SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEX

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Abstract: the study of Schiff bases containing salicylaldehyde and their metal complexes. have their remarkable antifungal, antibacterial, antitumor and anticancer activity. Thus the main aim of this study was to design new Schiff base containing salicylaldehyde unit and its metal complexes could be synthesized in a novel way. To fulfill this Schiff base 2-(salicylimino)-3-hydroxypyridine (SIHP) was selected as a starting point and the Cu (II) and Mn (II) complexes were prepared and characterized

Keywords: Study of Schiff bases, Transition metal, salicylaldehyde.

1. INTRODUCTION:

Heterocyclic compounds found momentous applications in the synthesis of agrochemicals and pharmaceuticals (Gomtsyan 2012; Taylor et al. 2016; Verma et al. 2020). The majority of the synthesized drug molecules contain heterocyclic moiety with significant physiological activities. Among them, nitrogen-containing heterocyclic compounds are pointedly noted for antibacterial, anti-inflammatory, antidiabetic and anticancer activities (Dadiboyena et al. 2009; Gottmann et al. 2018). Moreover, the active natural products were found to have nitrogen in the aromatic rings, especially in the pyridine-like compounds (Makary; Padmavathi et al. 2008; Fustero et al. 2011; Ansari et al. 2017). Pyridine is one of the most important organic compounds for various organic syntheses. Due to its Lewis base character, pyridine can act as a very good ligand and form metal complexes (Lesley et al. 1998). In addition, owing to the biological importance of pyridine, researchers have been using pyridine derivatives as ligands for synthesizing various metal complexes. Pyridine-based ligands have a strong tendency to form complexes with many transition metals; specifically copper and zinc have a good affinity toward these ligands (Huheey et al. 2006). Govindharajan et al have synthesized many metal complexes using a pyridine derivative 2, 6-dipicolinate as the ligand and hydrazinium moiety as the counterion (Saravanan and Govindarajan 2002; Saravanan et al. 2004; Saravanan and Govindarajan 2005). These metal complexes have been found to exhibit better biological properties compared to the ligands (Sarkar et al. 2014). Copper, nickel, cobalt and zinc play a crucial in the human biological system. They are involved in many biological processes such as respiration, catalytic activity and redox reactions (Chang et al. 2010; Vijayan et al. 2015; Murugan et al. 2017; Murugan et al. 2018; Vinusha et al. 2019). Further, these elements have high bioavailability and lower toxicity in a biological system. Hence, several researchers have been synthesizing a wide range of pyridine-based first-row transition metal complexes for various biological applications (Liu et al. 2009; Donde 2015). Like pyridine, morpholine is a potent bioactive molecule. It has two functional groups such as ether and amine, which can donate electrons to the receptors present in various proteins and after protonation, through the lone pair on the N atom, it can act as a counter ion in the complex compounds to stabilize the structure (Hashemian et al. 2018; Arshad et al. 2019). Numerous reports have confirmed the antioxidant, antimicrobial, antidepressant, antidiabetic, anti-inflammatory and anti-tuberculosis activities of morpholine. Morpholines are also used as local anesthetics, platelet aggregation inhibitors, HIV-protease inhibitors and antitumor agents (Al-Ghorbani et al. 2015; Rupak et al. 2016; Nithyabalaji et al. 2020). Based on the above ideas, an attempt is made to synthesize a series of transition metal complexes derived from dipicolinic acid with morpholinium counter ion. The complexes have been characterized and subjected to in silico studies and biological evaluations.

