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Research Article

A SIMPLE, GREEN AND EXPEDITIOUS SYNTHESIS OF SALEN OF 2-HYDROXY 1- NAPTHALDEHYDE WITH ETHYLENE DIAMINE IN WATER AND ITS COMPLEXATION WITH VARIOUS TRANSITION METALS (CU, CO, FE AND NI) EXPLORING ULTRASOUND WAVES.

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ABSTRACT

A salen type ligand of 2-hydroxy 1- napthaldehyde with ethylene diamine was synthesized by sonochemical process. The synthetic process is simple yet efficient using environmentally benign water as a solvent. The synthesized salen ligand was characterized by physical constant, ^{1}H NMR, FT-IR, HRMS, and UV-visible spectroscopy. The ligand was then coupled with various transition metals (Cu, Co, Ni, and Fe) under sonication and metal complexes were prepared. The metal complexes are obtained in excellent yield under sonication within short period of time. The metal complexes are identified by FT-IR, HRMS and UV-visible spectroscopic analysis.The developed protocol is simple, clean, high yielding, green, and with reduced reaction times by application of sonication. The products are purified by simple filtration followed by washing with water/alcohol and drying processes.

Keywords: Sonication, 2-Hydroxy 1- napthaldehyde, Ethylene Diamine, Salen, Aqueous

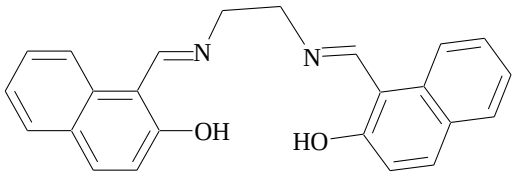
1. INTRODUCTION

Sustainable methodologies for the synthesis of organic molecules have got tremendous importance in last few decades because of increase in awareness towards impact of chemicals on environment. Several green chemistry protocols are emerged as sustainable methods for synthesis of chemicals. The use of sonication methods is one of them, which many times give alternatives to harsh condition and unusual solvents for the synthesis protocols. Reactions carried out under sonication are having many advantages over conventional reactions, mainly in terms of reaction rates, yields of product, purity and ease in operations. As a result, sonication technique is now a day's widely used for organic synthesis, preparation of inorganic compounds, ionic liquids, nano materials and many other applications in the field [1-12].

Schiff base ligands are proven to be versatile ligands for many transition metals, because of their catalytic activities in organic synthesis and biological properties. Schiff base ligands are well explored in last century and there are numerous reports on the synthesis and application of Schiff base ligands [13-19]. Salen types Schiff base ligand of 2-hydroxy 1- napthaldehyde with diamines are not much explored and there are only few reports on synthesis of such molecules in literature [20-25]. In general the synthesis of such Schiff base are reported in organic solvents like alcohol, DMF etc. at reflux temperature and reaction needs 4-5 hrs to complete in general. Thus, there is scope for the development of salen ligands of 2-hydroxy 1-napthaldehyde exploring green alternatives like sonication and aqueous medium.

In continuation of our previous work on synthesis of Schiff base ligand of 2-hydroxy 1- napthaldehyde and there complexes with transition metals [26-27], in the current article authors claim synthesis of Salen of 2-hydroxy 1- napthaldehyde with ethylene diamine (SL) in aqueous medium using sonication as an accelerator for the first time. The synthesized ligand was well characterized by physical constant, ^{1}H NMR, FT-IR and HRMS analysis. The complexation of Salen ligand with four different transition metals (Ni, Cu, Fe, and Co) was achieved exploring sonication technique. The SL metal complexes are characterized by FT-IR UV-Visible and HRMS analysis. The developed protocol is advantageous

in terms of time required for reaction to complete, use of sonication, green and ecofriendly solvent and high yields of product with purity.



SL

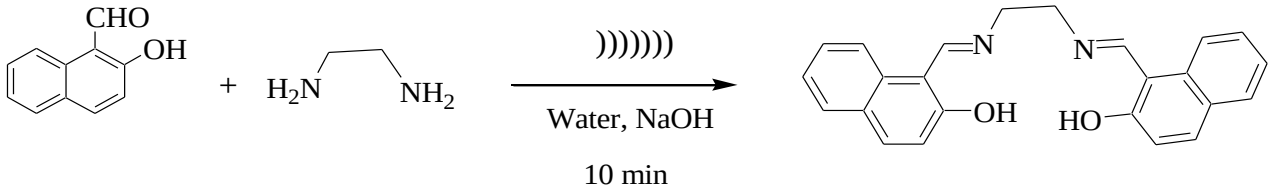
2. EXPERIMENTAL AND RESULTS

2.1. Material 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. UV-Vis absorption of solid compounds was recorded on Shimadzu UV 2450 spectrophotometer at room temperature. High resolution mass spectra (HRMS) were recorded on a Brucker impact HD LCMSMS. 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.

