

SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, ELECTROCHEMICAL AND ANTIMICROBIAL STUDIES OF COPPER (II), NICKEL (II), COBALT (II), ZINC (II) AND OXOVANADIUM (II) COMPLEXES DERIVED FROM NAPHTHYLIDENE-4-AMINOANTIPYRINE AND TRYPTOPHAN

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ABSTRACT: Neutral tetradentate N_2O_2 complexes of Cu(II), Ni(II), Co(II), VO(II) and Zn(II) have been synthesized from naphthylidene-4-aminoantipyrine and tryptophan. All the complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility data, IR, ¹H-NMR, UV-Vis., FAB-Mass and ESR spectral studies. The physico-chemical studies and spectral data indicate that the ligand act as a divalent tetradentate chelating agents. All the complexes have the general composition [ML] (where, M= Cu(II), Ni(II), Co(II), VO(II) and Zn(II), L = Schiff base). The IR, UV-Vis., magnetic susceptibility and ESR spectral data of the complexes suggest that all the complexes are square planar geometry around the central metal ion except VO(II) complexes which exhibit square pyramidal geometry. The lower conductance data confirms the non-electrolytic nature of the complexes. The effect of redox potential on metal ion by the ligand environment is studied by cyclic voltammetric measurements. These redox studies of copper complexes suggest that the ligand system stabilises the unusual oxidation states Cu(III), Cu(I) and Cu(0) under electrochemical condition. The Schiff bases and their metal complexes are utilized to test the *in vitro* antimicrobial activities, which give good results in the presence of metal ion than the free ligand environment against the different species of microorganisms.

KEYWORDS: naphthylidene-4-aminoantipyrine, tryptophan, Cyclic Voltammetric measurements, Neutral tridentate N_2O_2 complexes.

I. INTRODUCTION

The transition metal complexes of 4-aminoantipyrine and its complexes have been extensively examined due to their wide applications in various fields like biological, pharmacological, clinical, analytical and industrial area. These ligands have been playing an important part in the development of coordination chemistry as they easily form stable complexes with most of the transition metal ions. The interaction of these donors and metal ion give complexes of different geometries and these complexes are potentially biologically active. Schiff base complexes of transition metals containing ligands with N,O- donors play an essential role in agricultural, pharmaceutical, industrial chemistry, antifungal, antibacterial, anticancer and catalytic activities. Schiff bases itself have some antimicrobial activities which have been further enhanced by chelating it with metal ion. Earlier works reported that some drugs show the increased activity when administrated as metal chelates rather than as organic compounds [1-10]. The coordinating property of

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4- aminoantipyrine has been modified into a flexible ligand system by condensing with a variety of reagents like aldehydes, ketones, thiosemicarbazides, carbazides, etc. More recent literature reveals that very little work has been done on the condensation of 4-aminoantipyrine derivatives with semicarbazide/thiosemicarbazide [11-15] . But no work has been done on the reaction of carbonyl group present in the pyrazolone ring with amino acids. In this chapter, we report new ligand systems by using naphthylidene-4-aminoantipyrine and tryptophan.