Schiff's base is a functional group or type of chemical compound containing a carbon nitrogen double bond with the nitrogen atom connected to an aryl group or an alkyl group but not hydrogen [1]. Schiff bases are formed by condensation of an amine and the carbonyl group of aldehydes. Schiff for the first time reported condensation of this kind and hence the condensation products are referred as Schiff bases. Many procedures have been described in literature for the synthesis of Schiff bases [2]. The simplest method appears to the one in which equimolar quantities of amines and aldehydes are condensed by boiling in methanol or ethanol [3, 4]. Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different fields. Schiff bases derived from the salicylaldehydes are well known as polydentate ligands coordinating in neutral forms. The interaction of these donors ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active. A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group, photochromic properties, and complexing ability towards some toxic metals. The high affinity for the chelation of the schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Many Schiff base complexes showed excellent catalytic activity in various reactions at high temperature (>100°C) and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis [5, 6]. In the past two decades, the synthesis, structure and properties of Schiff base complexes have stimulated much interest for their noteworthy contributions in single molecule-based magnetism, material science, catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis, etc [7, 8]. A great deal of work has been reported on the synthesis, structural investigations, various crystallographic features, mesogenic characteristics, structure-redox relationships and catalytic properties of different types of Schiff bases and their complexes with transition and non-transition element [9-12]. The lot of attention is being given to the study of Schiff bases containing salicylaldehyde and their metal complexes. In recent years metal complexes of Schiff bases derived from salicylaldehyde have attracted considerable attention due to their remarkable antifungal, antibacterial, antitumor and anticancer activity. Thus the main aim of this study was to design new Schiff base containing salicylaldehyde unit and its metal complexes could be synthesized in a novel way. To fulfill this Schiff base 2-(salicylimino)-3-hydroxypyridine (SIHP) was selected as a starting point and the Cu (II) and Mn(II) complexes were prepared and characterized

2. EXPERIMENTAL SECTION:

Scheme 1.

Synthesis of SIHP An ethanolic solution of 2-amino-3-hydroxypyridine (5g, 1 mmol) was added to the ethanolic solution of salicylaldehyde (5.54 g, 1mmol) in 250 ml round bottom flask. To this reaction mixture 3-4 drop of Conc. HCl was added with vigorous stirring. The reaction mass was refluxed on water bath at 80 ºC for 6 hr with constant stirring. The hot reaction mass was then quenched on crushed ice. Yellow crystals obtained were filtered, washed with hot water and recrystallized twice from distilled ethanol.

Scheme 2.

Synthesis of the metal complexes Aqueous solution of metal salt (1mmol) was mixed with warmed ethanolic solution of SIHP (2 mmol). To this reaction mixture 3-4 drop of Conc. HCl was added with vigorous stirring. The reaction mass was refluxed on water bath at 90-100 ºC for 3 hr with constant stirring. The appropriate pH of the solution was maintained by adding 0.1N NH4OH solution. The precipitate obtained was cooled, filtered, washed with warm water followed by 50 % ethanol and dried in vacuum.

3. RESULTS AND DISCUSSION:

1H NMR Spectra The paramagnetic nature and the limited solubility in the solvents CDCl3 and DMSO, metal complexes leads to noisy base line and broadening of the signals, and did not yield 1H NMR spectra to satisfactory quality. The NMR signals for SIHP. FTIR Spectra The infrared spectra of the complexes are quite complex, however, important bands have been assigned on the basis of their correlation with other similar complexes. Characteristic FTIR bands of the compounds. The frequency due to O-H vibrations observed in the spectrum of SIHP (3329 cm-1) was also present in the spectra of complexes, which suggested presence of one -OH group. This observation confirmed the replacement of proton of one –OH group by metal ion during complexation; where as other –OH group was remained unchanged after colmplexation. The sharp band observed at 1576 cm-1 in spectrum of SIHP was assigned for C=N stretching vibrations, these vibrations were remained unchanged in the spectra of complexes. This observation also suggested non involvement of C=N in the complexation. The another sharp band observed at 1455 cm-1 in the spectrum of SIHP was assigned for C-N vibrations of pyridine, these vibrations were shifted to lower frequency (1281-1396 cm-1) in the FTIR spectra of metal complexes. This observation suggested that, the nitrogen atom on pyridine ring formed coordinate bond during the complexation. The weak intensity bands observed around 533-618 and 466-547 cm-1 in the FTIR spectra of the metal complexes were assigned to M-N and M-O stretching modes, respectively. These assignments are based on the fact that oxygen is more electronegative than nitrogen, the M-O bond tends to be more ionic than the M-N bond and, therefore, M-O vibrations were expected to appear at lower frequencies than the M-N vibration.

