



Designing, structural, redox and biological investigation of copper(II), nickel(II), cobalt(II), Zinc(II) and vanadium(IV) complexes derived from 1-phenyl-2,3-dimethyl-4-imino-(3-oxo-N-phenylbutamide)-pyroazol-5-(a-imino)-indole-3-propionic acid.

Thavuduraj Kavitha^{1*}, Antonysamy Kulandaisamy² and Ponnusamy Thillaiarasu³

¹Department of Chemistry, Sri Ramasamy Naidu Memorial College, Sattur - 626203, India.

²Department of Chemistry, Raja Doraisingam Government Arts College, Sivagangai – 630561, India.

³Department of Chemistry, Kalasalingam University, Krishnan koil - 626190, India.

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ABSTRACT

A Schiff base namely tetradentate N_2O_2 donor has been prepared by condensation of acetoacetanilido-4-aminoantipyrine and 5-(α -imino)-indole-3-propionic acid (tryptophan) in 1:1 molar ratio. Copper(II), Nickel(II), cobalt(II), Zinc(II) and VO(II) complexes of this Schiff base have been synthesized and characterized by elemental analysis, molar conductance, Magnetic measurements, IR, UV- Vis., ¹H- NMR, FAB Mass, and ESR spectral data. The IR data show that the ligand is coordinated to the metal ion in a tetradentate manner with N_2O_2 donor site of the enolic –OH group, carboxylate oxygen and two azomethine nitrogen. Magnetic measurements and electronic spectral data of the chelates suggested that all the complexes are square planar geometry except VO(II) complex which has square pyramidal geometry. ¹H-NMR spectra of the Schiff base and its zinc complex reveal that carboxylate proton of amino acid and enolic hydroxyl proton of acetoacetanilido-4-aminoantipyrine moiety were displaced during complexation. The ligand and the metal complexes were evaluated for antibacterial and antifungal activities against various bacterial and fungal strains. The results showed that all the chelate have better activity than the free ligand.

KEYWORDS: Biological screening studies, Cyclic voltammogram, ESR spectra, acetoacetanilido-4-aminoantipyrine, Tryptophan.

INTRODUCTION:

The Schiff base and their metal complexes derived from 4-aminoantipyrine are more important because of their applications in biological, biochemical, anticancer, analytical, catalysis, food industry, dye industry, and antimicrobial activity. Additionally, tetradentate Schiff bases composed of N_2O_2 donor atoms are very important chelating ligands for designing medicinally and catalytically useful metal chelates¹⁻⁶. Amino acids play an important role in many physiological activities of the human body and also helpful in understanding biological functions of macromolecules such as proteins. In particular histidine and tryptophan amino acids analogues are useful in antimicrobial therapeutics⁷. A careful literature survey reveals that Schiff bases derived from tryptophan and acetoacetanilido-4-aminoantipyrine and their coordination behavior towards the transition metals have yet not been studied⁸⁻²⁰. Here, we report that the synthesis, characterization, redox and antimicrobial studies of transition metal complexes containing Schiff base derived from acetoacetanilido-4-aminoantipyrine and tryptophan. The metal com-

plexes have shown moderate to good antibacterial activity against gram positive, gram negative bacteria and fungi.

MATERIAL AND METHODS:

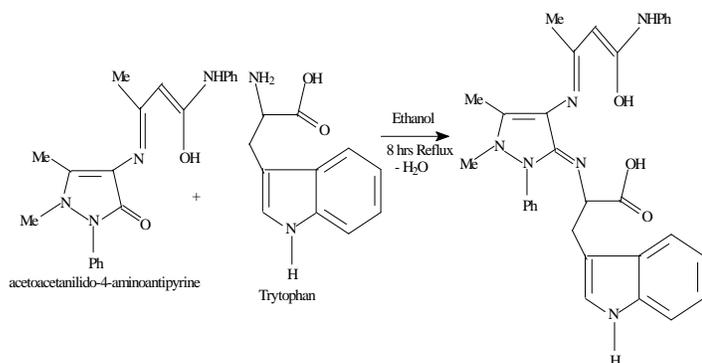
All the reagents, 4-aminoantipyrine, acetoacetanilide, tryptophan and the metal salts were purchased from Merck. Melting points of ligands and complexes were determined on electrochemical capillary apparatus. Elemental analysis was obtained by using a thermal finger- flash CA, 112 series at sophisticated 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. Cyclic voltammogram of the complexes was recorded in MeCN solution at 300 K using BAS CV 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 elec-

