

SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE AND ITS TRANSITION METAL COMPLEXES DERIVED FROM 3-ETHOXYALICYLALDEHYDE AND P-TOLUIDINE

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ABSTRACT

By Micro elemental analysis, FTIR, Ultra Violet-Visible, Thermal analysis, ¹H & ¹³C NMR, ESR and Antimicrobial studies a total of four new metal complex derivatives of 2-((p-tolyliminomethyl)-6-ethoxyphenol (EST-L) with the metal ions Mn(II), Co(II), Cu(II) and Zn(II) have been synthesized and characterized quantitatively and qualitatively. It is shown through the spectral study that the geometrical, structural and octahedral geometries for Mn(II), Co(II), Cu(II) complexes and square planar for Zn(II) complex respectively. The presence of unpaired electrons in dx²-y² orbital and distortion in octahedral geometry of Cu(II) complex is confirmed by the ESR spectra. Under the biological evaluation, all the synthesized compounds were closed.

Keywords: Schiff Base, Metal Complexes, Spectral Characterization, Biological Studies.

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INTRODUCTION

In many biological aspects, the Schiff bases are a very important class of organic compounds with a wide range of applications.¹⁻² The metal complexes of Schiff bases possess extraordinary properties as catalysts in numerous biological systems, polymer dyes, antimicrobial activities, antifungal activities, antiviral and antibacterial activities, insecticides, antitumor, plant growth regulator, enzymatic and pharmaceutical fields³⁻⁷. Because of its biological relevance, several model systems including those with bidentate, tridentate, tetradentate, multidentate Schiff base ligands and their coordination complexes attract much attention. This study presents the synthesis, characterization, and biological activities of 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and its transition metal complexes.

EXPERIMENTAL

Without using further purification, the chemical and solvents used are of inorganic and bio-applications grade. At room temperature, all the experiments are carried out, unless otherwise stated. All the metal (II) salts are used as chlorides.

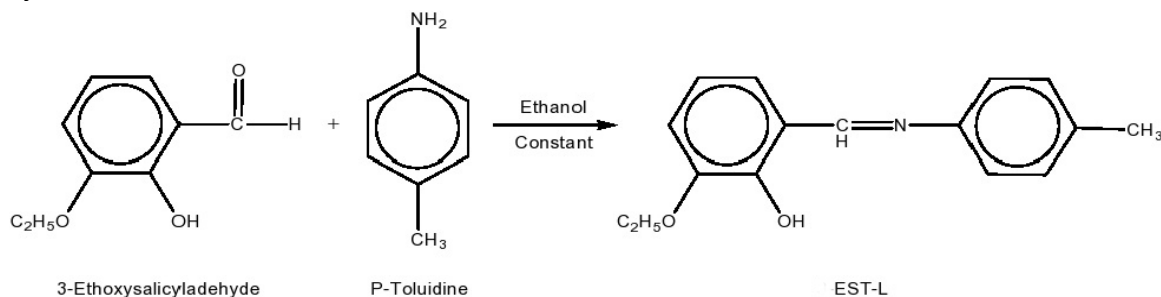
Physical Measurements

On CHNS Perkin Elmer 2400 elemental analyzer, microanalytical data (C, H and N) is collected. From the following studies, the spectroscopic data is obtained in the range of 200-800 nm, spectra Perkin Elmer UV-Visible spectrophotometer model lambda 25, using NMR spectrometer Bruker Advance (II) (400 MHz, d₆-DMSO - solvent). ¹H and ¹³C NMR spectra of 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and their complexes are recorded. On STH 6000 Perkin Elmer instrument the Thermo Gravimetric Analysis is done under an inert N₂ gas atmosphere. In dimethyl formamide, the Electron Proton Resonance spectra

are recorded at room temperature (298K) and liquid nitrogen temperature (77K) using Bruker EPR spectrometer EMX 10/(2) X-bond ER 4119 HS cylindrical resonator.

