

# Synthesis and characterization of some transition metal complexes of Schiff base derived from o-mercaptoaniline and 2-formylthiophene

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## Abstract

Schiff bases are the compounds which are mainly formed by the condensation of the aldehyde and amines. These compounds can be synthesized by various synthetic routes. The Transition metal complexes derived from Schiff bases have been among the most widely studied coordination compounds in recent years. These complexes containing certain metal ions are active in many biological processes. A new series of transition metal complexes of Mn(II) and Ni(II) were synthesized from the Schiff base ligand derived from o-mercaptoaniline and 2-formylthiophene and characterized by elemental analysis, IR,<sup>1</sup> HNMR and electronic absorption spectroscopy. Antimicrobial effects of representative ligand and their complexes on different species of pathogenic fungi and bacteria have also been recorded. It was found that the complexes were more effective against all the bacteria and fungi.

**Key Words:** Schiff bases, o-mercaptoaniline, metal complexes, Antimicrobial, bacteria.

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## INTRODUCTION

Schiff bases and their coordination compounds have gained importance recently because of their application as models in biological, biochemical, analytical, antimicrobial system, anticancer, antibacterial and antifungal activities. Studies of new kinds of chemotherapeutic Schiff bases are now attracting the attention of biochemists. Intramolecular hydrogen bonding between OH hydrogen and C=N nitrogen atoms of Schiff bases determines the properties of various molecular systems and plays a significant role in many

biochemical mechanisms<sup>1</sup>. Schiff bases have been extensively used as ligands in coordination chemistry because of their excellent donor abilities<sup>2-5</sup>. Schiff base metal complexes have many industrial uses, especially in catalysis, dyeing and analytical chemistry. Although the coordination compounds of Schiff bases of terephthalaldehyde have been extensively studied, reports are scanty on Schiff bases derived from terephthalaldehyde and ortho substituted aromatic amines. Presence of such metallizable groups at suitable position markedly influences their coordination characteristics<sup>6</sup>. As part of our investigation on Schiff bases and their metal complexes<sup>7,8</sup> we report herein the synthesis and characterization of a new series of Schiff bases produced from 2-formylthiophene and o-mercaptoaniline. Typical metal complexes of these ligand systems were also studied. In the present study, we are reporting the synthesis, characterization and antimicrobial activities of Schiff base ligand 2-formylthiophene-o-mercaptoaniline and its complexes with Mn (II) and Ni (II).

## MATERIAL AND METHODS

**Chemicals and reagents:** All the chemical and solvents used were A.R. grade including o-mercaptoaniline, 2-formylthiophene,  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , absolute ethanol, acetone. The water use throughout the work was doubly distilled.

**Physical measurements:** Elemental analysis was carried out on Perkin Elmer 240c model Elemental Analyzer from IIT Powai, Mumbai. The infrared spectra were recorded on Model RZX (Perkin Elmer) Spectrophotometer using KBr pellets from SAIF, Punjab University, Chandigarh. Electronic spectra were recorded on a UV-VIS-NIR-Spectrophotometer Model Synthesis Lambda 750 Perkin Elmer from SAIF, PU, Chandigarh. The magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer (VSM) from IIT, Roorkee. The melting points of the ligand and the complexes were determined in open capillaries with electronic melting point apparatus and are uncorrected.

**Preparation of Schiff base ligand:** The Schiff base ligand 2-formylthiophene-o-mercaptoaniline (FTMA) was prepared by slow addition of ethanolic solution of o-mercapto-aniline 0.1 mol (0.63g) to 0.1 mol of 2-formylthiophene (0.56g) in 50 ml ethanol. The reaction mixture was refluxed for 2 hrs at 40-50°C. The product so formed were filtered, washed with ethanol and finally recrystallized with ethanol.

**Preparation of metal complexes:** 0.1 M ethanolic solution of the metal(II)chlorides (M=Mn, Ni) was separately added to 0.2 M ethanolic solution of Schiff base ligand (2.19 g) with continuous stirring. Few drops

of dilute ammonium hydroxide solution were added to the above solution to adjust the pH. Resulting mixture was refluxed for 2hrs at 70°C. The product formed were filtered and washed with ethanol and dried over  $\text{CaCl}_2$  in a desiccator.

**Biological Activity:** *In vitro* antibacterial activity of the newly synthesized compounds was investigated against two Gram-negative species *E. coli* and *Pseudomonas aeruginosa* by the agar well-diffusion method<sup>19,20</sup>. Nutrient agar (Hi-Media, India) was used as the bacteriological medium. The extracts were dissolved in 10% aqueous dimethylsulfoxide (DMSO) to a final concentration of 50 $\mu\text{g}/\mu\text{L}$ . Pure DMSO was taken as the control. 100 $\mu\text{L}$  of inoculums was aseptically introduced on to the surface of sterile agar plates and sterilized cotton swabs were used for even distribution of the inoculums. Wells were prepared in the agar plates using a sterile cork borer of 6.0 mm diameter. 50  $\mu\text{L}$  of test and control compound was introduced in the well. The same procedure was used for all the strains. The plates were incubated aerobically at 35°C and examined after 24 hours. The diameter of the zone of inhibition produced by each agent was measured with a ruler.

## RESULTS AND DISCUSSIONS

The structures of Schiff base ligand and their complexes were confirmed by elemental analysis, IR, <sup>1</sup>HNMR and electronic spectra. Elemental analysis data, formula weight, and melting point of the ligand and the complexes are given in Table-1.

