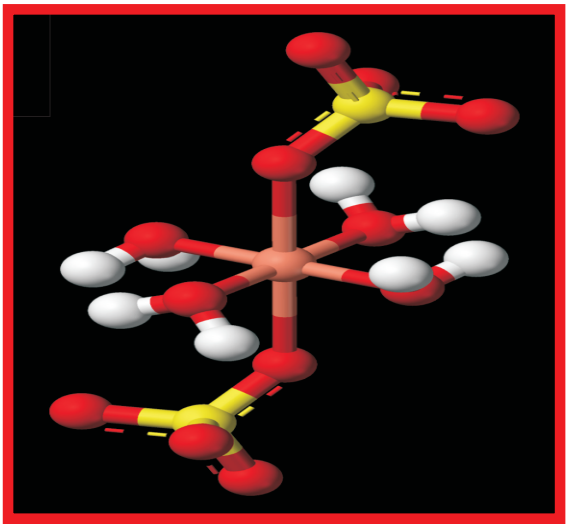
ISSN 2231-5063 IMPACT FACTOR : 3.4052(UIF) | VOLUME-4 | ISSUE-9 | MARCH-2015

GOLDEN RESEARCH THOUGHTS

GREEN, ECO-FRIENDLY SYNTHESISAND CHARACTERISATION OF COPPER(II) COMPLEXES WITH SCHIFF BASES OF 2-HYDROXY-1-NAPHYHALDEHYDE



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Abstract:-

A green, timeliness, workable, rapid and eco-friendly exclusive synthesis of Schiff bases and their complexes with copper(II) ions has been developed using condensation of 2- hydroxyl-l-naphthaldehyde with aryl amines, under microwave irradiation. The use of microwave for assisting different organic synthesis has blossomed into an important tool in organic chemistry. This method provides advantages like short reaction time, energy saving, workable procedure, non-toxic and excellent yield of products. The results are compared with conventional methods. All the prepared Schiff bases were used for complexation with copper(II) ions. The synthesized Schiff bases and their copper(II) complexes were characterized by analytical and spectral methods.

The red to orange red coloured copper(II) complexes have general formula [(ML)2], where 'L' is a Schiff base molecule, The Schiff bases and metal complexes were characterized by elemental analysis data, conductivity data, electronic spectral data and infrared spectral data. With the help of analytical and spectral data it may be suggested that the complexes have coordination number four with a square planar to pseudotetrahedral structure.

Keywords: Microwave irradiation, Schiff bases, copper(II) complexes,Co-ordination compounds.

1.INTRODUCTION :

Metal complexes of Schiff bases have been found to be useful(1,2) in organic synthesis, pigment industries, polymer industries, textile and rubber industries etc. Schiff bases play an important role in structural as well as synthetic research. They also find applications in dye-stuff, silk, varnishes and printing ink(3-5). In recent years simple, eco-friendly, environmentally bening synthetic methods have received considerable attention(6-9). Microwave irradiation is well known to promote the synthesis of various organic compounds(10-12). Catalytic synthesis of Schiff bases using microwaves have been reported (13). Due to the structural aspects and flexibility of Schiff bases and their metal complexes these compounds have been synthesized by conventional methods as well as by using microwave irradiations(14-18). Microwave assisted synthesis of various compounds is a branch of green chemistry. These synthesis are very attractive offering pollution free, timeliness, eco-friendly and simple with high yields. Based on this the author reports synthesis of Schiff bases and their complexes with copper(II) ions by conventional methods as well as by using microwave irradiations. Spectral analysis and structural characterization of Schiff bases and metal complexes have been also reported.

2.MATERIALS AND METHODS :

2.1Materials :

All the aromatic amines used were of L.R. grade, which were purified by conventional methods. 2. Hydroxy-1-naphthaldehyde used in synthesis of Schiff bases was of Fluka made. The metal salt copper(II) nitrate used was of B.D.H. A.R. grade.

2.2.Preparation of Schiff Bases :

2.2.1 Conventional Method:

Schiff bases were prepared by mixing 2-hydroxy–l-naphthaldehyde and the corresponding amines in 200 ml ethanol for two hours.On cooling solidification occurs rapidly. All the ligands crystallizes as light yellow to orange yellow coloured crystal

2.2.2 Microware Assisted Method :

2-hydroxy-1-naphthaldehyde and the corresponding amines were refluxed in 5-10 ml ethanol in microware (720W) for 2-3 minutes. On cooling all the ligands crystallizes as yellow to range yellow coloured crystals.

2.3 Preparation of Metal complexes.

2.3.1 Conventional Method.

The copper(II) complexes were prepared by refluxing copper(II) nitrate and the ligands in 1:2 ratio in ethanol for two to two and half hour. The pH was adjusted to 7.0 by adding alcoholic ammonia. The precipitate obtained was filtered, washed with hot ethanol and dried in vacuum. The metal complexes obtained were red to orange red coloured compounds.

2.3.2Microware Assisted Method :

Copper(II) nitrate and the ligands were refluxed in 1:2 ratio in ethanol in microware (540 W) for 2-3 minutes in alcoholic ammonia. The precipitate obtained was filtered, washed with hot ethanol and dried in vacuum. The metal complexes obtained were red to orange red coloured compounds.

