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# Synthesis, IR, and NMR Study of Some Cu(II), Ni(II), Co(II) complexes of O-Vanillin and 2-amino pyridine

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## ABSTRACT

In the present work the study of antimicrobial activity of ligand N(3-ethoxy-2-hyroxybenzylidine)-pyridine-2-amine, and its metal complexes was investigated. Ligand (L4) was synthesized by condensation of 2-aminopyridine and o-vanillin and by making some alterations in the previous method, synthesis of Cu(II), Co(II), and Ni(II) complexes was also carried out. The structure of the synthesised complexes has been defined using microanalysis, conductivity measurement, electronic spectra, IR spectra, and NMR spectra. It has been observed that the activity of complexes was more towards *Staphylococcus aureus*, *Bacillus subtitles*, *Escherichia coli*, and *Klebsiella pneumonia* in comparison to the ligand. It was noticed that the presence of $OCH_3$ group magnifies the antibacterial as well as antifungal activity of the ligand.

**Keywords:** O-Vanillin, Electronic spectra, Elemental analysis, Magnetic moment.

## INTRODUCTION

The -HC=N group in the bidentate ligand is normally an admirable chelating agent. Five or six-membered rings with metal ion form particularly when electronic donating groups –OH and $–OCH_3$ are attached near azomethine group[1-3]. Organic reagents play a dynamic role in modern analytical devices, Schiff bases have brilliant features and structural similarities among these reagents. Azomethine moiety forms complexes with a diversity of metals[4,5]. Many Cu (II) complexes have seemed in the literature with various biological activities[6,7]. The presence of a heterocyclic ring in the Schiff base moiety leads to adding stability to the structure of Schiff base metal complexes[8]. Cobalt, Nickel, and Copper are known to have a great attraction for coordination to the heteroatoms as of their small size and high nuclear charge[9]. Aryl group or heterocyclic groups containing Schiff bases remain to possess good biological activities. Therefore, research scholars have been attracted to this topic recently. 2,3-aminopyridine and o-vanillin containing Schiff bases used as ionophores have been used as ionophores in Cu(II) selective electrochemical sensors[10]. Structural elucidation. salicylamide show significant photochromic nature where interconversion through intramolecular hydrogen transfer[11] is caused between enolimine and keto-imine tautomer due to the absorption of light. O-Vanillin is a natural compound that encloses -$OCH_3$, -OH, and –CHO group which shows contradictory effects. Schiff bases from o-vanillin and 2-amino pyridine and its complexes with metal have been found to keep biological activity[12-15]. o-vanillin Schiff bases are similar to salicylaldehyde Schiff bases, as their denticity is two or more than two due to the presence of the hydroxyl (–OH) group at the ortho position[16]. The most prominent flavor is vanillin and the aroma compound present in vanillin is used as a flavoring agent in foods, pharmaceuticals, and beverages.[17] There is a shortage of research on o-vanillin, the Schiff base that contains o-vanillin moiety forms stable complexes with several metal ions. Therefore ortho vanillin is the ideal contender in the synthesis of different aromatic Schiff bases[18-19].

## EXPERIMENTAL

In the present study here we tried to synthesize a novel ligand of Schiff base and its metal complexes of Ni(II), Co(II), and Cu(II) using Schiff base of ortho Vanillin and 2-aminopyridine. The easy availability and low cost make our work easier. Acetate of metal salts was used.

### Synthesis of N (3-methoxy-2-hydroxybenzylidine) pyridine-2-amine.[L4]

0.001M o-vanillin (1.522 g) is dissolved in 10 mL methanol and mixed with 0.001M 2-aminopyridine (0.94 g) in 10 mL methanol. The resulting yellow solution was exposed to sunlight and refluxed for 2 h in a round bottom flask attached with a water condenser, a dark orange precipitate was obtained. The completion of the reaction was tested by TLC. TLC was done using n-hexane and acetone in the ratio 8:2. The obtained product was filtered under suction, cleaned using ethanol, recrystallized using ethanol as solvent, and further dried over silica gel. The compound obtained had a pleasant fragrance. The reaction is given below.