**Table 1:** Analytical and physico-chemical data of Schiff base ligand and its complexes

Ligand/ Complexes	Mol. Wt.	Elemental analysis found (calcd.)%					Colour (yield%)	M.Pt. (°C)
		C	H	N	S	M		
$\text{C}_{11}\text{H}_9\text{NS}_2$ (FTMA)	234.19	69.12 (69.96)	4.20 (4.77)	7.11 (7.42)	16.33 (16.96)	-	Yellow 72%	185
$\text{Ni}(\text{C}_{11}\text{H}_9\text{NS}_2)_2$ $\text{Ni}(\text{FTMA})_2$	471.88	50.49 (51.18)	3.10 (3.50)	6.33 (6.41)	14.99 (15.02)	11.90 (12.05)	Red 65%	287
$\text{Mn}(\text{C}_{11}\text{H}_9\text{NS}_2)_2$ $\text{Mn}(\text{FTMA})_2$	432.18	53.20 (53.18)	3.72 (3.98)	5.71 (5.98)	13.55 (13.67)	11.43 (11.03)	Grey 52%	265

**Infrared spectral studies:** The infrared spectra for the present compounds taken in the range 400-4000  $\text{cm}^{-1}$  help to indicate regions of absorption vibrations. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. The peak between 1602 and 1565  $\text{cm}^{-1}$  have been assigned to  $\nu_{\text{C=N}}$  band<sup>11</sup>. This band shows a downward or upward shift by about 15-20  $\text{cm}^{-1}$  in the spectra of all the metal complexes, indicating the participation of the azomethine nitrogen in coordination with metals<sup>11-12</sup>. On comparison, it was determined that the  $\nu$  (C=N) stretching vibration is found

in the free ligands at 1596  $\text{cm}^{-1}$ . This band was shifted to higher or lower wave numbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (M-N)<sup>13</sup>. The bands appearing between 1520 and 1600  $\text{cm}^{-1}$  have been assigned to aromatic or thiophene  $\nu_{\text{C=C}}$ . The shifted band in many cases is coincident with the C=C band, which then shows greater intensity or broadening. The  $\nu_{\text{C=N}}$  modes are often mixed with higher frequency  $\nu_{\text{C=C}}$  (near 1600  $\text{cm}^{-1}$ ) and are seen as a strong band<sup>12,14</sup>. The bands appearing at 1320-1410  $\text{cm}^{-1}$  (specially the highest frequency ones near 1400  $\text{cm}^{-1}$  have been assigned to  $\nu_{\text{C-N}}$  mode<sup>11,12</sup>. It was observed that

the symmetric vibrations of C-S, which appeared as a band near  $706\text{ cm}^{-1}$  in the ligand spectrum, has been shifted to lower frequencies after complexation. Similarly a weak band of S-H, which appeared at  $2644\text{ cm}^{-1}$  in the case of ligand, has been disappeared in the spectrum of all complexes. The participation of the SH group in chelation is ascertained from the shift of the  $\nu_{\text{asym(C-S)}}$  and  $\nu_{\text{sym(C-S)}}$  from  $698\text{ cm}^{-1}$  and  $745\text{ cm}^{-1}$  to lower or higher wave numbers in the spectra of the complexes<sup>15</sup>. The sharp IR ligand bands at  $824\text{ cm}^{-1}$  assigned as  $\nu_{\text{(C-S-C)}}$  of thiophene moiety, for the ligand, shifted to  $827\text{-}828\text{ cm}^{-1}$  for metal complexes<sup>16</sup>.

**Electronic Spectral Studies:** The present Ni(II) complex shows spectral bands around 400-550 nm which may be attributed to the d-d transition. The Ni(II) complexes reported herein are high-spin with room temperature magnetic moment values of 3.80B.M., which are in the normal range observed for octahedral Ni (II) complexes. Their electronic spectra, in addition to showing the  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  bands of free ligands, display 3 bands 20870, 18565 and  $12470\text{ cm}^{-1}$  in the solid reflectance spectra at  $\nu_1: {}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  $\nu_2: {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  $\nu_3: {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ . The spectra show a band at  $25,641\text{-}27,173\text{ cm}^{-1}$ , which may be attributed to ligand to metal charge transfer. The electronic spectrum of Mn(II) complex shows four weak bands at 16000, 19810, 20746 and  $26740\text{ cm}^{-1}$ , which can be assigned to  $\nu_1: {}^6A_{1g} \rightarrow {}^6T_{1g}$ ,  $\nu_2: {}^6A_{1g} \rightarrow {}^4T_{2g}$ ,  $\nu_3: {}^6A_{1g} \rightarrow {}^4E_g$  and  $\nu_4: {}^6A_{1g} \rightarrow {}^4T_{1g}$ , respectively, for a Mn(II) ion in an octahedral field<sup>17</sup>.

**Antimicrobial Study:** Antibacterial activity of ligand and its metal complexes were tested in vitro against representative Gram-negative bacterial species such as *E. coli*, and *Pseudomonas aeruginosa* by agar well diffusion method. Compounds inhibiting growth of one or both microorganisms were further tested for their minimum inhibitory concentration (MIC) of the compound. Ligand(L) is more active against almost all microbes. Also all the complexes showed very good activity against all organisms (MIC =  $25\mu\text{g/mL}$ ). However, the synthesized compounds showed relatively higher activity than the standard drug, Streptomycin. It may be due the nature of the metal ion, the nature of the ligand, and orientation of the ligand around the metal ion.

## CONCLUSION

The Schiff base ligand derived from the condensation of 2-formylthiophene with o-mercapto- aniline acts as tridentate ligand. Spectral results show the involvement of azomethine N, thiophene S and deprotonated thiophenol S in coordination to the central metal ion. On the basis of spectral and analytical investigations octahedral geometry is proposed to Ni (II) and Mn (II) complexes. It is found that the formed complexes show better antibacterial activity in comparison to the Schiff base ligand.

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