Synthesis of Schiff base ligand:

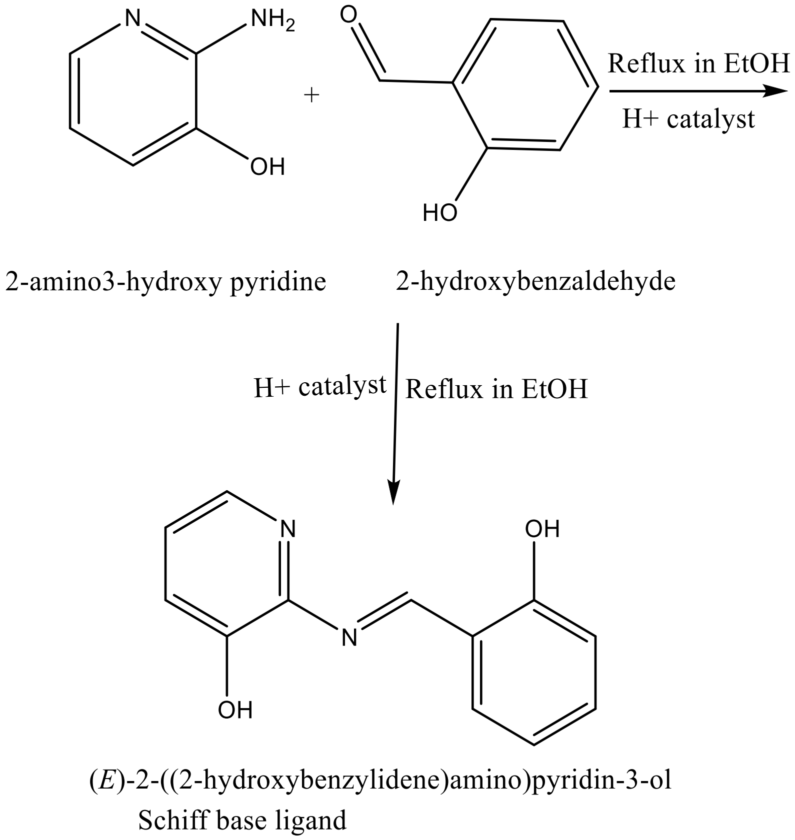

Fig: Synthesis of (E)-2-((2-hydroxybenzylidene) amino) pyridin-3-ol Schiff base ligand

Synthesis of metal complexes:

