

Synthesis, Characterization and spectral studies of Microwave Assisted Metal Complexes of Schiff Bases.



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ABSTRACT

The use of microwave for assisting different organic reactions has blossomed into an important tool in synthetic organic chemistry. Due to efficient, ease of workability and eco-friendliness microwaves provides an alternative to environmentally unaccptable procedures which may be time consuming or use toxic and expensive reagents. A rapid, clean and environmentally being synthesis of Schiff bases has been developed using condensation of 2- hydroxyl-1-naphthaldehyde with aryl amines. The results are compared with conventional methods. All the Schiff bases were used for complexation with cobalt (II) ions. The synthesized Schiff bases and their metal complexes were characterized by analytical and spectral methods. The red to orange red coloured binuclear cobalt (II) complexes have general formula $[(ML)_2Cl_2]$, where 'L' is a Schiff base molecule, with the help of elemental analysis data, conductivity measurements, electronic spectral data and infrared spectral data it may be suggested that the complexes have coordination number six with a planar to pseudotetrahedral structure.

Keywords: Schiff bases, Bivalent metal complexes, Microwave irradiation.

Introduction:

Day by day Schiff bases are more frequently applied for the betterment of human welfare. The applications of Schiff bases and their metal complexes have aroused considerable attention, mainly because of preparative accessibility and structural variability (1, 2) Schiff bases play an important role in both synthetic and structural research. Binuclear complexes with Schiff bases of various aldehydes with aromatic amines are known (3-5.) The oxygen bridged homo and hetero binuclear and trinuclear complexes have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical processes and homogeneous catalysis (6-8.) In recent years environmentally benign synthetic methods have received considerable attention and some methods are reported (9-10.) Catalysed synthesis of Schiff bases using microwaves have been reported (11-12.) Based on this, the author reports synthesis of Schiff bases and their metal complexes by conventional methods, as well as by using microwave radiations. Structural characterization and spectral analysis of Schiff basis and metal complexes have been also reported.

Materials And Methods:

2.1 Materials:

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 cobalt (II) chloride 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-1-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 Microwave Assisted Method:

2-hydroxy-1-naphthaldehyde and the corresponding amines were refluxed in 5-10 ml ethanol in microwave (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 binuclear cobalt(II) complexes were prepared by refluxing cobalt (II) chloride and the ligands in 1:2 ratio in 200 ml ethanol for half an hour on water bath. The PH was adjusted to 11.0 by adding excess of ammonium hydroxide. The precipitate obtained was filtered, washed with hot ethanol and dried in vacuum. The metal complexes obtained were red to orange red coloured compounds.

2.3.2 Microwave Assisted Method:

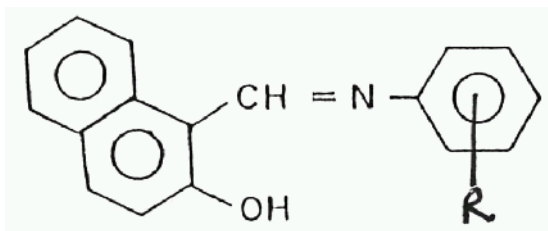
Cobalt (II) chloride and the ligands were refluxed in 1:2 ration in 5-10 ml ethanol in microwave (540 W) for 1-2 minutes in excess of ammonium hydroxide. The precipitate obtained was filtered, washed with hot ethanol and dried in vacuum. The metal complexes obtained were red to orange red colored compounds.

Table 1

Sr.No.	R	Symbol	Name of Ligand
1	H	SB1	2-Hydroxy-1-naphthalidene - a / nil
2	Chloro	SB2	2-Hydroxy-1-naphthalidene-21-chloro-anil
3	Chloro	SB3	2-Hydroxy-1-naphthalidene-31-chloro-anil
4	Chloro	SB4	2-Hydroxy-1-naphthalidene-41-chloro-anil

The structure of ligand is as

Structure - 1



2.4 Elemental Analysis :

Carbon, hydrogen and nitrogen content in the ligands and complexes were estimated micro analytically. Cobalt 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.