Synthesis of 2-((p-tolylimino)methyl)-6-ethoxyphenol (EST-L)

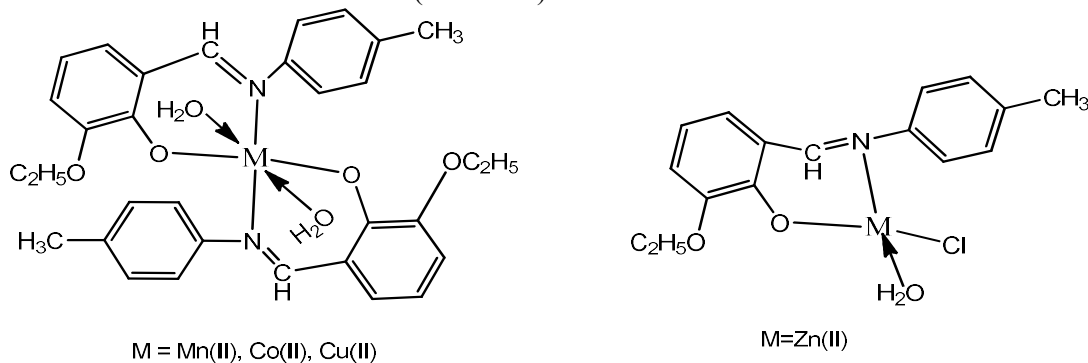
The 2-((p-tolylimino)methyl)-6-ethoxyphenol (EST-L) is synthesized from the solution of 3-ethoxysalicylaldehyde (0.05 mol) dissolved in absolute ethanol (20ml) and P-toluidine (0.05 mol) is added in an equimolar (1:1) ratio. At room temperature the reaction mixture is then stirred for 1-2 hrs. The solid product is separated, filtered and washed from ethyl alcohol. The typical yield 74%; FTIR (KBr, cm^{-1}): 3435(H_2O), 3048($-\text{OH}$), 1660($-\text{HC}=\text{N}$), 1251($\text{C}-\text{O}$); ^{13}C NMR (100MHz, d_6 -DMSO) δ = 77.34-76.70(OC_2H_5), 114.6-147.7(Ar-Carbon), 151.7($\text{HC}=\text{N}$), 161.6($\text{Ph}-\text{C}-\text{O}$); ^1H NMR (400 MHz, d_6 -DMSO, ppm) δ = 13.89(s, 1H, Ar-C-O), 8.62(s, 1H, $\text{HC}=\text{N}$), 6.84-7.20(m, 8H, Ar-H) 4.17-3.93(m, 5H, $-\text{OC}_2\text{H}_5$); Analytical: C-75.27, H-6.71, N-5.49; Found: C-74.93, H-6.96, N-5.14.



Scheme-1: Formation of 2-((p-tolylimino)methyl)-6-ethoxyphenol (EST-L)

Synthesis of Mn(II), Co(II), Cu(II) and Zn(II) Complexes

To a hot ethanolic solution (20ml) of respective metal chlorides (0.05 mol) is added with the hot solution corresponding 2-((p-tolylimino)-6-ethoxyphenol (EST-L) (0.05 mol) in ethanol (20ml) and the reaction mixture is refluxed for about 5-6 hrs on the mantle with a water condenser and then cooled with an ice bath. The obtained colored solid precipitates are collected by filtration washed with a sufficient quantity of ethanol and are dried in a hot air oven (Scheme-2).



Scheme-2: Structures of Metal Complexes

[Mn(EST)₂(H₂O)₂]

The typical yield 67%; Solid; FTIR (KBr, cm^{-1}): 3394(H_2O), 1634($\text{CH}=\text{N}$), 1238($\text{C}-\text{O}$), 532(M-O), 490(M-N); Analytical: C-64.10, H-6.05, N-4.67; Found: C-65.32, H-6.01, N-4.21.

[Co(EST)₂(H₂O)₂]

The typical yield 68%; Solid; FTIR (KBr, cm^{-1}): 3392(H_2O), 1636($\text{HC}=\text{N}$), 1242($\text{C}-\text{O}$), 575(M-O), 492(M-N); Analytical: C-63.38, H-6.01, N-4.64; Found: C-65.61, H-6.23, N-4.12.