*Corresponding author.

Thavuduraj Kavitha
Department of Chemistry,
Sri Ramasamy Naidu Memorial College,
Sattur - 626203, India.

trolyte. The X-band ESR spectra of the copper and vanadyl complexes 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.

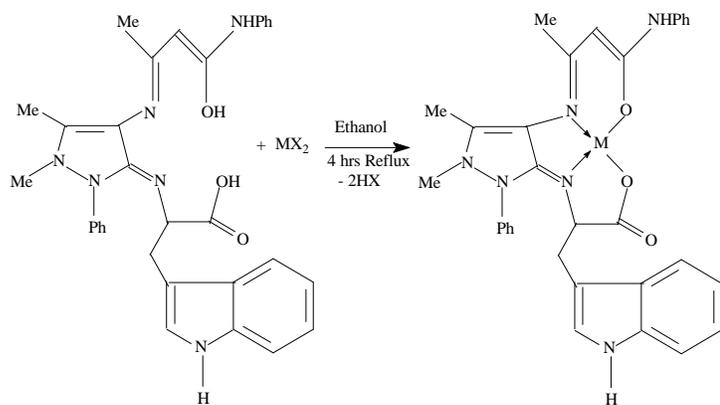
Synthesis of Schiff base (H₂L): An ethanolic solution (50 mL) of acetoacetanilido-4-aminoantipyrine (3.62 g, 0.01 mol) and tryptophan (2.04 g, 0.01 mol) was boiled under reflux on a water bath for 8 h. Then the resulting solution was concentrated to 10 mL and stirred with 5 mL of (30 %) ammonia solution. The solid obtained was collected by filtration and recrystallised from ethanol. The scheme for the synthesis of Schiff base is given below:



Scheme 1

Synthesis of complexes

An ethanolic solution of CuCl₂/NiCl₂/CoCl₂/ZnCl₂/VOSO₄ (0.05 mol) and Schiff base (0.05 mol) was stirred for 4 h and then concentrated to 10 mL. The mixture was cooled at room temperature for 12 h and the precipitated complexes were filtered, washed with ethanol and dried. The reaction scheme for the synthesis of Schiff base is given below



Where, MX₂ = CuCl₂ or NiCl₂ or CoCl₂ or ZnCl₂ or VOSO₄

Scheme 2

Procedure for antimicrobial activity

In vitro antimicrobial activity of the Schiff base and its chelates was performed by disc diffusion method using nutrient agar as medium for bacteria and potato dextrose agar as medium for fungi respectively. The Schiff base and its metal complexes were tested against bacteria such as *Escherichia coli*, *salmonella typhi*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* and fungi *Aspergillus niger* and *Candida albicans*. The stock solutions were prepared by dissolving the compounds in MeCN and the solutions are serially diluted in order to find the minimum inhibitory concentration values (MIC). All the blank discs were moistened with the solvent. For disc assays, the compounds containing disc (6 mm) with various concentrations were placed on the surface of the nutrient agar plate previously spread with 0.1 ml of overnight culture of microorganisms. Then, the plates were incubated at 37 °C for 48 hrs. During this period, the test solution was diffused and affected the growth of the microorganisms. Hence, the inhibition zones were developed on the plate around the disc. The concentration at which the zone developed was noted as MIC values of the synthesized compounds.