2.5 Physical Measurements :

The conductance measurements of all the complexes in DMF were recorded on a systronic direct reading conductivity meter, having cell constant of 1.0 cm-1. Infra red spectra 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 :

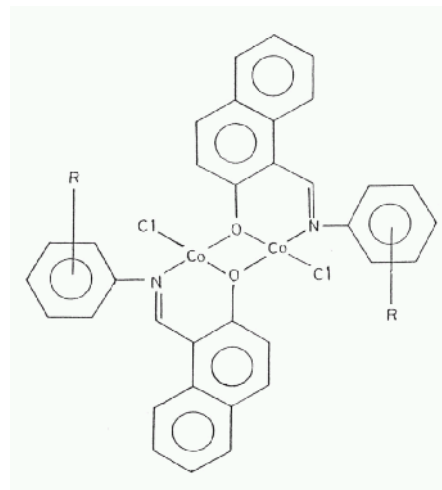
3.1 Analytical data and conductance measurements:
The analytical data of the compounds is reported in table 2. The elemental analysis indicated that the complexes are binuclear in nature and are represented by the general formula [(CoL)₂Cl₂](5). The molar conductance values fall in the range 9.60 to 23.00 Ohm-1 cm² mole-1. The values clearly indicate that they are non-electrolytes (13)

3.2 Electronic Spectra:

Electronic absorption bands for binuclear cobalt (II) complexes are observed at 3731-30674 cm-1, 31250-25253 cm-1 and 26253-23923 cm-1. The first two intensity bands are assigned to $\pi \rightarrow \pi^*$ transitions whereas third band is $n \rightarrow \pi^*$ transition. (13)

3.3. Infrared Spectral Studies :

The infrared (IR) spectra of ligand show a broad peak band in the region 3080-3005 cm-1, which has been



assigned to intermolecularly bonded (HO...O) bond occurring at 1625-1620 cm-1 in the spectra of ligand and 1619-1607 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 2956-2930 cm-1, which is assigned to the aromatic C-H stretching vibrations. The strong and sharp band appearing in the region 1540-1508 cm-1 is attributed to C=C stretching vibrations. Very strong band at 1459 cm-1 in all complexes is assigned to aromatic C-N frequencies in the complexes. The strong and sharp bond at 1376 cm-1 in all the complexes is assigned to C-O stretching vibrations. Thus a shift of 25 -40 cm-1 in C-O frequency is observed from ligand to Binuclear Cobalt (II) complexes. The shifting of this frequency is characteristic feature (13) of the formation of binuclear complexes and therefore, can be used as a criteria for the formation of binuclear complexes. Further this shifting suggests (16-18). The formation of Cobalt-Oxygen (Co-O) bond and bridging through phenolic oxygen in the complexes.

3.4 The Proposed Structure:

With the help of elemental analysis data, conductivity measurements, infrared spectral data and electronic spectral data it may be suggested that the

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

Cobalt (II) Complex of	Colour	Mol. wt	Elemental Analysis				Conductance $\text{Ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$
SB1	Red	683.34	60.30 (59.71)	3.2 (3.8)	4.20 (4.10)	12.50 (12.74)	9.60
SB2	Brown	752.22	55.30 (54.23)	4.20 (3.19)	4.20 (3.72)	16.40 (15.67)	21.42
SB3	Red	752.22	55.20 (54.23)	3.20 (3.19)	3.95 (3.72)	15.50 (15.67)	16.34
SB4	Brown	752.22	55.20 (54.23)	3.20 (3.19)	3.90 (3.72)	16.20 (15.67)	23.10

Table 3 Electronic Absorption Spectra of Binuclear

Cobalt (II) Complex of	Electronic Spectral band energies (cm^{-1})		
SB1	26253	31250	37313
SB2	23981	25188	30674
SB3	23923	25380	30769
SB4	23981	25253	30769

Table 4 Selected Infra red frequencies (cm^{-1}) of binuclear cobalt (II) complexes

Cobalt (II) Complex of	Aromatic C-H Stretching	C=N Stretching	Aromatic C=C Stretching	Armatic C-N Stretching	C-O Stretching
SB1	2932	1613	1536	1459	1376
SB2	2941	1619	1537, 1508	1459	1376
SB3	2956	1600	1536	1459	1376
SB4	2936	1607	1540	1459	1376

complexes have co-ordination number six with a planar to pseudotetrahedral structure. The molecular struc-

ture of the complexes is represented as.

Structure - 2
See Table 2, 3,4

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