[Cu(EST)₂(H₂O)₂]

The typical yield 67%; Solid; FTIR (KBr, cm^{-1}): 3425(H_2O), 1637($\text{HC}=\text{N}$), 1244($\text{C}-\text{O}$), 575(M-O), 492(M-N); Analytical: C-63.20, H-5.97, N-4.61; Found: C-62.19, H-5.82, N-4.82.

[Zn(EST)(Cl)(H₂O)]

The typical yield 67%; Solid; FTIR (KBr, cm⁻¹): 3367(H₂O), 1639(-HC=N), 1240(C-O), 577(M-O), 491(M-N); ¹³C NMR (100MHz, d₆-DMSO): δ=77.36-56.21(-OC₂H₅), 114.6-137.0(Ar-Carbons), 151.7(HC=N), 161.6(Ph-C-O); ¹H NMR (400MHz, d₆-DMSO): δ= 8.78(s, 1H, HC=N), 6.85-7.26(m, 8H, Ar-H), 3.93-2.00(m, 5H, -OC₂H₅); Analytical: C-51.50, H-4.86, N-3.75; Found: C-52.41, H-4.76, N-4.01.

RESULTS AND DISCUSSION

Elemental analysis (C,H,N), UV-Visible, FTIR, ¹H and ¹³C NMR, ESR, TGA and Antimicrobial studies characterize the synthesized 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and metal complexes.

Infrared Spectra

Due to the azomethine, the IR spectra of the ligand exhibit a strong band at 1660 cm⁻¹. A shift of this band towards lower frequency by 20-30 cm⁻¹ in all the complexes suggests that the azomethine nitrogen coordination to the metal centers.⁸ The ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L) IR spectrum shows a band at 3048 cm⁻¹ which corresponds to the phenolic ν(OH) group. OH phenolic group bands disappear in the complexes which indicate the coordination of phenolic oxygen to the metal atom. Further, a strong sharp band characteristic of ν(C-O) in the region 1251 cm⁻¹ observed in the free Schiff base ligand was shifted to lower frequencies 1244–1238 cm⁻¹ in the metal complexes.⁹ To ν(M-N) the presence of a new band around 495–490 cm⁻¹ is assignable. The emergence of the new band in the region of 530-580 cm⁻¹ in all the complexes is due to ν(M-O).¹⁰

UV-Visible Spectra

The banding range 412–665 nm is assigned in the spectra of metal complexes to LMCT and d-d transition respectively. In respect of ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L), the absence of these charge transfer bands confirms the coordination of metal complexes¹¹. In the UV part of the spectrum as well as in the visible part, the colored complexes exhibit a series of the overlapping absorption band. A distorted octahedral geometry is shown by the metal complexes of Mn(II), Co(II), Cu(II) and the Zn(II) complex shows distorted square planar as a stable geometry.

¹H and ¹³C NMR Spectra

In DMSO-d₆ ¹H NMR spectra of Schiff base ligand and Zn(II) complex were noted. In the free ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L), the signal due to the azomethine proton at 8.62 ppm(s, 1H, CH=N)⁹ and the multiplet which extends from 6.84–7.20 ppm corresponds to the protons of the aromatic ring (m, Ar-H). the peak at 13.89 ppm confirms the presence of OH proton in ligand¹². In the spectrum of Zn(II) complex, the OH proton is disappeared by complexation with a metal ion. The signal appeared at 8.78 ppm and multiplets in the region of 6.85–7.26 in ¹H NMR spectrum of the Zn(II) complex are due to azomethine proton and aromatic protons respectively. The signals due to proton have been shifted towards downfield strengths confirming the complexation of metal (II) ion with the ligand. In addition, the signals of ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and Zn(II) complex appeared in the region 3.93-4.17 and 2.00-3.93 ppm has been assigned to the -OC₂H₅ proton. In ¹³C NMR spectra of the ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L), the phenolic C-O, HC=N and aromatic carbon atoms appear in the region of 165.13, 159.20, 132.49–121.05 ppm, which is in agreement with various values reported in the literature. In Zn(II) metal complex, the signal appeared at δ 151.50 ppm(C=N, 1C) was assigned to azomethine carbon atom and the signal at δ 161.63 ppm(ph-C-O, 1C) was assigned to phenolic carbon. The phenyl rings of complexes showed signals between δ 114.07-147.20 ppm(Ar-C). The -OC₂H₅ signals appeared at 77.34-76.70 and 77.36-56.21 ppm in ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and Zn(II) complex.