II.MATERIAL AND METHODS

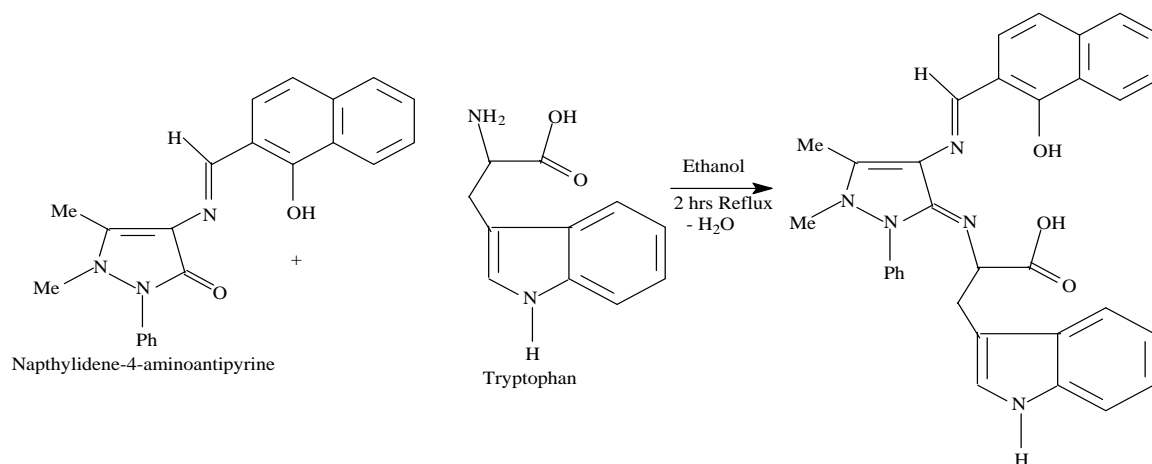
2.1 Materials

All the reagents, 4-aminoantipyrine, tryptophan and the metal salts were purchased from Merck. Melting point of the ligand and complexes were determined on electrochemical capillary apparatus. Elemental analysis was obtained by using a thermal finger- flash CA, 112 series at sophisticated analytical instrumentation facility, IIT, Mumbai. The IR spectra of the samples were recorded on a FT- IR shimadzu model (8400S) in a KBr pellets and electronic spectra in acetonitrile were recorded using Shimadzu model (1800) spectrophotometer. Conductivity measurements were carried out at room temperature on freshly prepared 10^{-3} M acetonitrile solution was measured using a 305 model systronic conductivity bridge with a dip type cell. ^1H NMR spectra of the Schiff base and its zinc complex were recorded in CDCl_3 solution on a Bruker 300 MHz FT-NMR spectrometer using TMS as internal standard at Madurai Kamaraj University, Madurai. Cyclicvoltammogram of the complexes was recorded in MeCN solution at 300 K using BASCV 50 electrochemical analyzer. CV measurements were performed using a glassy carbon working electrode, platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Tetrabutyl ammonium bromide was used as supporting electrolyte. The X-band ESR spectra of the copper complex in MeCN solution at 300 K and 77 K using TCNE (Tetracyanoethylene) as the g – marker were recorded on a Varian E-112 ESR spectrometer at Sophisticated Analytical Instrumentation facility, IIT, Mumbai. Magnetic susceptibility of the complexes was measured by Guoy balance using copper sulphate as calibrant. The antimicrobial activities of the ligand and their complexes were carried out by disc diffusion method.

2.2 Synthesis of Schiff base

An ethanolic solution (50 ml) of naphthylidene-4-aminoantipyrine (3.07 g, 0.01 mol) and tryptophan (2.04 g, 0.01 mol) was boiled under reflux on a water bath for 2 hrs. Then the resulting solution was concentrated to 10 ml and stirred with 5 ml of (30 %) ammonia solution. The solid obtained was collected by filtration and recrystallised from ethanol. The Schiff base derived by the condensation of naphthylidene-4-aminoantipyrine and tryptophan is given in the following scheme I .

Scheme I :



