

## ONE POT TANDEM SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE AND METAL COMPLEXES

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### ABSTRACT

In the present study of one pot tandem reductive Schiff base formation from nitroarenes carried out in the presence of iron powder and dilutes acid. In the present study new Schiff base compound derived from 2 hydroxy acetophenone with 2 nitro thiophenol and metal complexes. Schiff base and metal complexes are characterized.

### INTRODUCTION

Tandem reactions have several advantages over a series of individual reactions. First, they allow construction of complex structures in as few steps as possible. In theory, they also eliminate the need for a purification step (or steps). Since the intermediates are not isolated it becomes easier to work with sensitive or unstable intermediates. [1-2]

Multistep synthesis of specialty chemicals normally requires stoichiometrically excess reagents, leading to high effluent loads. Hence, search is now on for clean, non-hazardous and 'green' chemical transformations, which will have negligible bi-products and high selectivity.

### Green Context

In view of human health and environmental concerns, much attention is being paid to 'Green Chemistry', which is a chemical methodology to decrease or eliminate the use or generation of hazardous substances in the design, preparation and application of chemical production.

Schiff bases and their metal complexes are considered as an important branch in coordination chemistry, current studies proved that are used as antibacterial, antifungal and oxygen carrier properties. The investigations of structure and bonding of Schiff base complexes help understand the complexes. Schiff base ligand forms a stable complex with different transition metal ions and has been the subject for thorough investigation because of their extensive application in wide ranging areas from material science to biological sciences. Schiff bases are important intermediates for the synthesis of various bioactive compounds. Furthermore, they are reported to show a variety of biological activities including antibacterial, antifungal, anti-cancer and herbicidal activities [3-7].

New vistas have opened up in the field of coordination chemistry with the designing of structure of complexes by the influence of metal ions [8].

A perusal of literature showed major developments have been achieved in the research of coordination compounds with special emphasis on metal complexes of Schiff bases containing nitrogen, oxygen and sulphur atoms as donors [9].

The Schiff bases derived from 2-Hydroxy acetophenone are very interesting due to their ability to

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form various types of metal complexes. Biological activity of complexes derived from amino thiophenol has been extensively studied with respect to their antiviral, antitumor and antibacterial activities [10].

### Materials and methods

All the chemicals and solvents used were of AR grade. Completion of the reaction was monitored by thin layer chromatography. IR spectra of the metal in KBr pellets in the range of 4000-350  $\text{cm}^{-1}$  were recorded making use of FTIR-SCHIMADZU 8400 Spectrophotometer and  $^1\text{H}$  NMR spectra were recorded in DMSO on AVANCE 300 MHz spectrophotometer using TMS as an internal standard. ( $\delta$  ppm). Molar conductivity measurements were carried out in DMSO on an Elico digital conductometer model 180. The magnetic susceptibility measurements were made on Guoy balance at room temperature using Hg [Co (NCS) 4] as standard. UV visible spectra in DMF were recorded on a SCHIMADZU multipurpose recording spectrophotometer. Elemental analysis were analysed for metal and sulphur by standard methods [11-12]. Hydrochloric Acid (7.5 mmol) was added to a mixture of 2-nitro thiophenol (0.72 mmol), 2 hydroxy acetophenone (0.72 mmol), and iron powder (7.32 mmol) in 30 mL of EtOH-H<sub>2</sub>O (2:1 v/v) solution. The reaction was heated to 65°C for 6.5 h. cool to RT. The pale yellow precipitate formed was filtered, washed and dried over anhydrous CaCl<sub>2</sub>. The melting point was found to be 105°C.

### Synthesis of the Complexes

The complexes were prepared by slowly adding a hot aqueous solution of the metal acetate to a refluxing ethanolic solution of the 2-(1-(2-mercapto phenyl)limino)ethylphenol containing sodium acetate (0.5 gm), until the metal ligand ratio reached 1:1. The reaction mixture was refluxed for 1 hour and the complexes were precipitated. The precipitated complexes filtered, washed with water and alcohol and dried over anhydrous calcium chloride.

## RESULTS AND DISCUSSION

All the complexes are photo stable and non hygroscopic. They are soluble in DMSO and in other common organic solvents. On the basis of elemental analysis Co(II), Ni(II), Cu(II) and Zn(II) complexes can be represented by the general formula  $\text{ML}(\text{H}_2\text{O})_3$  where M is the metal and L is the Schiff Base.

