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An Efficient and Green Protocol for the Synthesis of Schiff's Base Ligand of 2-Hydroxy 1- Napthaldehyde With Glycine in Water and its Complexation with Iron Metal under Sonication

P. J. Tambade[1*] and B. N. Shelke[2]

[1]*Department of Chemistry, Maratha Vidya Prasarak Samaj's Arts, Commerce & Science College, Nandgaon, Nashik, INDIA.*
[2] *Department of Chemistry, Maratha Vidya Prasarak Samaj's Arts, Commerce & Science College, Ozar (Mig), Nashik, INDIA*

[*] *Correspondence: E-mail: pjtambade@nandgaoncollege.com*

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ABSTRACT: The synthesis of Schiffs base ligand of 2-hydroxy 1- napthaldehyde with glycine in abundantly available water as a solvent is claimed in this paper. For the synthesis of this classical Schiffs base, potassium hydroxide (KOH) is used as a base under ultrasonic conditions. Various reaction parameters were explored to find out optimal reaction conditions viz. effect of solvent, temperature, time, and ultrasound wave. The synthesized ligand was identified by comparing with standard product on TLC and further confirmed by melting point, IR and mass analysis. The ligand is then used for complexation with transition metal (iron) using ultrasound as a facilitator.

Keywords: Schiffs base; 2-hydroxy 1- napthaldehyde; glycine; water and ultrasound.

INTRODUCTION: Transition metal chemistry plays important role in day to day life, with increase in awareness regarding use of transition metal complexes in various field of prime importance like catalysis, pharmaceutical, and many more, the attention on benign synthesis of transition metal complexes shows a paradigm shift. Furthermore, application of green methodologies in chemistry has its own importance and is explored for sustainable development of chemical science. Among the diverse areas of green chemistry use of aqueous medium and application of ultrasonic waves for accelerating reaction rates are enthralling.[1-13]

The exploration of sonication in chemistry offers synthetic chemist a method of activation of molecules which has its broad applications and it needs equipment's which are relatively easily available and inexpensive. Sonication has many advantages for chemists viz. it reduces the time required to complete the reaction by activating reactant molecules, needs mild reaction conditions, higher yields of product are obtained and clean reactions as evident from many scientific reports. Schiff's base arte the compound containing azomethine groups (-C=N-) in the structure, usually synthesized by the condensation of primary amines and carbonyl compounds. Schiff bases are important class of compounds in medicinal and pharmaceutical field. They exhibits numerous biological applications, plays vital role in pharmaceuticals, rubber additives and as amino protective groups in organic synthesis.[14-17]

There are reports on use of 2-hydroxy 1-napthaldehyde for preparation of Schiff bases with various amines under normal conditions. Usually, the reaction needs use of organic solvents like alcohol, acetonitrile, DMF etc., use of high temperature, drastic reaction conditions, use of acid reagent as a catalyst and low reaction yields are issues associated with synthesis of Schiff bases of 2-hydroxy 1-napthaldehyde with amines.[18-21]

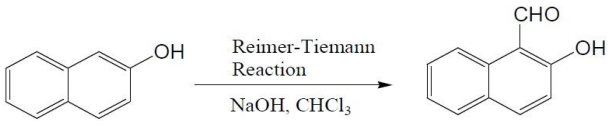
In current findings we are reporting a simple, green, yet efficient methodology for the synthesis of Schiff bases ligand of 2-hydroxy, 1-napthaldehyde with glycine in water using sonication as an accelerator at room temperature. The synthesized Schiff bases ligand was characterized and compared with standard compound, and was use to form complex with iron utilizing ultrasound as an accelerator. The synthesized

metal complex was then characterized with the aid of physical constant, IR spectroscopy, EDS and mass analysis.

MATERIALS AND METHODS: All the reagents used were of analytical reagent type and were used without further purification. Analytical grade solvents were purchased from S D Fine chemicals and are used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and are corrected. Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. Mass spectra were recorded on a Shimadzu LC-MS: EI QP 2010A mass spectrometer with an ionization potential of 70eV. Reactions were monitored by thin layer chromatography (TLC), carried out on 0.2 mm silica gel 60 F254 Merck plates using UV light (254 and 366 nm) for detection.