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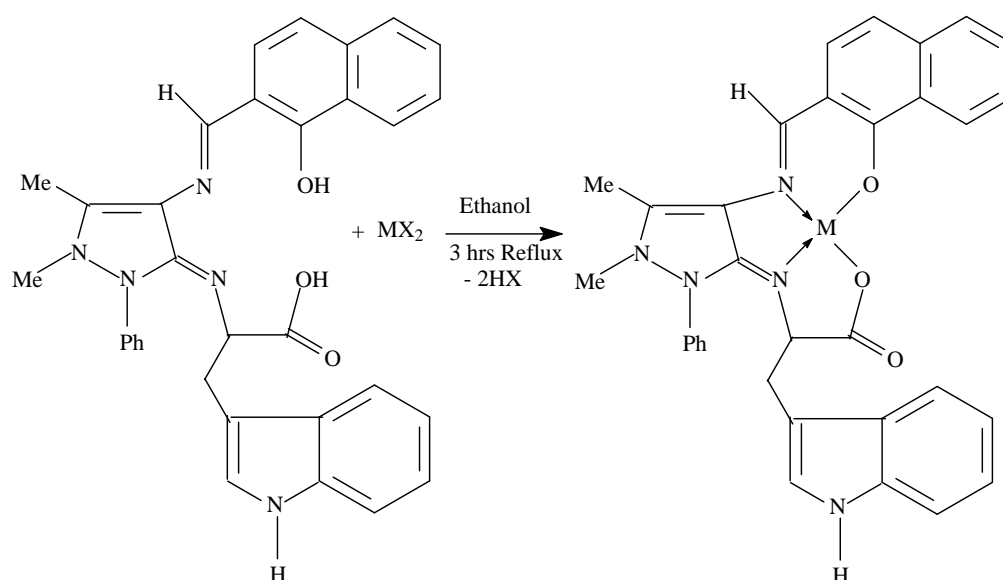
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2.3 Synthesis of metal complexes

An ethanolic solution of $\text{CuCl}_2/\text{NiCl}_2/\text{CoCl}_2/\text{ZnCl}_2/\text{VOSO}_4$ (0.05 mol) salts and 0.05 mol of Schiff base was stirred for 3 hrs under reflux and then concentrated to 10 ml. The mixture was cooled at room temperature for 12 hrs and the precipitated complexes were filtered, washed and recrystallised from ethanol. The preparations of the above metal complexes are given by the following scheme II.

Scheme II :



Where, $M = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Zn(II)}$ and VO(II)

III RESULTS AND DISCUSSION

The analytical data of the ligand and their complexes together with some physical properties are summarized in Table 3.1. The analytical data of the complexes correspond well with the general formula $[\text{ML}]$, where, $M = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Zn(II)}$ and VO(II) ; L is Schiff base. The magnetic susceptibility data of the complexes in the solid state shows that $\text{Cu(II)}, \text{Co(II)}$ and VO(II) are paramagnetic and Ni(II) & Zn(II) are diamagnetic at room temperature. The lower conductivity values of the chelate support their non-electrolytic nature [16].

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Table 3.1 The % of yield, melting point, colour, analytical, molar conductance and magnetic susceptibility data of the compounds.

| Compound | Yield(%) | Melting/Decomp. Point (°C) | Color | Found (Calcd) (%) | | | | $\Lambda_M \times 10^{-3}$ (mho cm ² mol ⁻¹) | $\mu_{\text{eff.}}$ (B.M.) |
|----------|----------|----------------------------|-------|-------------------|------------------|----------------|------------------|---|----------------------------|
| | | | | M | C | H | N | | |
| HL | 75 | 125 | Red | - | 72.13 (72.93) | 5.31 (5.43) | 12.43 (12.89) | - | - |
| CuL | 68 | 232 | Green | 10.84 (10.51) | 64.61 (65.5) | 4.86 (4.47) | 11.68 (11.58) | 0.32 | 1.78 |
| NiL | 72 | 168 | Green | 9.08 (9.79) | 66.01 (66.03) | 4.91 (4.50) | 11.92 (11.67) | 0.21 | - |
| CoL | 74 | 197 | Brown | 9.11 (9.82) | 66.18 (66.01) | 4.28 (4.50) | 11.78 (11.67) | 0.42 | 3.94 |
| VOL | 69 | 241 | Green | 8.01 (8.38) | 65.18 (65.14) | 4.21 (4.44) | 11.68 (11.51) | 0.31 | 1.80 |
| ZnL | 70 | 179 | Red | 10.62 (10.83) | 65.18 (65.27) | 4.13 (4.45) | 11.96 (11.54) | 0.66 | - |

3.1 MASS SPECTRA

The mass spectra of Schiff base HL and its copper complex show a molecular ion peak at 543 and 605 respectively. These data are in good agreement with the proposed molecular formula for copper complex *i.e.*, [CuC₃₃H₂₇N₅O₃]. In addition to molecular ion peak, the spectra exhibited peaks assignable to various fragments arising from the thermal cleavage of the ligand and its complex.