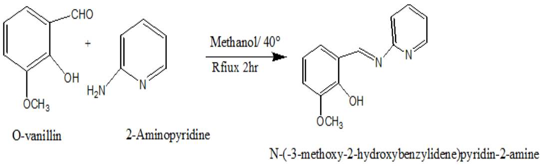

Fig. 1. Reaction of Schiff base synthesis

### Synthesis of metal complexes Synthesis of Co [L4] complex

Solution of Cobalt chloride ($Co(OAc)_2.6H_2O$), (0.5984 g, 2.5mmol) in 20 mL methyl alcohol was added to (0.76 g, 5mmol) of Schiff base ligand(L4). The mixture was refluxed in a 250 mL round bottom flask for two hours. The complex was allowed to precipitate. A blue coloured precipitate was obtained that was filtered and washed with ethanol and then dried in the oven at 50⁰C. Further, it was dried for analysis.[7] The complexes of Ni(II) and Cu(II) were prepared similarly by using ($Ni(OAc)_2.6H_2O$) and ($Cu(OAc)_2.6H_2O$) respectively.

## RESULT AND DISCUSSION

All compounds are inert at room temperature and have a sharp MP that indicates the purity of the compound. The elemental analysis of compounds cooperating with the composition suggested for compounds, colour, yield, melting point, and percentage of composition of C, H and N are given in Table 1.

**Table 1: The analytical and physical data of Schiff base ligand and its metal complexes**

| Compounds | Formula | M.W. g/mol | Colour | Yield % | m.p. ⁰C | μeff B.M. | Elemental Analysis C | H | N | M |
|---|---|---|---|---|---|---|---|---|---|---|
| (L4) | $C_{13}H_{12}N_2O_2$ | 198.24 | Dark orange | 73 | 80-82 | - | 68.32<br>(68.43) | 5.42<br>(5.26) | 12.18<br>(12.28) | - |
| $Co(L4)_2$ | $C_{26}H_{22}N_4O_4Co$ | 513.38 | Blue | 82 | 316-317 | 3.85 | 60.71<br>(60.82) | 4.30<br>(4.32) | 10.80<br>(10.91) | 11.88 |
| $Ni(L4)_2$ | $C_{26}H_{22}N_4O_4Ni$ | 513.14 | Light green | 49 | >3oo | 2.8 | 60.69<br>(60.85) | 4.28<br>(4.32) | 10.87<br>(10.92) | 11.44 |
| Cu(L4) | $C_{13}H_{13}O_3N_2ClCu$ | 344.23 | Deep blue | 67 | - | 1.94 | 45.30<br>(45.35) | 3.80<br>(3.81) | 8.10<br>(8.14) | 18.46 |

**Table 2: Conductance study**

| Compounds | Co(L4)$_2$ | Ni(L4) | Cu(L4) |
|---|---|---|---|
| Ω (DMSO) Scm$^2$mol$^{-1}$ | 15.33 | 19.92 | 16.08 |

Molar conductance value for complexes ranges from 15.33 to 19.92 Scm$^2$mol$^{-1}$ which predicts the non-electrolyte type behavior of Schiff base complexes in DMSO. The higher value is due to steric factors and donor behavior. The conductance behavior of metal complexes is different from those of p-block elements like Te show weak electrolytic nature.

**Table 3: IR Spectra of Compound**

| Compounds | μ(O-H) cm$^{-1}$ | μ(C=N) cm$^{-1}$ | μ(-OCH$_3$) cm$^{-1}$ | Pyridine (C-N-C) | μ(M-N) cm$^{-1}$ | μ (M-O) cm$^{-1}$ |
|---|---|---|---|---|---|---|
| (L4) | 3355 | 1675 | 1299 | 1475 | - | - |
| Co(L4)$_2$ | - | 1661 | 1232 | 1450 | 496 | 521 |
| Ni(L4)$_2$ | - | 1500 | 1320 | 1495 | 481 | 575 |
| Cu(L4) | - | 1550 | 1310 | 1500 | 470 | 578 |