RESULTS AND DISCUSSION: Synthesis of Schiff base ligand using water as a medium:

Synthesis of 2-hydroxy -1- napthaldehyde: 2-Hydroxy -1- napthaldehyde has been synthesized according to reported method (Scheme 1).[22] In a three-necked round-bottomed flask fitted with a reflux condenser and a dropping funnel are placed 10 gm of β-naphthol and 30 mL ethanol. The stirrer is started, and a solution of 20 gm of sodium hydroxide in 45 mL water is rapidly added. The resulting solution is heated to 70–80°C, and the drop wise addition of chloroform is started (15 mL). The reaction mixture was stirred for 2 hrs, after completion of reaction the excess solvent was evaporated and hydrochloric acid was added to solidify the crude product. The crude product so obtained was washed several times with water and finally is crystallized using ethanol. At the end of reaction received 4.2 gm of product. The product so obtained was determined by TLC and melting point (81°C) and is used in further reaction without any purification.



Scheme 1: Synthesis of 2-hydroxy-1-napthaldehyde.

Ultrasound mediated Synthesis of Schiffs base of 2-hydroxy-1-napthaldehyde with glycine: The reaction of 2-hydroxy-1-napthaldehyde and glycine is well explored earlier, however, we attempted its synthesis using ultrasound as an accelerator. To get optimum conditions for its synthesis using ultrasound, the reaction of 2-hydroxy-1-napthaldehyde and glycine (Scheme 2) was carried out in different solvents at room temperature and reflux temperatures to ensure the suitable solvent for the reaction (Table 1). After initial scrutiny of effect of solvent on reaction outcome, we noticed that the reaction progresses in water as solvent, so we explored other parameters for further enhancement of yield of product using water as a green solvent. The reaction was found to give better yield using KOH as a base instead of NaOH for this reaction. The model reaction was tried in different solvents at room temperature and at reflux temperature (Table 1). While using water as a solvent the improvement in yield was noticed at reflux temperature (Table 1, entry 8), however, time required for completion of reaction is more than 5-6 hrs. Further, reaction in water was explored using ultrasound as an accelerator, and we noticed enhanced yield of product upto 84% in just 25-30 min (Table 1, entry 9), further raise in time was found to have minimal effect on reaction outcome. During this exploration of reaction in water as a solvent, we noticed that the mode of addition of reactant plays crucial role.

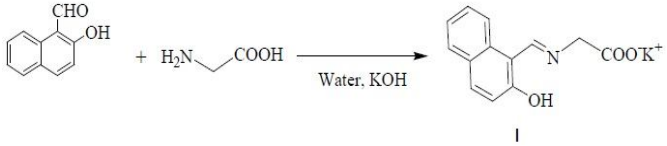
Table 1: Effect of various parameters on reaction outcome[a].

Sr. No.	Solvent	Temp.	Time	Yield (%)[b]
1	Water	25°C	4hr	42
2	Ethanol	25°C	4hr	74
3	THF	25°C	4hr	40
4	$CHCl_3$	25°C	4hr	----
5	Acetonitrile	25°C	4hr	55
6	Ethanol	Reflux	3hr	92
7	THF	Reflux	3hr	58
8	Water	Reflux	3hr	62
9	Water	25°C	25-30 min	84

[a]Glycine (0.01 mol), 2-hydroxy -1-napthaldehyde (0.01 mol), KOH solution, Solvent (15-20 mL).[b] Crude product.

Preparation of Ligand under ultrasonic condition: To a solution of 0.01 mole of glycine (0.75 g) in 10 ml of water, was added a premade solution 0.01 mole 2-hydroxy-1-napthaldehyde (1.72 g) in 0.01 mole of KOH. The resulting reaction mixture was then subjected for sonication for 30 min at room temperature. The yellow green mass formed was filtered, washed with water, hot water followed by diethyl ether. After repeated wash with, the free flowing solid product obtained (2.2 gm; 84%) was dried in oven and used for complexation with iron. The product so obtained was analyzed without any purification by melting

point (238°C), IR and mass analysis. IR: (KBr) ν 1637 cm^{-1}, MS (m/z) calculated 267.03; observed 268.03 (M+1) (Figures 1 & 2).