3.2 ¹H-NMR SPECTRA

The ¹H-NMR spectra of the Schiff base and its zinc complexes were recorded in CDCl₃ solution. The ¹H-NMR spectrum of the Schiff base shows two peaks at 8.62 ppm and 10.92 ppm which are attributable to the –OH group of 2-hydroxy naphthaldehyde and –COOH group of tryptophan moiety respectively. Absence of these two peaks in the Zinc complex which favours the loss of phenolic –OH and –COOH proton due the coordination with zinc ion. A slight down field shift was noted in all other signals in the zinc complex. ¹H-NMR spectra of Schiff base and its zinc complex are given in Figure 3.1.

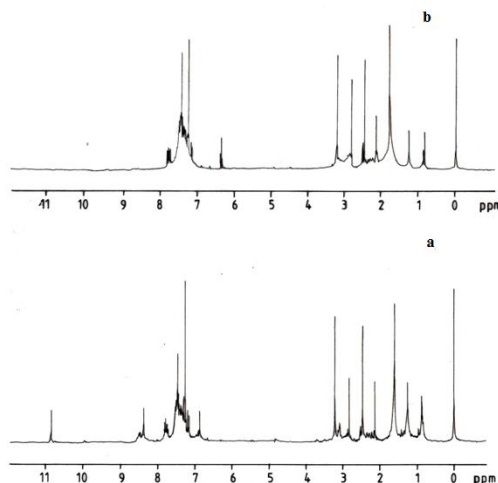


Figure: 3.1 ¹H-NMR spectra of Schiff base (a) and its zinc complex (b) in CDCl₃ solution

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3.3 IR SPECTRA

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The IR spectra of the ligands and their complexes are shown in Figure 3.2. IR spectra of the ligand shows a merged strong band at 3500- 3000 cm^{-1} region which is assigned to phenolic -OH group of naphthaldehyde and -COOH group of tryptophan moiety. Disappearance of this band indicates the deprotonation of these groups upon coordination. IR spectra of all the complexes shows a new strong band at 3150 cm^{-1} region which are assigned to cyclic -NH- group of tryptophan moiety and the same peak is also appeared in the IR spectrum of ligand as a weak node due to merging of -OH groups. It indicates that there is a free existence of this group and not involved in coordination with metal ion. In the spectra of the Schiff bases also show a strong bands at 1615 - 1600 cm^{-1} region which are attributable to -C=N groups. On chelation, due the possible drift of lone pair electron density towards the metal ion, the azomethine -C=N band is expected to absorb at lower frequency in the complex. The observed bands at 1591 - 1550 cm^{-1} region indicate the coordination of azomethine nitrogen atoms to the metal ion. Moreover, the Schiff base and their complexes exhibit an intense peak at 1645 cm^{-1} , a characteristic feature of the -C=O stretching frequency indicating the existence of -C=O of acid group in tryptophan moiety. IR spectra of the complexes also show a new peaks at 510 cm^{-1} and 430 cm^{-1} region due to the formation of M-N and M-O bonds respectively. In addition to other bands, the vanadyl complexes show their characteristic V=O frequency at 960 cm^{-1} region [17-19].