RESULTS AND DISCUSSION

The analytical data for the ligand and the complexes together with some physical properties like colour, melting point, molar conductance, magnetic susceptibility are summarized in Table I. The analytical data of the complexes is in good agreement with general formula ML, Where M=Cu(II),Ni(II),Co(II),Zn(II) and VO(II); L=C₃₂H₃₀N₂O₃. The magnetic susceptibility data of the complexes in the solid state shows that Cu(II), Co(II) and VO(II) are paramagnetic, Ni(II) and Zn(II) are diamagnetic at room temperature. The electrolytic nature of the complexes was measured in DMSO at 10⁻³M. The lower conductivity value of the chelates supports the non-electrolytic nature of the metal complexes²¹.

Mass Spectra:

The FAB mass spectra of the ligand H₂L and its copper complex were recorded and they are used to compare their stoichiometric composition. The mass spectra of Schiff base and its copper complex shows a molecular ion peak at 546 m/z and 610 m/z respectively confirms the stoichiometry of metal chelates as [ML] type. This composition is also supported by the mass spectra of other complexes.

¹H-NMR spectra:

¹H-NMR spectra of the Schiff base (H₂L) and its zinc complex were recorded in CDCl₃ (Fig. 1). The Schiff base shows peak at 12.40 ppm and 13.30 ppm which are attributable to the enolic –OH group of acetoacetanilide and -COOH group of tryptophan moiety respectively. Absence of these two peaks in the zinc complex which favours the loss of enolic –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.

Infrared spectra:

The infrared spectra of the Schiff base and its complexes recorded in the region 400-4000 cm⁻¹ using KBr as solvent. The spectra of the