Thermal Analysis of Zn(II) Complex

Under nitrogen gas at a heating range 25-1000 °C and heating rate (10 °C/min) (Fig.-1) Thermo gravimetric analysis of Zn(II) complex are studied, to prove the suggested structures and studies the thermal stability of the complexes, the thermal analysis is performed. TGA curves of the Zn(II) complex

were represented and the thermal decomposition takes place in three stages. Between the temperatures range of 120-150°C water (H₂O) molecules decomposed and the observed mass loss was recorded as 15.87%. The second stage corresponds to the decomposition of Cl atom at 190-210°C. The major step of decomposition takes place ligand was decomposed in the temperature range 270- 340°C and the observed mass loss was recorded as 49.14%.

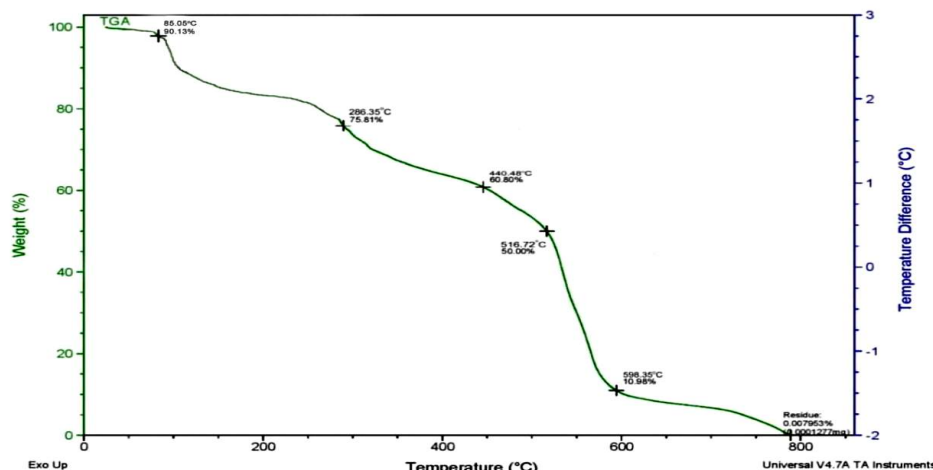


Fig.-1: TGA Spectrum of Zn(II) Complex

ESR Spectra

At room temperature (Fig.-2), the Electron Spin Resonance Spectra of the Cu(II) complex is recorded. The unpaired electron is localized in that dx^2-y^2 orbital which is further supported by the values of exchange interaction, in term of G value estimated from the expression is suggested that,

$$G = (gH - 2.0023/g_H - 2.0023)$$

If $G > L$; slightly misaligned (or) the local axis is aligned parallel. If $G > L$, a significant exchange coupling is presented and misaligned is appreciable. The local tetragonal axes are aligned parallel (or) slightly aligned and the unpaired electron is present in the dx^2-y^2 orbital is suggested that the observed value for the exchange interaction parameters for the Cu(II) complex $Cu(EST)_2(H_2O)_2$.

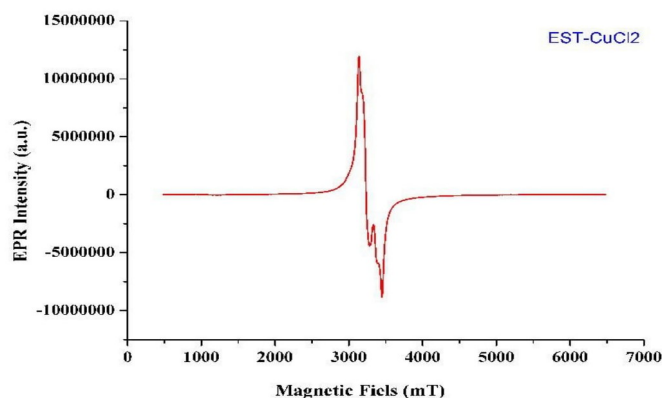


Fig.-2: ESR Spectrum of Cu(II) Complex

Antimicrobial Activity of 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and its Metal Complexes

As a result, in this study, the metal complexes have high inhibition efficiency than the EST-L against the bacterial species. And they were also taken to determine the antifungal activity of the metal complexes.