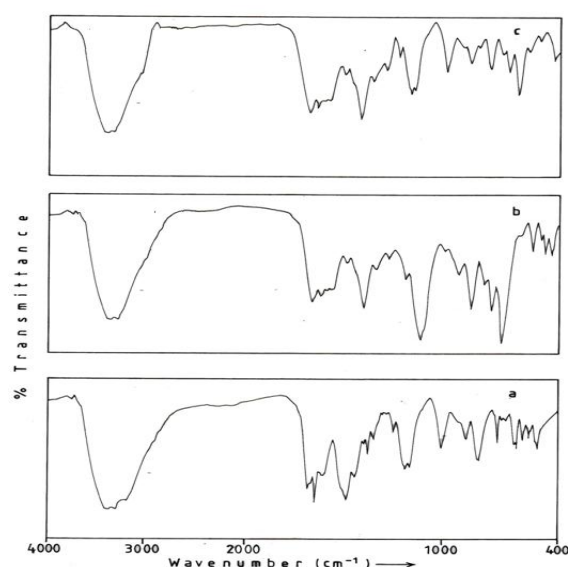


Figure: 3.2 IR spectra of the Schiff base (a), copper complex (b) and vanadyl complexes (c).

3.4 ELECTRONIC ABSORPTION SPECTRA

The electronic spectra serves as a useful tool to distinguish between the square planar, octahedral and tetrahedral geometries of the complexes. The absorption regions, assignments and the proposed geometry of the complexes are shown in Table 3. 2. [20]

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Table : 3.2 Electronic absorption spectral data of the Schiff bases and their complexes in MeCN solution at 300 K.

| Compound | Absorption region (nm) | Band assignment | Geometry |
|----------|--------------------------|---|------------------|
| HL | 312 | INCT | - |
| CuL | 290 459 854 | INCT ${}^2B_{2g} \rightarrow {}^2B_{1g}$ ${}^2B_{2g} \rightarrow {}^2A_{1g}$ | Square planar |
| NiL | 235 & 275 605 | INCT ${}^1A_{1g} \rightarrow {}^1B_{1g}$ | Square planar |
| CoL | 301 678 | INCT ${}^1A_{1g} \rightarrow {}^1T_{1g}$ | Square planar |
| VOL | 295 482 673 865 | INCT ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2E$ ${}^2B_2 \rightarrow {}^2A_1$ | Square pyramidal |

3.5 ELECTROCHEMICAL STUDY

Cyclic voltammogram of copper complex was recorded in MeCN solution using tetrabutylammonium bromide as supporting electrolyte. The scan rates were varied from 25 to 100 mVs^{-1} . Several peaks were observed in the cathodic and anodic sections of the cyclic voltammogram. The plot of peak currents of all the peaks was correlated with the square root of the sweep rate, resulting in a straight line in all the complexes. This demonstrates the diffusion controlled mass transport.

The cyclic voltammogram of the complexes in MeCN solution at room temperature (Figure 3.3) shows a reversible peak for the couple: $\text{Cu(II)} \rightarrow \text{Cu(III)}$ with the direct cathodic peak for $\text{Cu(III)} \rightarrow \text{Cu(II)}$. Further, it exhibits two irreversible peaks characteristic for $\text{Cu(II)} \rightarrow \text{Cu(I)}$ and $\text{Cu(I)} \rightarrow \text{Cu(0)}$ reduction. In the anodic side, the direct oxidation of $\text{Cu(0)} \rightarrow \text{Cu(II)}$ is observed with a strong stripping peak. The two-electron transfer nature of the process is established by the comparison of I_{p_c} and I_{p_a} values. The cyclic voltammogram data of copper complexes are summarised in Table 3.3.

Table 3.3 The cyclic voltammetric data of copper complex in MeCN (2×10^{-3} M) solution containing 0.1 M TBAB at 300 K with scan rate 100 mVs^{-1} .

| Complex | Couple | E_{p_a} (V) | E_{p_c} (V) | I_{p_a} (μA) | I_{p_c} (μA) |
|----------------|--|---------------|---------------|-----------------------------|-----------------------------|
| Copper complex | Cu(II)/Cu(III) | 0.56 | 0.52 | 46.81 | -42.22 |
| | $\text{Cu(II)} \rightarrow \text{Cu(I)}$ | -- | -0.34 | -- | -35.61 |
| | $\text{Cu(I)} \rightarrow \text{Cu(0)}$ | -- | -0.83 | -- | -18.83 |
| | $\text{Cu(0)} \rightarrow \text{Cu(II)}$ | -0.15 | -- | 54.62 | -- |

