahedral geometry for the prepared metal complexes. Mixed ligand Copper complex chloride ion is more strongly coordinated to copper. Consequently, it is easier, for the alcohol ate, to enter the copper coordination sphere when it is the counter -ion chloride. This is plausible explanation for the activities observed. A new and very mild oxidation of primary alcohol to aldehydes with excellent conversion has been developed. The reaction is carried out under air at room temp. and is catalysed by a [CuCl₂L(Phen)] catalyst which is very easy to handle. In the reaction mechanism, TEMPO seems to be involved as a Hydrogen acceptor. The mechanism of the oxidation is under investigation and further investigation is aimed at improving the rate of oxidation of aliphatic alcohols. For this purpose, studies using other N legends are currently in progress.

Table 1 Analytical and physico-chemical data of the metal complexes

Complex	M. F.	Colour	Yield%	M.P. °C	Analytical data				$\Lambda_M \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$	μ_{eff}
					% Found(calculated)					
					Cu	C	H	N		
L	C ₁₄ H ₁₂ N ₂ O ₂	Brown	78	146		66.99	5.03	11.66		
[CuL(phen)Cl]	C ₂₆ H ₁₉ N ₄ O ₂ ClCu	Green	81	>230	12.26	60.23	3.69	10.81	16	1.74

Table 2: Infrared spectral data of the ligands and metal complexes

Compound	$\nu_{\text{C=N}}$	ν_{COO^-}	1, 10- phenanthroline	Cl ⁻	Py-N
L	1617	1672			659
[CuL(phen)Cl]	1614	1591, 1325	1538, 1409, 869, 717		644

Table 3: UV-VIS- spectral data of the ligand and metal complex.

Compound	μ_{eff} μ_B	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and charge transfer transitions (cm ⁻¹)	d → d transitions (cm ⁻¹)
L		252, 275, 345	
[CuL(phen)Cl]	1.74	250, 275	650, 730

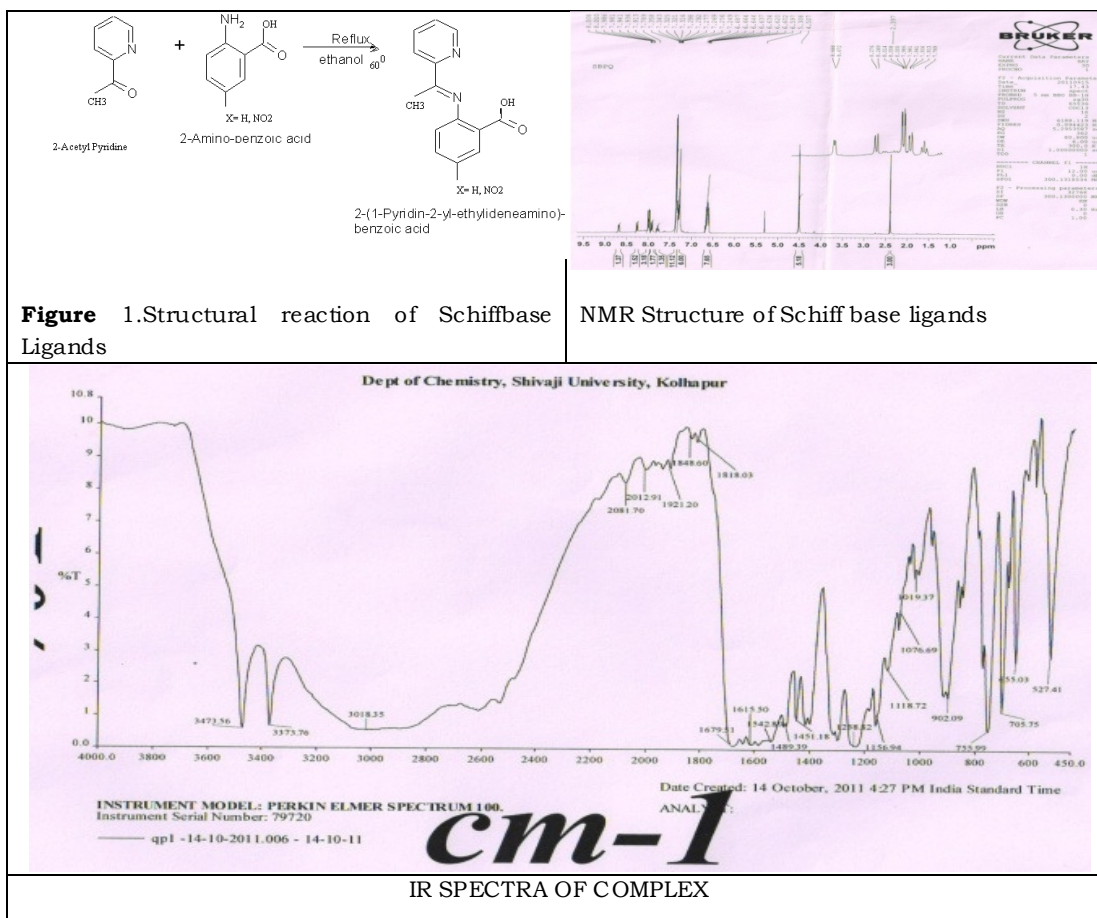
Catalytic Reaction:-

CuCl ₂ (L)(phen) catalysed oxidation of benzyl alcohol to benzaldehyde ^a				Conversion (%)	
Entry	Phen	TEMPO	t-BuOK	0.5 h	1.5h
1	No	Yes	yes	<1	6
2	Yes	No	yes	No reaction	
3	Yes	Yes	no	10	27 ^b
4	Yes	Yes	yes	38	83 ^c

^aSelectivity >99% based on GC. ^b100% conversion after 24h. ^c100% Conversion after 2.5h.

CuCl ₂ (L)(Phen)-TEMPO-catalysed oxidation of alcohol to aldehydes under air			
Entry	Alcohol	Time / h	Conversion (%)
1	Benzyl alcohol	2.5	100

^aSelectivity always >99%. ^bReaction performed at 40 °C with 7.5 mole % TEMPO.



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