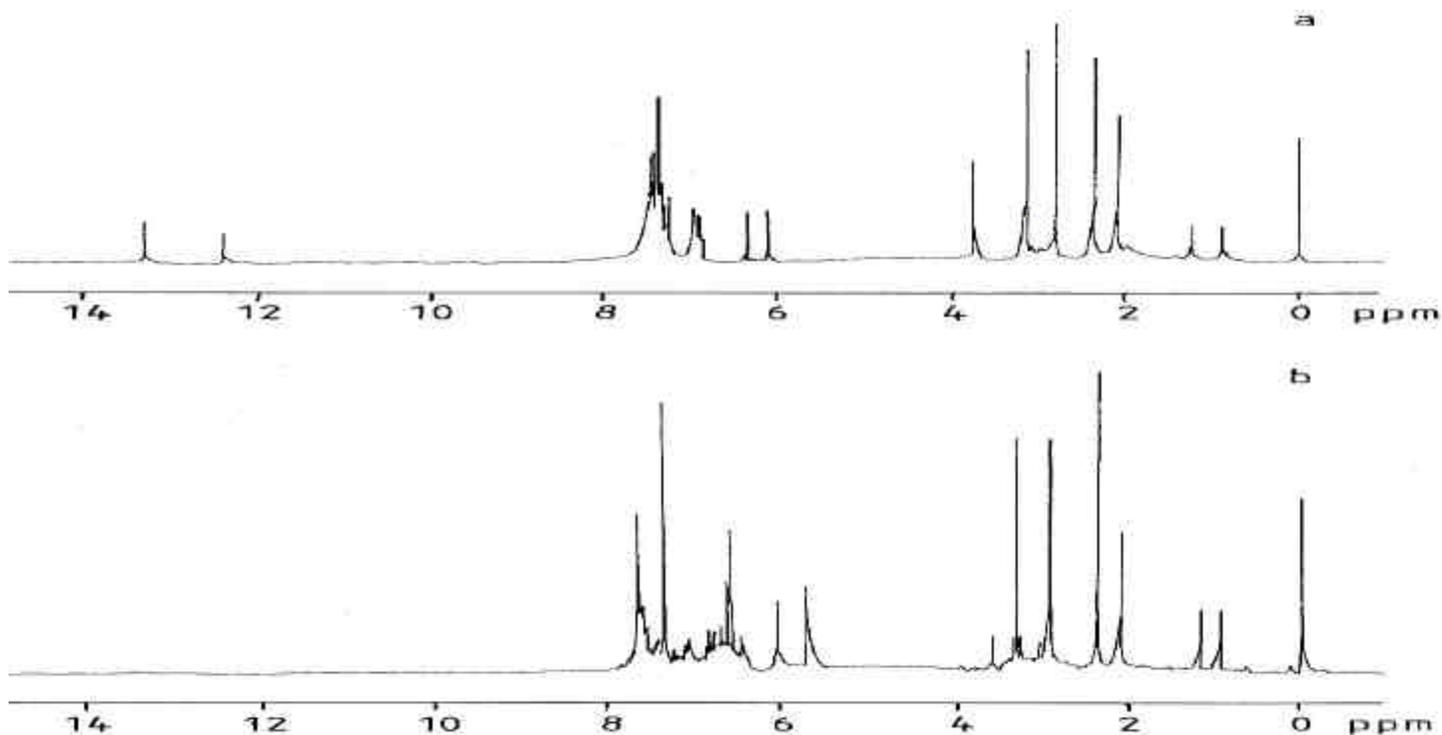


Fig. 1 - $^1\text{H-NMR}$ spectra of the Schiff base (H_2L) and zinc complex in CDCl_3 solution.

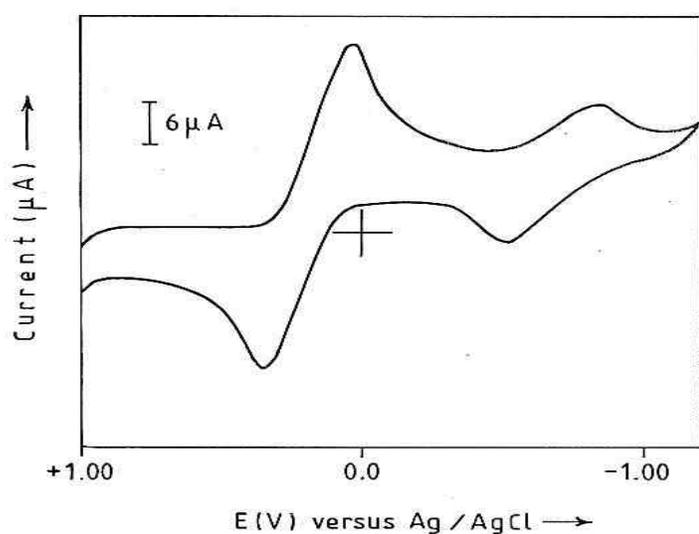


Fig. 2 - The cyclic voltammogram of the $[\text{CuL}]$ complex in MeCN solution (0.1 M TBAB; scan rate 100mVs^{-1}).

complexes were compared with those of the free ligand. There are some significant changes between the metal(II) complexes and their free ligand due to chelation was expected. The IR spectrum of the ligand shows a merged strong broad band at $3500\text{--}3300\text{ cm}^{-1}$ region which are assigned to enolic -OH group of acetoactanilide -COOH group of tryptophan moiety. Disappearance of these bands indicates the deprotonation of these groups upon coordination. IR spectrum of all complexes shows a new strong band at 3150 cm^{-1} and 3320 cm^{-1} region which are assigned to cyclic -NH- group of tryptophan moi-