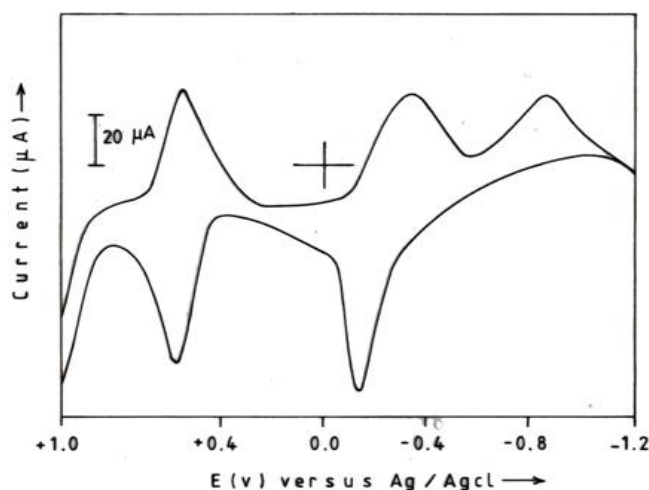


Figure 3.3 The cyclic voltammogram of the copper complex in MeCN solution (0.1 M TBAB) (Scan rate 100 mVs^{-1}).

3.6 ESR SPECTRA:

The X-band ESR spectra of copper and vanadyl complexes in MeCN solution at a concentration of *ca.* 0.1 M were recorded at 300 K and 77 K. The spectra of copper complexes at 300 K and 77 K are shown in Figure 3. 4 and 3. 5

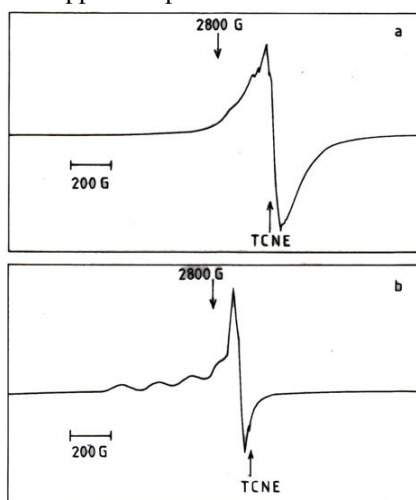


Figure 3.4 The ESR spectra of copper complex at 300 K (a) and 77 K (b) in MeCN solution.

The spectra of the copper complex at 300 K show one intense band in the high field region, which are isotropic due to tumbling motion of the molecules. However this complex at 77 K shows well-resolved peaks with low intensities in the parallel region and one intense peak in perpendicular region. The absence of a half field signal at 1600 G corresponding to the $\Delta M_s = \pm 2$ transition, rules out any Cu-Cu interaction in the ESR spectrum.

The ESR parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} were determined from the anisotropic spectra of the frozen solution (magnetically diluted solids). The g tensor values of the copper complexes can be used to derive the ground state. In square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ${}^2B_{1g}$ as the ground state with $g_{\parallel} > g_{\perp} > 2$, while the unpaired electron lies in the d_z^2 orbital giving ${}^2A_{1g}$ as the ground state with $g_{\perp} > g_{\parallel} > 2$.