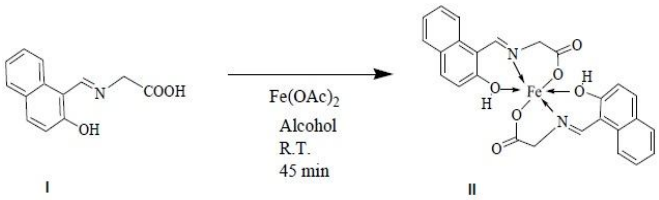


I

Scheme 2: Synthesis of Schiffs base of 2-hydroxy-1-napthaldehyde with glycine (I).

Preparation of iron I complex (II): For the synthesis of metal complex of ligand, iron was chooses as a metal as it can show catalytic as well as biological properties. For preparation of complex anhydrous iron acetate (0.0025 mol) 0.43 gm and Schiff's base ligand I (0.005mole), 1.34gm were added in alcohol and the resultant suspension was irradiated with ultrasound at room temperature. The reaction was completed in 45 min, as monitored by TLC for consumption of ligand (I). After complete consumption of ligand in reaction mixture, the resultant green colored solid was filtered using suction and washed with alcohol and diethyl ether repeatedly. The free flowing solid obtained (2.0gm; 80%) was then dried, physical constant was recorded and is confirmed by IR, EDS and mass analysis (Figures 3-5).

The physical constant (248°C), mass and IR analysis confirms the formation of iron metal complex. IR: (KBr) ν 1612 cm^{-1}, EDS: Fe (Calculated 10.90 %; Observed 10.77 %), MS (m/z) calculated 512.07; observed 512.06.



I II

Scheme 3: Ultrasound assisted synthesis of iron complex with ligand I.

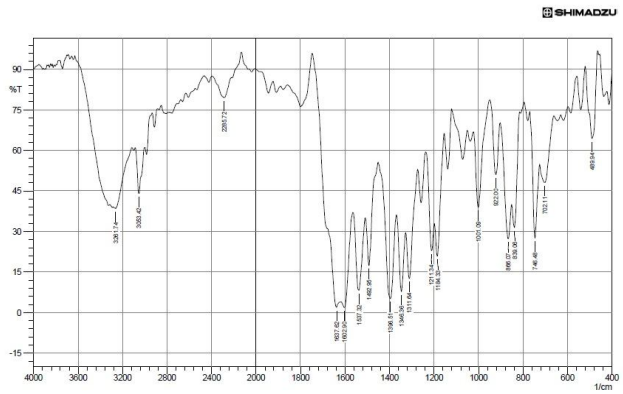


Figure 1: IR spectrum of Ligand.

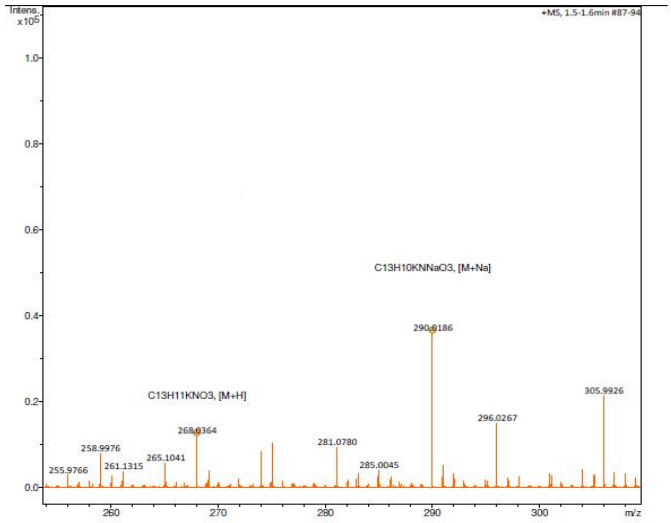


Figure 2: Mass analysis of Ligand.