2.2. Synthesis of Salen ligand (SL) under ultrasonic condition in water:

The salen ligand was prepared by sonochemical method using water as a medium. During synthesis, 2-hydroxy - 1- napthaldehyde 0.01 mmol (1.72 g) was added in distilled water and stirred for 2 minutes then 0.01 mole of NaOH solution was added dropwise. After addition of NaOH, ethylene diamine 0.005 mmol (0.3 gm) was added and resultant solution was located in an ultrasonic bath at room temperature (scheme 1). The reaction was found to complete within 10 min as shown by TLC analysis, which was compared with standard.



Scheme 1: Sonication assisted synthesis of salen ligand (SL)

The yellow mass formed was filtered, washed with water, hot water followed by diethyl ether. After repeated washing, the free flowing solid product obtained (1.72 gm; 94 %, MP 230-232 °C), which was dried in oven and was used for complexation with transition metals without any purification.

Color: Yellow, Yield: 94 %, MP 230-232 °C, selected FT-IR peaks (KBr, cm^{-1}) 3049, 1635.^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ = 4.012 (s, 4H), 6.72-6.74 (d, 2H), 7.19 (2H), 7.40 (2H), 7.62-7.63(d, 2H), 7.71-7.73 (d, 2H), 8.02-8.04 (2H), 9.15 (s, 2H).HRMS: [M+1] 369.1599 (Expected M+1 = 369.15).

2.3. Sonochemical synthesis of complexes of SL with transition metals:

The synthesis of metal complex of LS was also tried in water initially, but unfortunately rate of reaction was found to be very low and thus reaction conditions for synthesis of metal complexes were optimized. The reaction between SL and nickel chloride ($Ni(Cl)_2$) was considered as a model reaction and other parameters were optimized.

Table 1: Effect of various parameters on reaction between SL and $NiCl_2$[a].

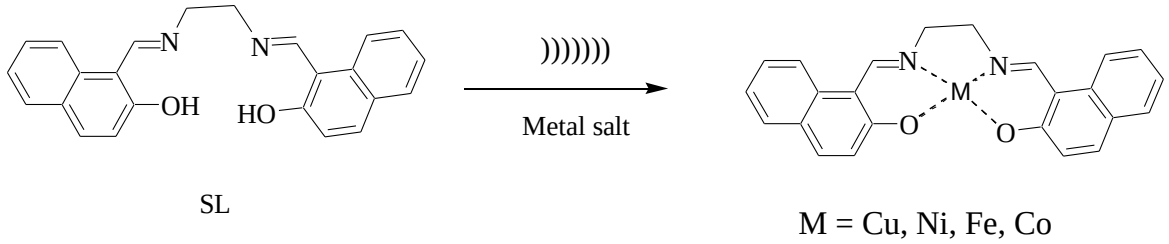
Solvent	Temp.	Time	Yield (%)[b]
Water	Reflux	4 hr	Traces
Ethanol	Reflux	4 hr	94
Acetonitrile	Reflux	4 hr	64
$CHCl_3$	Reflux	4 hr	------
DMF	Reflux	4 hr	88
**Ethanol ((((((((**	**25 °C**	**10 min**	**96**

[a]Ligand SL (0.005 mol), nickel chloride (0.005 mol), Solvent (20 mL).[b] Crude product; ((((((((= Ultrasound

The reaction was carried out in different solvents (Table 1), the desired complex was found to obtain in good amount when reaction was carried out in ethanol and DMF at reflux conditions (Table 1; entries 2 and 5). The reaction in ethanol was found to give better yield with easy work up procedure and hence similar reaction was carried out under sonication and it has been noticed that

reaction is completed within 10 min which is confirm by consumption of ligand on TLC (Table 1; entry 6).

The dark red colored complex formed was filtered, washed with alcohol and dried in oven and finally weighed to find out crude yield.



SL

M = Cu, Ni, Fe, Co

Scheme 2: Sonication assisted synthesis of transition metal complexes of SL

Table 2: Sonication assisted synthesis of metal complexes with SL[a]

Metal precursor	Product	Method of preparation	Time required	Color	Yield[b] (% w/w)
$NiCl_2 6H_2O$	Ni SL complex	Ultrasound	10 min	Dark red	96
$Cu(OAc)_2 5H_2O$	Cu SL complex	Ultrasound	20 min	Light green	94
$FeSO_4$	Fe SL complex	Ultrasound	10 min	Green	90
$CoCl_2$	Co SL complex	Ultrasound	30 min	Gray	84

[a]Ligand SL (0.005 mol), metal precursor (0.005 mol), Solvent (20 mL).[b] Crude product.