Antibacterial Activities

The antibacterial activity of the complexes and 2-((p-tolylimino)-6-ethoxyphenol (EST-L) was determined by disc diffusion method on *E.coli* and *S.aureus* and compared with the metal

complexes Streptomycin is used as standard. The ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and the metal complexes exhibited variable antibacterial activities against both *E. coli* and *S. aureus* are summarized in Table-1. The result shows that the metal complexes have good activity compared to that of the free ligand 2-((p-tolylimino)-6-ethoxyphenol (EST-L). This fact confirms the tweedy chelation theory. Thus, the order of activity of the metal complexes and 2-((p-tolylimino)-6-ethoxyphenol (EST-L) against gram-negative bacterium *E. coli* is $\text{Cu(EST)}_2(\text{H}_2\text{O})_2 > \text{Mn(EST)}_2(\text{H}_2\text{O})_2 > \text{Zn(EST)(Cl)(H}_2\text{O)} > \text{Co(EST)}_2(\text{H}_2\text{O})_2 > \text{EST-L}$. It is clear from the above order of activity that Cu(II), Zn(II) and Mn(II) complexes are highly active against *E. coli* and Co(II) complex is moderately active. The order of activity of the metal complexes and 2-((p-tolylimino)-6-ethoxyphenol (EST-L) against gram-positive bacterium *S. aureus* is $\text{Cu(EST)}_2(\text{H}_2\text{O})_2 \approx \text{Co(EST)}_2(\text{H}_2\text{O})_2 > \text{Mn(EST)}_2(\text{H}_2\text{O})_2 > \text{Zn(EST)(Cl)(H}_2\text{O)} > \text{EST-L}$. Similarly, the order of activity shows that Cu(II) and Co(II) complexes are highly active against *S. aureus* and Mn(II) and Zn(II) complexes are moderately active.

Antifungal Activities

Based on the results obtained the order of resistivity of the metal complexes against the fungal species *A. niger* is given as $\text{Cu(EST)}_2(\text{H}_2\text{O})_2 \approx \text{Co(EST)}_2(\text{H}_2\text{O})_2 > \text{Mn(EST)}_2(\text{H}_2\text{O})_2 > \text{Zn(EST)(Cl)(H}_2\text{O)} > \text{EST-L}$. According to the values, it explains that Cu(II), Co(II) and Mn(II) complexes are highly resistive against *A. niger* fungal species. Zn(II) complex is moderately resistive against *A. niger*.

Table-1: Antimicrobial Activities of 2-((p-tolylimino)-6-ethoxyphenol (EST-L) and its Metal Complexes

Compound	Zone of Inhibition (mm)		
	<i>E. coli</i> (-)	<i>S. aureus</i> . (+)	<i>A. niger</i>
EST-L	5	5	5
[Mn(EST) ₂ (H ₂ O) ₂]	8	7	7
[Co(EST) ₂ (H ₂ O) ₂]	6	8	8
[Cu(EST) ₂ (H ₂ O) ₂]	11	12	8
[Zn(EST)(Cl)(H ₂ O)]	7	6	6
Streptomycin – Std.	8	8	11
DMF – solvent control	2	1	1

CONCLUSION

The analytical data and spectral data discussed above suggest that the metal complexes Mn(II), Co(II) and Cu(II) have the proposed geometry is octahedral and Zn(II) has the proposed geometry is a square planar. The antimicrobial study shows that, metal complexes are more active than ligands. The antimicrobial activity of Cu(II) complex is more biologically active than other complexes.

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