### Molar Conductance

Table 1 shows Conductance measurements of the complexes in methanol at a concentration of 10<sup>-4</sup> M at room temperature are in the range of 2-10  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ . The very low values indicate that these complexes behave as non-electrolytes and are neutral in nature.[13]

### Magnetic Measurements

Magnetic susceptibility of the complexes was determined by Gouy balance. The measurements were made at room temperature and instrument was standardized using Hg [Co(NCS)<sub>4</sub>] as calibrant.[14] Table I shows effective magnetic moment values calculated from the corrected magnetic susceptibility. Some indications of the structures and geometries of the complexes can be obtained from these magnetic moment values [15].

### Electronic Spectra

The electronic spectra of all the complexes of HAPATP are recorded in DMSO. Octahedral geometries are commonly found in Co(II) Complexes and such complexes are pale pink in colour. In the octahedral Co(II) complex, 4T<sub>1g</sub>(F)- 4T<sub>2g</sub>(F) and 4T<sub>1g</sub>(F)- 4A<sub>2g</sub>(F) transitions occur in the region 1250-1000nm and 700-500nm respectively [16].

In the present case the electronic spectrum of Co(II) Complex shows bands at 1066nm and 665nm which can be assigned to the d-d transitions of octahedral geometry. Low intensity of bands and the pink colour of the complex support octahedral geometry.

### Infrared Spectra

IR Spectra of the Schiff base ligand show the absence of bands corresponding to  $\nu$  NH<sub>2</sub> and  $\nu$ C=O. Instead of this a new prominent band at 1550-1690 $\text{cm}^{-1}$  due to azomethine linkage appeared in the ligand indicating the condensation of ketonic group with amino group.[17]

A peak ~3400 $\text{cm}^{-1}$  and ~1300 $\text{cm}^{-1}$  corresponds to  $\nu$ (OH) stretching and bending vibrations. A weak band ~2550 $\text{cm}^{-1}$  corresponds to the  $\nu$ (SH) vibration. Bands at ~760 $\text{cm}^{-1}$  probably indicate the C-S symmetric vibrations and this band are shifted to lower frequencies in all the complexes. The band at 1612 $\text{cm}^{-1}$  is the characteristic of the azomethine group ( $>\text{C}=\text{N}$ ) present in the free ligand.

A downfield shifting in this frequency region (1570-1595 $\text{cm}^{-1}$ ) can be observed in all the complexes indicating that the ligand is coordinated to the metal through azomethine nitrogen. This also indicates the reduction of electron density in the azomethine ligand. Broad and strong band around 3300-3400 $\text{cm}^{-1}$  indicates coordinated water molecules present in the complexes. In the chelates of Co(II), Ni(II) and Cu(II), coordinated nature of water molecules is further supported by the appearance of new bands of medium intensity between 750-850 $\text{cm}^{-1}$  [18].

The weak  $\nu$  (SH) vibration band at 2552 $\text{cm}^{-1}$  in the ligand disappears in the complexes showing the participation of SH group in chelation. The C-O band which appears ~1246  $\text{cm}^{-1}$  in the ligand is shifted to lower frequency in the complexes indicating the co-ordination of the metal through phenolic oxygen. The new band found in complexes in the range 540-560 $\text{cm}^{-1}$  is assigned to  $\nu$  (M-N) stretching mode. The  $\nu$ (M-S) bands of the complexes appear in the range 450-500 $\text{cm}^{-1}$  and the new



bands in the region 420-440cm<sup>-1</sup> are correspond to  $\nu(\text{M-O})$  stretching vibrations [19].

The above data indicate that the ligand is dianionic tridentate ligand (ONS) coordinating to the metal through the deprotonated thiophenol, deprotonated phenol and azomethine nitrogen.