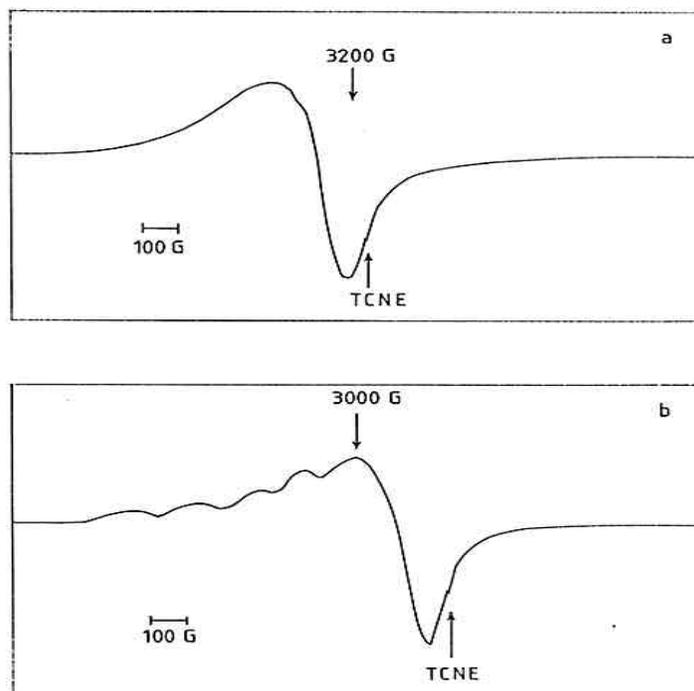


Fig. 3 - The ESR spectra of copper complex at 300 K (a) and 77 K (b) in MeCN solution.

ety as well as -NHPh group of acetoactanilide moiety and these peaks are 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 these groups and not involved in coordination with metal ion.

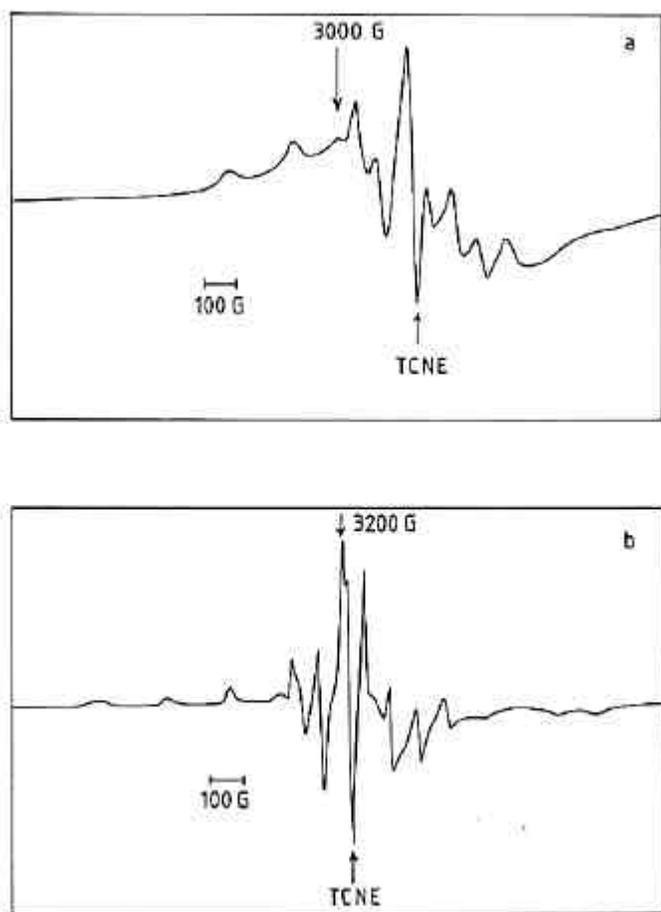


Fig. 4 - The ESR spectra of vanadyl complex at 300 K (a) and 77 K (b) in MeCN solution.