The stretch vibration due to the hydroxyl group in the ligand was found at 3355 cm$^{-1}$ which is absent in all complexes and shows the formation of the O-M bond by deprotonating the hydroxyl group. The strong band between 1500-1675 cm$^{-1}$ is due to ν(-HC=N) showing a slight decrease in IR value than free ligand indicates metal nitrogen bond formation coordinating through the nitrogen of azomethine. The bands observed in the complexes' spectra at 470-496 cm$^{-1}$ and 521578 cm$^{-1}$ region are due to ν(M-N) and ν(M-O) bonds respectively. The value above 300 cm$^{-1}$ in the complexes for aromatic compounds. The value is between 2800-2900 cm$^{-1}$ for metal chelates in all complexes. The spectral value shows in Table 3. The ν(C-N-C) strong band at 1462 cm$^{-1}$ upon complexation, shifts to a higher frequency which is due to coordination with the nitrogen atom of the pyridine ring.

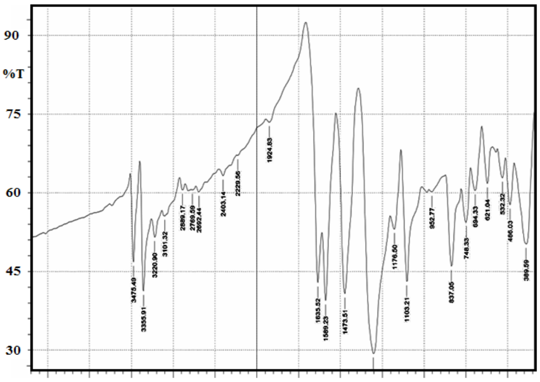

Fig. 2. FT-IR Schiff base

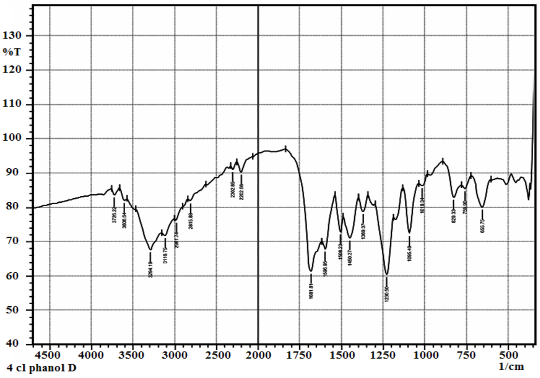

Fig. 3. FT-IR Co(II) complex

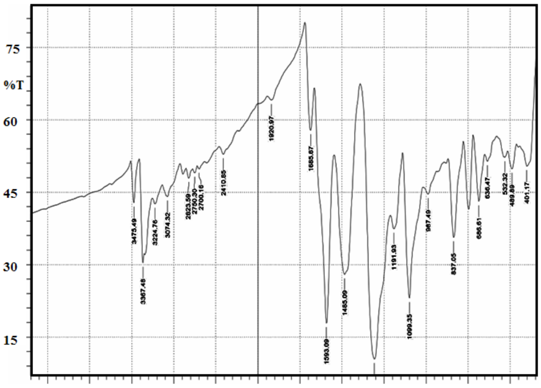

Fig. 4. FT-IR of Ni(II) complex

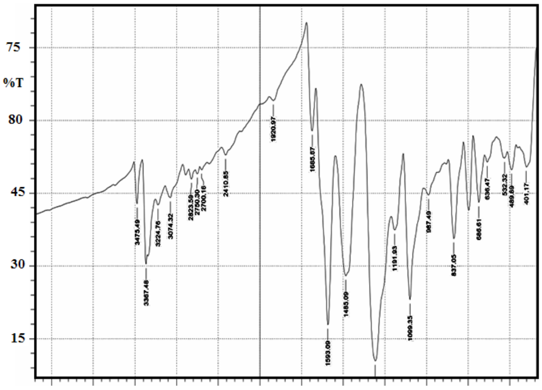

Fig. 5. FT-IR Cu(II) complex

**Table 4: $^1$H-NMR spectra**

| Compounds | Phenolic OH δppm | Azomethine HC=N) δppm | At ring proton δppm | -$OCH_3$ |
|---|---|---|---|---|
| (L4) | 11.65(s,1H) | 8.75(d,1H) | 6.98 (m,7H) | 3.68(s,3H) |
| Co$(L4)_2$ | - | 7.52(s,1H) | 6.85-7.91(m,7H) | 3.81(s,3H) |
| Ni$(L4)_2$ | - | 7.37(s,1H) | 6.83-8.31(m,7H) | 3.99(s,3H) |
| Cu(L4) | - | 7.53(s,1H) | 6.83-8.09(m,7H) | 3.92(s,3H) |