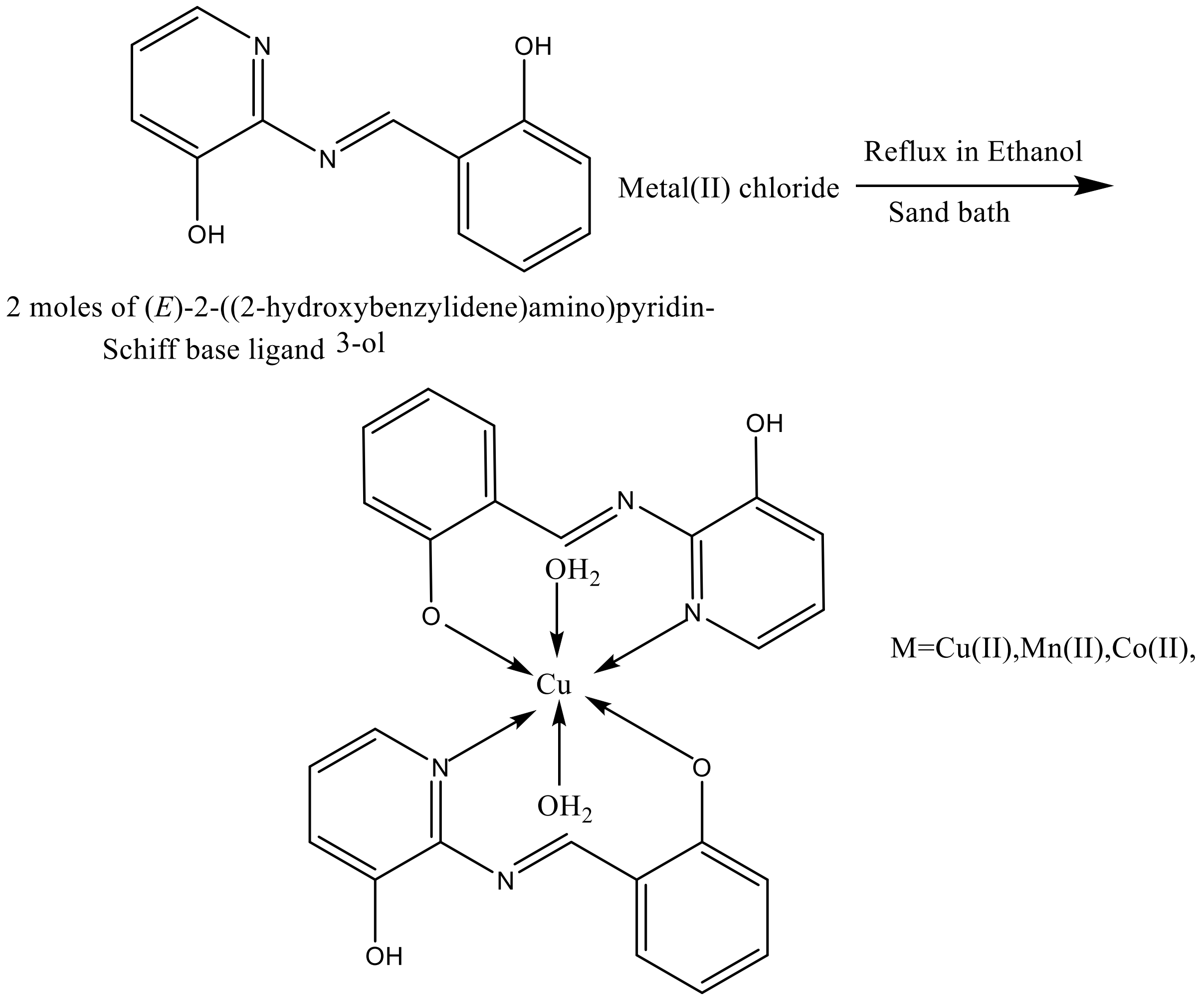

Fig: Synthesis of metal complexes of (E)-2-((2-hydroxybenzylidene) amino) pyridin-3-ol Schiff base ligand

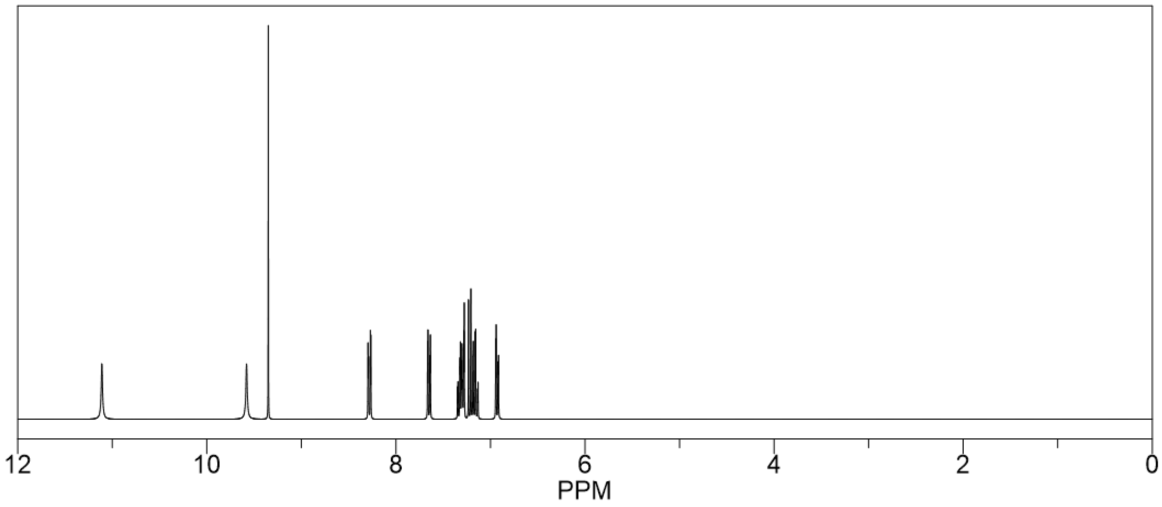

Fig- ^{1}H NMR spectra of (E)-2-((2-hydroxybenzylidene) amino) pyridin-3-ol Schiff base ligand