In the spectrum of the Schiff base, the strong bands at 1610 - 1590 cm^{-1} region are attributable to $-\text{C}=\text{N}$ groups. On chelation, due to the possible drift of lone pair electron density towards the metal ion, the azomethine $-\text{C}=\text{N}$ band is expected to absorb at lower frequency in the complex. The observed band at 1585 - 1565 cm^{-1} region indicates the coordination of azomethine nitrogen to the metal. Moreover, the Schiff base and all the complexes exhibit an intense peak at 1670 cm^{-1} , a characteristic feature of the $-\text{C}=\text{O}$ stretching frequency indicating the existence of $-\text{C}=\text{O}$ of acid group in tryptophan moiety. IR spectra of the complexes also show a new peaks at 510 - 490 cm^{-1} and 470 - 450 cm^{-1} region due to the formation of M-N and M-O bond respectively²². In addition to other bands, the vanadyl complex shows its characteristic V=O frequency at 943 cm^{-1} region²³.

Electronic spectra:

The electronic spectrum of the Schiff base in MeCN shows two predominant bands at 246 nm and 283 nm region, which are assigned as intra ligand charge transfer (INCT) bands. These transitions are also found in the spectra of the complexes but they shifted towards lower frequencies, confirming the coordination of the ligand to the metal ions

The UV-Vis., spectra of copper complex in MeCN solution shows a well-defined shoulder at 515 nm and strong broad band at 910 nm, which are assignable to ${}^2\text{B}_2\text{g} \rightarrow {}^2\text{B}_1\text{g}$ and ${}^2\text{B}_2\text{g} \rightarrow {}^2\text{A}_1\text{g}$ transition respectively. It reveals that the copper complex exists in square planar geometry²⁵. It also shows two predominant INCT bands at 235 nm and 271 nm region.

The electronic spectrum of nickel complex in MeCN shows three bands at 235 nm, 275 nm and 612 nm. Comparison of this spectrum with the free ligand origin, first two bands are assignable to INCT transitions and the remaining one occurring at 612 nm region is due to ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{B}_{1\text{g}}$ transition which confirms square-planar geometry of the nickel complex. The observed zero magnetic moment also confirms the square planar environment for the nickel (II) complex, in conformity with the fact that all known square planar complexes of nickel (II) are diamagnetic^{25,26}.

The cobalt complex in MeCN solution shows three prominent bands at 238 nm, 265 nm and 642 nm. The two strong bands in the lower wavelength region are assignable to INCT transitions. The ground state configuration for the d^7 , Co^{2+} ion is ${}^4\text{F}$. The electronic absorption spectrum of the cobalt complex in MeCN show only one d-d band at 642 nm (${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{T}_{1\text{g}}$) which reveals that the cobalt complex is present in square planar environment^{25,26}.

The optical spectrum of vanadyl complex in MeCN solution shows five bands at 240 nm, 271 nm, 520 nm, 645 nm and 880 nm. The last three bands are assigned as ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ transition respectively which is consistent with that of square pyramidal geometry²⁶. The other two higher energy transitions are assigned as INCT. This is further confirmed by the magnetic susceptibility value (1.86 BM).

Redox Studies:

Cyclic voltammetry helps to evaluate the effect of ligands on the redox potential of the central metal ion in complexes. The electrochemical reversible nature of the Cu(II)/Cu(III) redox system in complexes depends on the nature of the ligand. Cyclic voltammetry has been shown to be a particularly useful technique in studies of this type, aiding one to measure the existence of short lived species, as well as to study the ligand's structural parameters such as size and degree of conjugation.

The cyclic voltammogram of the copper complex in MeCN solution (Fig. 2) shows a reversible peak for the couple: $\text{Cu(II)} \rightarrow \text{Cu(III)}$ at $E_{\text{p}_a} = 0.34$ V with the direct cathodic peak for $\text{Cu(III)} \rightarrow \text{Cu(II)}$ at $E_{\text{p}_c} = 0.06$ V. Further, it exhibits another one couple characteristics for $\text{Cu(II)} \rightarrow \text{Cu(I)}$ ($E_{\text{p}_c} = -0.66$ V) reduction and $\text{Cu(I)} \rightarrow \text{Cu(II)}$ ($E_{\text{p}_a} = -0.51$ V) oxidation. The one-electron transfer process is established by the comparison of I_{p_c} and I_{p_a} values²⁷⁻³⁰.