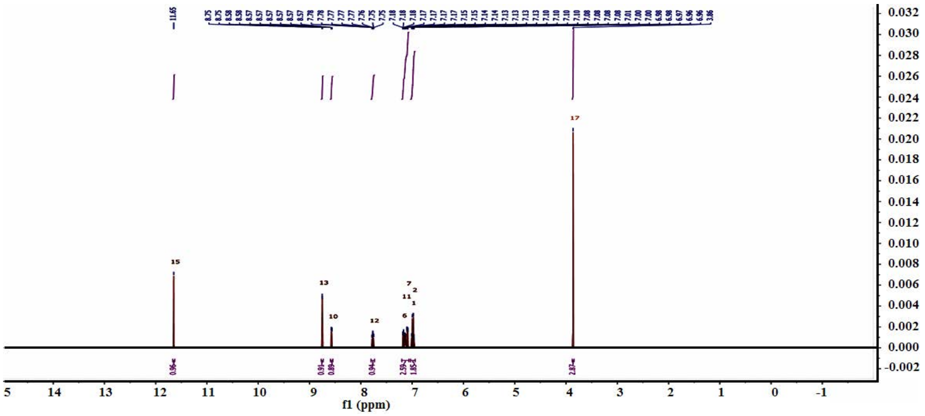

Fig. 6. $^1$H-NMR of Schiff base

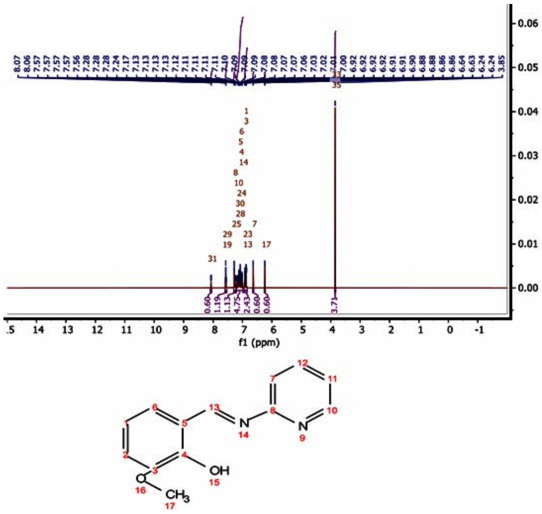

Fig. 7. $^1$H-NMR of Cu(II) complex

The $^1$H-NMR spectrum of the ligand displayed a signal by 8.75 ppm in free ligand for azomethine proton which shift to lower values after complex formation at 7.52 ppm, 7.37 ppm and 7.53 ppm for Ni(II), Co(II), Cu(II) respectively. The multiple corresponds to aromatic protons that appeared between 6.83-8.51 ppm are given to aromatic protons. The hydroxyl proton of ligand looks at 11.65 ppm which disappears in the complexes and indicates that the OH group has been deprotonated and bonded to the metal ion. Signal displays a downfield shift from 8.86 to 7.23 ppm suggesting the decrease of electron density and deshielding of azomethine proton as a result of which nitrogen of azomethine group coordinates to the metal atom.