### NMR Spectra

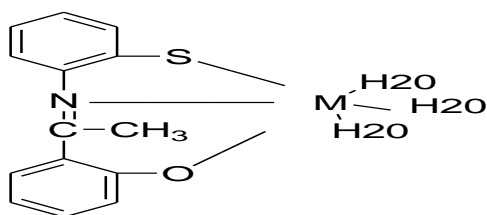
In the case of Schiff Base complexes the <sup>1</sup>H NMR Spectra of diamagnetic Zn Complex, [ZnL1 (H<sub>2</sub>O)<sub>3</sub>] was compared with free ligand. The ligand gave a singlet at 12.5 $\delta$  corresponding to OH protons, another singlet at 5.1 $\delta$  corresponding to SH, and a singlet at  $\delta$  2.5 for the methyl protons. Aromatic multiplet was observed at the range 6.9-

7.4  $\delta$  corresponding to 8 aromatic protons. In NMR spectra of the diamagnetic Zn complex it was found that the singlets due to SH and OH protons disappeared indicating the removal of these protons by chelation with Zinc [20].

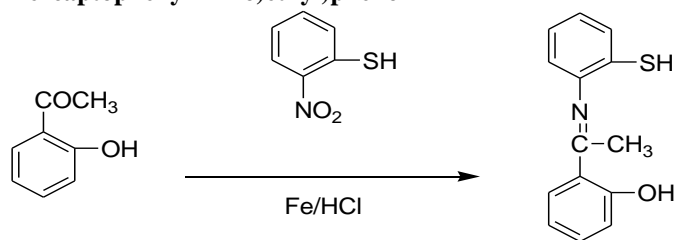
### TG Studies

Cu(II) and Zn(II) complexes of Schiff base were subjected to thermal studies by non-isothermal method. Three stage decomposition was observed for Cu (II) Complex whereas Zn (II) Complex undergoes two stage decomposition. The observed mass loss in TG studies, agrees fairly well with the values calculated from pyrolytic experiments.

**Figure 1.** Based on the above observations, the proposed structure of metal-Schiff base complexes



**Figure 2.** Synthesis of Schiff base ligand: 2-(1-(2-mercaptophenylimino)ethyl)phenol



**Table 1.** Physical characteristics and analytical data of ligand and its complexes

Compound	Elemental analysis					$\mu_{\text{eff}}$ B.M	$\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
	Carbon	Hydrogen	Nitrogen	Sulphur	Metal		
Schiff Base	68.32 69.00	5.21 5.33	5.18 5.23	12.55 13.05	---	---	---
SCBCo(H <sub>2</sub> O) <sub>3</sub>	47.85	47.89 47.44	4.02 4.56	9.10 9.05	16.22 16.49	4.85	3.72
SCBNi(H <sub>2</sub> O) <sub>3</sub>	47.28	4.54	4.06	9.34	16.15	3.55	5.54
SCBCu(H <sub>2</sub> O) <sub>3</sub>	47.12	4.18	3.96	8.92	17.14	1.97	2.55
SCBZn(H <sub>2</sub> O) <sub>3</sub>	47.21 46.97	4.67 4.74	3.90 3.89	7.99 8.14	18.03 18.15	D	2.4

**Table 2.** The selected IR spectral data of the ligand and complexes

Compound	$\nu(\text{H}_2\text{O})$ (cm <sup>-1</sup> )	$\nu(\text{C=N})$ (cm <sup>-1</sup> )	$\nu(\text{C-O})$ (cm <sup>-1</sup> )	$\nu(\text{C-S})$ (cm <sup>-1</sup> )	$\nu(\text{M-N})$ (cm <sup>-1</sup> )	$\nu(\text{M-})$ (cm <sup>-1</sup> )
Schiff base	3380 br	1615 s	1250 m	765 m	--	----
SBCCo	3310 br	1595 s	1230 m	745 m	540 m	425 w
SBC Ni	3325 br	1570 s	1225 m	750 m	525 m	425 w
SBCCu	3330 br	1585 s	1225 m	750 m	520 w	424 w
SBC Zn	3310 br	1590 s	1228 m	745 m	545 m	440 m

Br= broad, s= strong, m= medium, w= weak

### CONCLUSION

Green chemistry for chemical synthesis addresses our future challenges in working with chemical processes and products by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes that can simplify operations in chemical productions, and seeking greener solvents that are inherently environmentally and ecologically benign.

Schiff base have been prepared by a simple one pot tandem and environmentally friendly reductive imination procedure. This methodology uses only Fe (0) in acidic EtOH/H<sub>2</sub>O as a reductant for nitroarenes, which upon reduction spontaneously condense with an aldehyde. Since the intermediate (amine) is not isolated it becomes easier to work with sensitive or unstable intermediates.



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