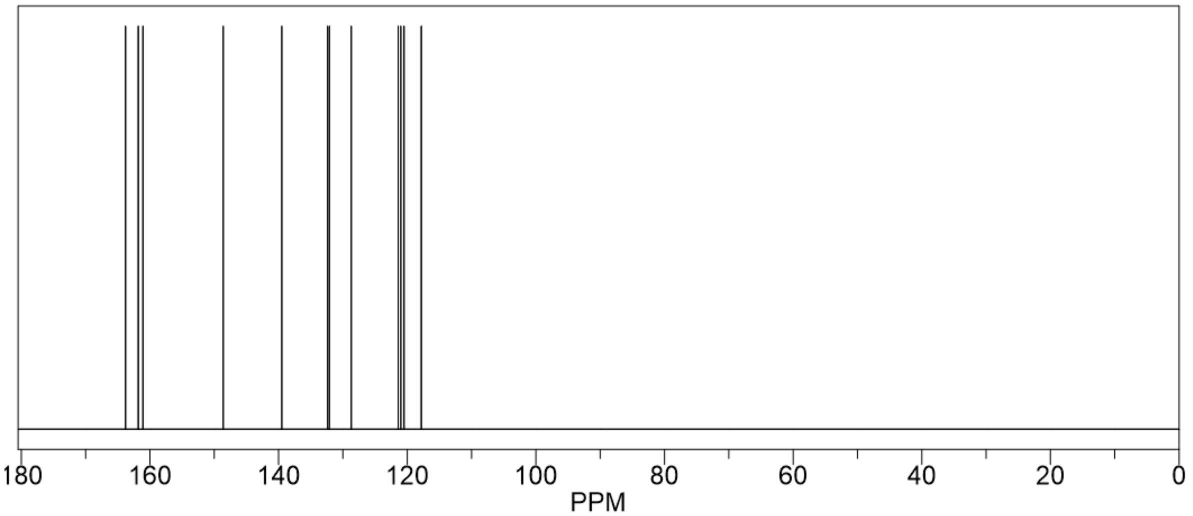

Fig- ^{13}C- NMR spectra of (E)-2-((2-hydroxybenzylidene) amino) pyridin-3-ol Schiff base ligand

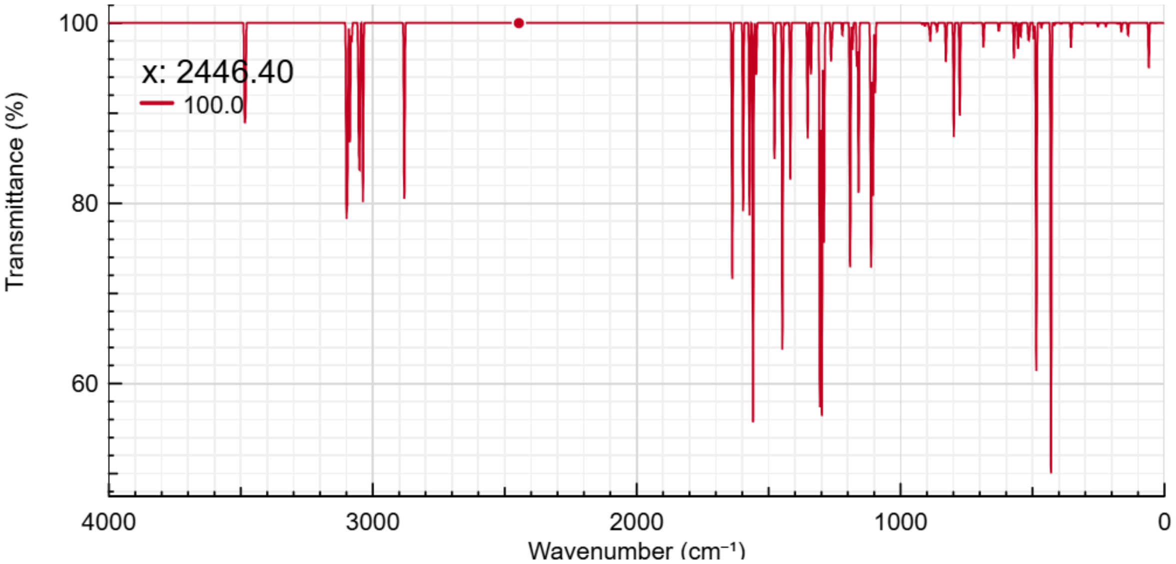

Fig- FT-IR spectra of (E)-2-((2-hydroxybenzylidene) amino) pyridin-3-ol Schiff base ligand

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