The optimized reaction conditions were used for the synthesis of metal complexes of SL with other transition metals (Scheme 2).Four complexes of SL were synthesized under sonication (Ni, Cu, Co, Fe). The time required for the synthesis of each of this metal complex was check by progression of reaction (Table 2), the reactions were found to complete within 10-30 minutes with good to excellent yield of expected product. The synthesized metal complexes were characterized by FT-IR, UV-Visible and HRMS analysis.

2.4. IR analysis

The characteristic infrared spectral data of ligand SL and its metal complexes are listed in Table 3.The IR spectrum of the ligand showed characteristics absorption band at1635 cm^{-1} for azomethine group (-C=N-). In case of metal complexes of SL the shift in band from 1635 cm^{-1} is observed; the band varies from 1602-1624 cm-1 in metal complexes. Apart from these new peaks in the range 565-665 cm^{-1} are observed which are due to interaction metal with oxygen.

2.5. UV-Visible analysis

The UV-Visible absorption study of all compounds is carried out in solid state by preparing pellets. The absorption spectrum of the SL shows intense peaks at 260 nm, 310 nm and 396 nm corresponding to n-π* and π-π* transitions. The SL is complexed with various metals and their UV-Visible absorption is noted, a new peaks with red shift is observed for all the prepared complexes (Table 3 and Fig. 1).

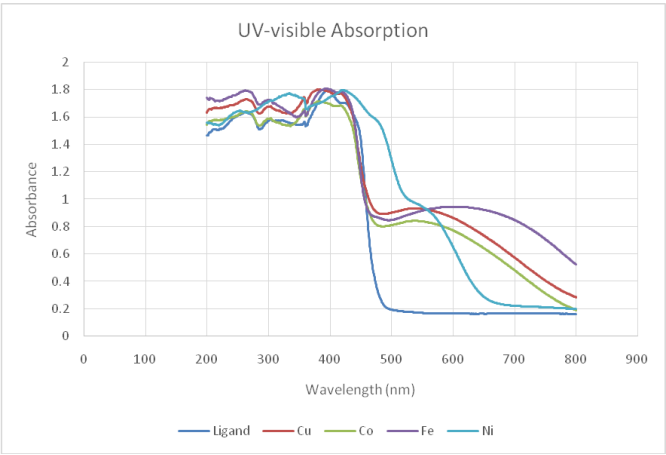
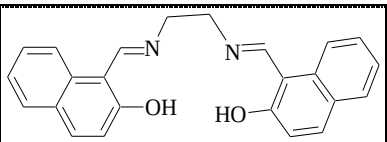
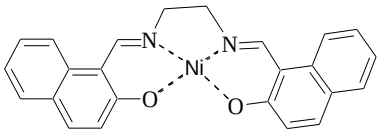
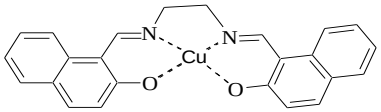
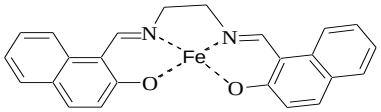
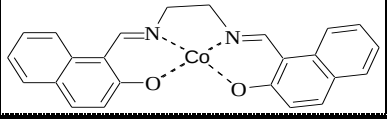


Fig. 1: UV-Visible analysis of SL and metal complexes

Table 3: Characterization data of SL and complexes

Molecule	Structure	Selected IR Peaks (cm^{-1})	UV Absorption maxima (nm)	HRMS (M+1) [M + Na]
SL Ligand		1635	396	369.1599 [391.1416]
Ni SL complex		1602, 665, 588	552	425.0796 [447.0617]
Cu SL complex		1622, 648, 565	535	430.0733 [452.0553]
Fe SL complex		1624, 663, 598	605	422.0714
Co SL complex		1618, 659, 597	529	425.0699 [448.0591]

3. CONCLUSIONS

In summary, an expeditious, simple, and environmentally friendly protocol has been developed for the synthesis of salen ligand of 2-hydroxy -1-napthaldehyde in water as a green solvent under sonication. Transition metal complexes of the ligand are prepared using sonication. The synthesized ligand and its complexes are well characterized by using available techniques like physical constant, FT-IR, and HRMS analysis. The time required for synthesis of ligand and complexes is reduced to many folds. To the best of our knowledge the developed protocol represents the first example of synthesis of SL of 2-hydroxy -1-napthaldehyde in water and its complexes exploring sonication. All these advantages make this protocol an alternative to the conventional methods. The synthesized metal complexes can be used as catalyst in organic transformation in future.

4. ACKNOWLEDGEMENTS

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