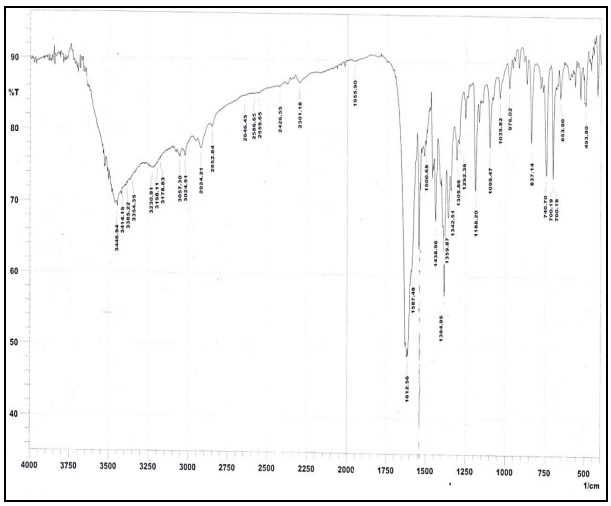


Figure 3: IR of iron complex.

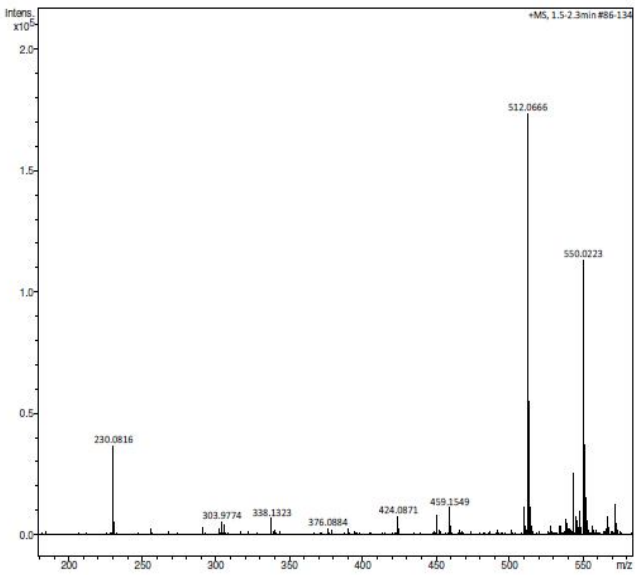


Figure 4: Mass of iron complex.

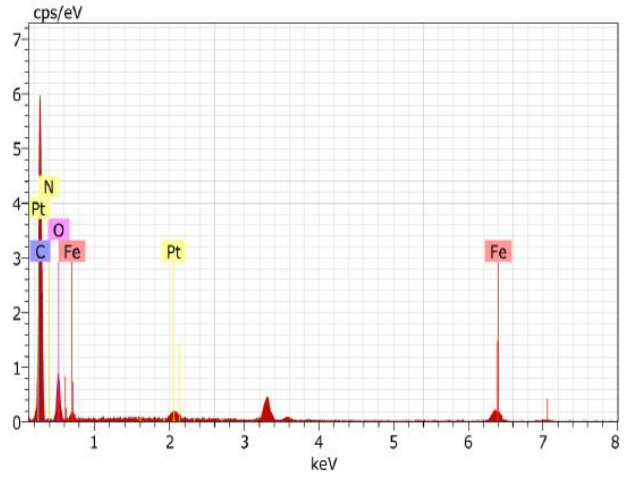


Figure 5: EDS analysis of iron complex.

CONCLUSION: An efficient, simple, and environmentally friendly protocol has been developed for the synthesis of Schiffs base ligand of 2-hydroxy -1- napthaldehyde with glycine using ultrasound in water as a green solvent. The protocol bestowed targeted ligand in good quantity at ambient conditions. The complexation of synthesized ligand with iron is also attempted under ultrasonic conditions. The prepared ligand and complex were analyzed by physical constant, IR and mass analysis.

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