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Table 3.4 The spin Hamiltonian parameters of copper and vanadyl complexes in MeCN Solution at 300 K and 77 K.

| Complex | $A_{ }$ | A_{\perp} | A_{iso} | $g_{ }$ | g_{\perp} | g_{iso} | α^2 | β^2 | γ^2 |
|-----------------|---------------------------------|-------------|-----------|----------|-------------|-----------|------------|-----------|------------|
| | $\times 10^{-4} \text{cm}^{-1}$ | | | | | | | | |
| Copper complex | 190 | 77 | 114 | 2.32 | 2.06 | 2.147 | 0.89 | 1.06 | 0.90 |
| Vanadyl complex | 178 | 77 | 111 | 1.98 | 1.94 | 1.95 | 0.85 | 0.98 | 1.1 |

From the observed values it is clear that $A_{||} > A_{\perp}$ and $g_{||} > g_{\perp} > 2$ and the parameters of the complex coincide well with related systems which suggest that the complex has square planar geometry and the system is axially symmetric. Furthermore, this conclusion is also supported by the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital, as was evident from the value of the term G , estimated from the expression:

$$G = g_{||} - 2.0023/g_{\perp} - 2.0023$$

If $G > 4$, the local tetragonal axes are aligned parallel or only slightly misaligned. The observed value for the exchange interaction parameter for the complexes are greater than 4 which suggest that the local tetragonal axes are aligned parallel or slightly misaligned and the unpaired electron is present in the $d_{x^2-y^2}$ orbital. The ESR parameters and the d-d transition energies were used to evaluate the bonding parameters α^2 , β^2 and γ^2 for the Cu(II) ion in various ligand field environments which may be regarded as a measure of the covalence of the in-plane σ -bonds, in-plane π -bonds (β^2) and out-of- plane π -bonds (γ^2) respectively.

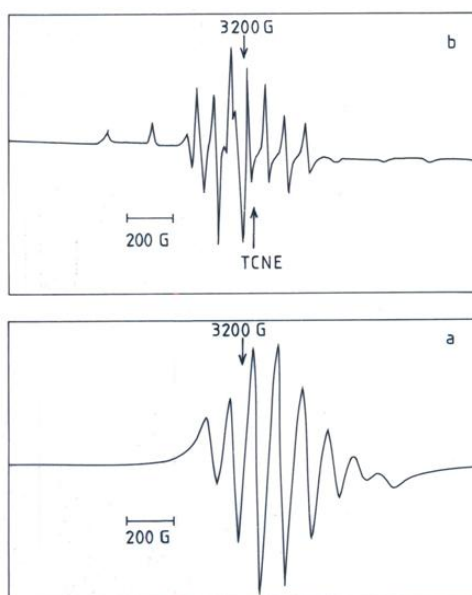


Figure 3.5 The ESR spectra of Vanadyl complex at 300 K (a) and 77 K (b) in MeCN solution.

The room temperature (300 K) spectra is a typical eight line pattern which shows that single vanadium is present in the molecule, *i.e.* it is a monomer. In the frozen solid state, the spectrum shows two types of resonance component: one set due to the parallel features and the other set due to the perpendicular features. It shows an axially symmetric anisotropy with well resolved sixteen-line hyperfine splitting characteristic of an interaction between the electron and the vanadium nuclear spin. The spin Hamiltonian parameters of the vanadyl complexes are summarised in

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Table 3.4. The various parameters calculated from the spectra of the complexes $[A_{\parallel} > A_{\perp}]$ and $[g_{\parallel} > g_{\perp}]$ indicate that the complexes are square pyramidal geometry, characteristic for the oxovanadium(II) chelates.

3.7 BIOLOGICAL SCREENING ACTIVITY

The *in vitro* biological screening effects of the investigated compounds were tested against the various bacteria such as *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* and fungi *Candida albicans* and *Aspergillus niger* by disc diffusion method. The minimum inhibition concentration values of the compounds against the growth microorganisms are summarized the Table 3.5.