ESR Spectra:

The X-band ESR spectra of copper complex in DMSO at a concentra-

tion of ca. 0.1 mol was recorded at 300 K and 77 K are shown in Fig. 3. The spectrum of the copper complex at 300 K shows one intense band in the high field region, which are isotropic due to tumbling motion of the molecules. The splitting of intense peak at 300 K may be due to internal standard (TCNE). 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 spectrum³¹. The ESR parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} were determined from the anisotropic spectra of the frozen solutions (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 dx^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 $g_{\perp} > g_{\parallel} > 2$. From the observed values, it is clear that A_{\parallel} ($167 \times 10^{-4} \text{ cm}^{-1}$) $> A_{\perp}$ ($98 \times 10^{-4} \text{ cm}^{-1}$) and g_{\parallel} (2.39) $> g_{\perp}$ (2.09) > 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^{30,31}.

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 measures of the covalence of the in-plane σ -bonds (α^2), in-plane π -bonds (β^2) and out-of-plane π -bonds (γ^2) respectively³². The observed value of α^2 (0.92) indicates that complex have some covalent character. The observed β^2 (1.22) and γ^2 (1.11) values indicate that there is no substantial interaction in the out-of-plane π -bonding and in-plane π -bonding which are completely ionic.

The ESR spectra of the vanadyl complex were recorded in DMSO solution at 300 and 77 K and are shown in Fig.4. The room temperature (300 K) spectrum 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 which show an axially symmetric anisotropy with well resolved sixteen-line hyperfine splitting characteristic of an interaction between the electron and the vanadium nuclear spin.

The various parameters calculated from the spectrum of the complex [A_{\parallel} ($203 \times 10^{-4} \text{ cm}^{-1}$) $> A_{\perp}$ ($97 \times 10^{-4} \text{ cm}^{-1}$) and g_{\perp} (2.13) $> g_{\parallel}$ (1.97)] indicate that the complex is square pyramidal geometry, characteristic for the oxovanadium (IV) chelates. The bonding parameters of this complex can be calculated with the help of optical spectra of the complex^{33,34}.

The in-plane π -bonding β^2 (1.02) and out-of-plane π -bonding coef-

ficients γ^2 (0.98) values do not deviate much from unity. This is consistent with Kivelson's conclusion³⁴, which suggests that the d_{xy} orbital is essentially non-bonding while π -bonding coefficients remain constant. Essentially, the delocalization of electrons into the ligand may be gauged from the in-plane σ -bonding coefficients (α^2) values. This follows the σ -donor strength of the ligand and it usually decreases as the covalent bonding increases. The observed α^2 (0.85) value indicates that the in-plane σ -bonding is significant. The molecule orbital coefficients also show that the metal ion has some covalent character in ligand environment.

Biological screening studies:

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 value of the compounds against the growth microorganisms are summarized the Table 2.

A comparison of the MIC value of ligand with those of the complexes indicates that the metal chelates exhibited higher antimicrobial activity than ligand and the control sample. Such increased activity of the complexes can be explained based on the Overtone's concept and the Tweedy chelation theory³⁵. According to the Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble materials, due to which liposolubility is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion will be reduced due to the partial sharing of positive charges with donor groups. Furthermore, it increases the delocalization of p-electrons over the whole chelate ring that enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and the blocking of the metal binding sites in the enzymes of microorganisms³⁷. Due to the presence of more functional groups (hydroxyl groups and azomethine groups), which forms hydrogen bonding with proteins present in the cell walls of the organisms, resulting in interference with the normal cell process³⁷⁻³⁹. Comparatively, zinc complex shows higher activity than all other complex which is due to its higher lipid solubility⁴⁰.

CONCLUSION

A Schiff base of acetoacetanilido-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.

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