## Electronic spectra

The electronic spectrum provides the information regarding the electronic atmosphere of the metal; The electronic spectra are resolved in DMF i.e. (dimethyl formamide) The spectra were observed i.e.(10,000-50, 000 $cm^{-1}$) The intensive bands at 42194 $cm^{-1}$, 37037 $cm^{-1}$ and 29850 $cm^{-1}$ suggested the presence of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. This $\pi \rightarrow \pi^*$ transition is transferred to a longer wavelength resulting from coordination to metal, confirming the formation of Schiff base metal complexes. Various bands are grouped into the range between 210-245nm, 280-290nm, 302372nm, and 421nm. The first and second band is due to the π to π* transition of benzene & the band above 400nm displayed by Schiff base is attributed to imino $n \rightarrow \pi^*$[6,7] The keto-enol tautomer of Schiff base is implied by the presence of these bands in methanol. The transition of these complexes shifted to a higher wavelength. All the maxima were observed due to the charge transfer band. The donation of lone pairs of a nitrogen atom (N→M) or oxygen atom (O→M) to the metal ion is considered to be the cause of this shift. In the Co(II) complex, the expected band of wavelength 840-960nm has shown low symmetry transition $^4A_2 \rightarrow {}^4T_1(F)$, and the band at 500-600nm has shown $^4A^2 \rightarrow {}^4T_1(P)$ transition which suggested the distorted tetrahedral geometry[7]. In the electronic spectra of the Cu(II) complex which is square planar, the transitions are $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2{}_{Eg}$ with particular absorption at 515-525nm and 645655 nm which was due to John Teller distortion (J-T)[6,8,17]. square planar complexes showed a broad absorption peak at 600-700nm, & the peak at 515-520nm merged with the broadband thus only a single band was observed[13]. One strong band at 555nm was displayed by the Ni(II) complexes. This is allocated to the square planar $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. This transition value lies within the range of 600-450nm which is responsible for the green color[18].

### Magnetic measurement

The value of magnetic moment (B.M.) of all metal(II) complexes was obtained at room temperature. The value of an observed magnetic moment of Co(II) complexes was seen in the range of 4.32-4.68 B.M. which signified three unpaired electrons in a tetrahedral atmosphere.[11] The value of a magnetic moment of the Ni(II) complex was 3.39-3.55 B.M. suggesting two unpaired electrons suggesting the square planar geometry. The measured magnetic moment value at 1.931.97B.M. for Cu(II) indicates one unpaired electron.

The study of the antibacterial activity of the ligand and its complexes was done using two antibacterial drugs including Streptomycin and ampicillin against two *Gram-positive* (*S. aureus* and *B. substilis*) and two *Gram-negative* (*E. coli* and *Pneumonia*). The results show that the antibacterial activity of metal complexes is improved than ligand[18]. This is due to changes in the structure due to the chelating and coordination trend to make metal complexes perform more powerful. The value of an antibacterial activity is given in Table 5.

**Table 5: Antibacterial activity**

| Name of compounds 1000 μg/mL | Inhibition zone | | | |
|---|---|---|---|---|
| | *Gram-positive* bacteria | | *Gram-negative* bacteria | |
| | *Staphylococcus aureus* | *Bacillus substillis* | *Escherichia coli* | *Klebsiella pneumonia* |
| Ligand | - | - | 13 | 12 |
| $Co(L5)_2$ | 14 | 11 | 15 | 1 9 |
| $Ni(L5)_2$ | 13 | 13 | 17 | 25 |
| $Cu(L5)_2$ | 7 | 6 | 15 | 1 8 |

## CONCLUSION

This part is used to discuss the results obtained from all the techniques used in characterizing the isolated Schiff base Synthesized from o-Vanillin and its metal complexes of Co(II), Ni(II), and Cu(II). The discussion will focus on some of the observed shrinking behaviours of the various synthesized ligands and complexes. The reaction of Schiff bases with transition metal compounds leads to different complexes. The most common of these is the inner sphere complex in which Schiff base bonded to metal atom through the oxygen atom of its deprotonated hydroxyl group and the nitrogen atom of its -C=N groups. That is those in which ligand binds as diatonic $N_2O_2$ donor system. All the complexes obtained possess tetrahedral geometry for Co, Ni, and square planar for Cu metals. The conclusions are based on Elemental analysis, IR, NMR, electronic spectra, and microanalysis results.

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### Conflict of interest

Authors do not have a conflict of interest with each other.

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