Table 3.5 Antimicrobial activities of Schiff bases and their metal complexes (MIC in mg)

| Compound | <i>Escherichia coli</i> | <i>Salmonella typhi</i> | <i>Pseudomonas aeruginosa</i> | <i>Staphylococcus aureus</i> | <i>Starptococci</i> | <i>Candida albicans</i> | <i>Aspergillus niger</i> |
|------------------|-------------------------|-------------------------|-------------------------------|------------------------------|---------------------|-------------------------|--------------------------|
| H ₂ L | 55 | 70 | 65 | 70 | 65 | 75 | 90 |
| CuL | 50 | 60 | 60 | 60 | 60 | 65 | 75 |
| NiL | 55 | 65 | 60 | 60 | 60 | 70 | 85 |
| CoL | 50 | 50 | 50 | 55 | 60 | 70 | 90 |
| VOL | 50 | 65 | 55 | 65 | 55 | 65 | 75 |
| ZnL | 35 | 45 | 45 | 50 | 45 | 45 | 50 |

The MIC (Minimum Inhibitory Concentration) values of the free ligands and their complexes indicate that all the metal chelates have higher antimicrobial activity than the free ligand. Such increased activity of the metal chelates can be explained on the basis of overtone's concept and the Tweedy's chelation theory. According to overtones concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid soluble material due to lipophilicity is an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a great extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion which donor groups [20-24]. Further, it increases the delocalisation of the π -electrons over the whole chelate ring and enhances the lipophilicity of the complex. The results are also presented as bar graphs (Fig 3.6)

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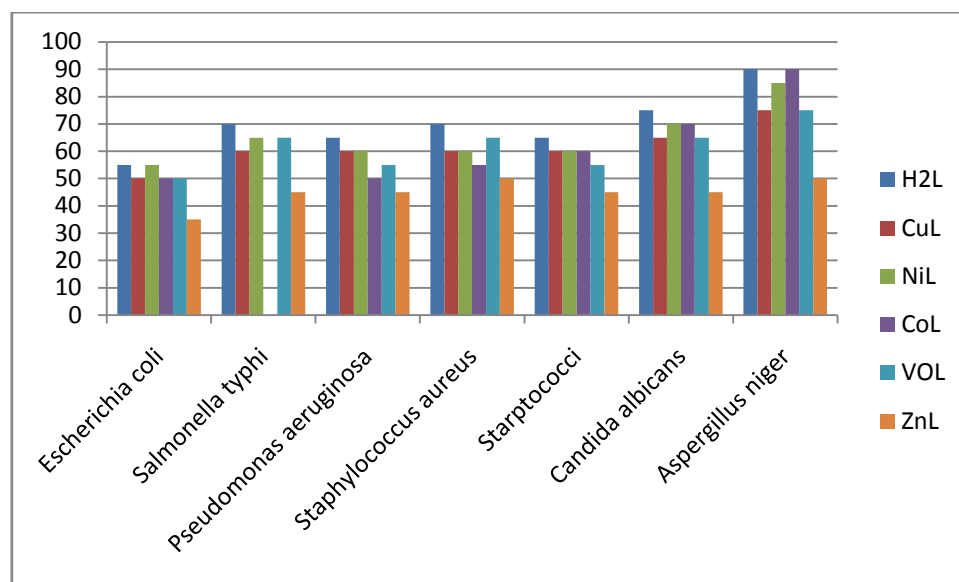


Figure 3.6 antimicrobial activities of the Schiff base complexes against bacterial and fungal pathogens

This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocks the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restrict further growth of the organism. Furthermore, the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in interference with the normal cell process. Comparatively zinc complex shows higher activity than all other complexes due to its higher lipid solubility.

IV.CONCLUSION

A Schiff base of naphthylidene-4-aminoantipyrine with tryptophan and their metal complexes of Cu(II), Ni(II), Co(II), Zn(II) and VO(II) were synthesized and structure was characterized using spectroscopic techniques. The metal complexes formed were non electrolytic in nature. Schiff base behaves as a tetra dentate ligand and is coordinated to the central metal ion through the azomethine. The metal complexes Cu(II), Ni(II), Co(II) and Zn(II) were square planar geometry except VO(II) complex has square pyramidal geometry. The biological activity of the complexes is higher than the free Schiff base.

V ACKNOWLEDGMENTS

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