Table 1

Sr. No.	R	Symbol	Name of Ligand
1	Hydrogen	SB_1	2-Hydroxy-1-naphthalidene – a / nil
2	Chloro	SB_2	2-Hydroxy-1-naphthalidene-2^1-chloro-anil
3	Chloro	SB_3	2-Hydroxy-1-naphthalidene-3^1-chloro-anil
4	Chloro	SB_4	2-Hydroxy-1-naphtualidene-4^1–chloro-anil

2.4Elemental Analysis :

Carbon, hydrogen and nitrogen content in the ligands and complexes were estimated micro analytically. Copper in the complexes was estimated by using complexometric titration method using a standard EDTA solution of disodium salt of ethylene diamine tetra-acetic acid of E-Merc-A.R. quality.

2.5Physical Measurements :

The conductance measurements of all the complexes in DMF were recorded on a systronic direct reading conductivity meter. Infra red specta of all the ligands and their complexes were recorded on Perkin Elmer IR spectrophotometer, in the region 4000-600 cm-1. The electronic spectra of all the complexes were recorded on Shimadzu u.v. spectrophotometer using quartz cell of 1cm3 optical path. Chloroform was used as solvent blank.

3. RESULTS AND DISCUSSIONS :

3.1 Analytical data and conductance measurements:

The analytical data of the compounds is reported in table 2. The elemental analysis indicated that the complexes are mononuclear in nature and are represented by the general formula $[(CuL)^{2}]$(5). The molar conductance values fall in the range 10.80 to 18.40 Ohm-1 cm2 mole-^{1}. The values clearly indicate that they are non-electrolytes (13)

3.2Electronic Spectra:

Electronic absorption bands for copper(II) complexes are observed at 40486-40000cm-1, 31250-30960cm-1 and 24390-24331cm-1, indicating formation of complexes. The shift in position of - * and n- * bands in these complexes show that there is -interaction between copper(II) and ligand orbitals(19).

3.3.Infrared Spectral Studies :

The infrared (IR) specta of ligand show a broad peak band in the region 2600-2350 cm-1 which has been assigned to intermolecularly bonded (HO……H). A band occurring at 1570-1560 cm-1 in the specta of ligand and 10-1600 cm-1 in complexes has been assigned to (C=N) stretching. The shifting of the frequency suggest the co-ordination through nitrogen of azomethine group (14, 15). The spectra of most of the complexes exhibit a weak band in the range 3060-3020 cm^{-1}, which is assigned to the aromatic C-H stretching vibrations. The strong and sharp band appearing in the region 1580-1460 cm-1 is attributed to C=C stretching vibrations. Very strong band at 1440-1400 cm-1 in all complexes is assigned to aromatic C-N frequencies in the complexes. The strong and sharp bond at 1360-1345 cm-1 in all the complexes is assigned to C-O stretching vibrations. This suggests the coordination of ligands to the metal through phenolic oxygen and azomethine nitrogen(20).

3.4Microwave Assisted Synthesis :

Microwave assisted synthesis are rapid, timeliness, eco-friendly, environmentally acceptable, involving non-toxic reagent and green synthesis.

3.5 CONCLUSION :

With the help of elemental analysis data, conductivity measurements, infrared spectral data and electronic spectral data it may be suggested that the complexes have co-ordination number four with a square planar to pseudotetrahedral structure.

TABLE – 2
Colour Molecular weight, Elemental Analysis and Conductance Data of Copper Complexes of Schiff Bases.

Copper (II) Complex of	Colour	Mol. wt	Elemental Analysis				Conductance Ohm^{-1} cm^{-1} mol^{-1}
SB1	Orange red	558.13	72.70 (73.18)	5.30 (4.66)	5.02 (5.02)	11.04 (11.37)	10.80
SB2	Red	618.19	69.20 (69.96)	4.40 (4.05)	4.90 (4.73)	10.87 (10.12)	18.40
SB3	Orange	618.19	69.90 (69.96)	4.80 (4.86)	5.04 (4.53)	10.38 (10.26)	13.72
SB4	Orange red	618.19	69.40 (69.96)	5.19 (4.86)	4.60 (4.53)	9.97 (10.26)	16.45

Table 3
Electronic Absorption Spectra of Binuclear Copper(II) Complexes.

Copper(II) Complex of	Electonic Spectral band energies (cm^{-1})		
SB1	24390	31250	40486
SB2	24390	30960	40000
SB3	24331	30960	40486
SB4	24390	31250	40000

Table 4
Selected Infra red frequencies (cm-1) of copper(II) complexes

Copper(II) Complex of	Aromatic C-H Stretching	C=N Stretching	Aromatic C=C Stretching	AroSmatic C-N Stretching	C-O Stretching
SB1	3040	1600	1520,1460	1440	1350
SB2	3060	1610	1540,1460	1400	1350
SB3	3020	1600	1570,1470	1430	1360
SB4	3040	1610	1580,1460	1440	1345

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