



RESEARCH ARTICLE

PREPARATION CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF CHELATES OF SCHIFFS BASE DERIVED FROM 4-AMINOANTIPYRINE VANILLIN AND O-PHENYLENE DIAMINE

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ABSTRACT

A new series of transition metal complexes of Mn (II), Co (II), Ni (II) and Cu (II) are synthesized from a new novel macro cyclic Schiff base ligand with four N donor atoms derived from 4-aminoantipyrine, vanillin and o-phenylenediamine. Several tools like elemental analysis, molar conductance methods, Infrared, electronic (UV-Vis), Electron spin resonance (ESR) and Nuclear Magnetic Resonance (NMR) spectroscopic techniques, thermo gravimetric analysis were used to investigate the chemical structure of the prepared ligand (L) and complexes. The elemental analysis data suggest the formation of 1:1 (M: L) anionic complex with formula $[ML]Cl_2$ (M=Co(II) and $[ML]SO_4$ (M= Mn (II), Ni (II) and Cu (II)). The higher molar conductivity values support the electrolytic nature of the complexes. The infrared spectral studies reveal that the involvement of azomethine nitrogen ($-C=N$) is coordinated to the metal resulted in to MN_4 chromospheres. The electronic absorption spectra of the complexes suggest a square planar geometry around the central metal ion. The NMR parameters of the free ligand and its Zinc (II) complexes were also compared. The X-band ESR spectra of Copper (II) complexes were recorded and the molecular orbital coefficients like $g_{||}$, g_{\perp} , Exchange interaction term (G), the covalence parameter (α^2), K , K_{\perp} and K^2 etc., were calculated. The thermal decomposition parameters of these complexes are also studied in static air atmosphere with a heating rate of 20°C per minute which represents a single stage decomposition with metal oxides as stable residue. Antibacterial screening tests were also performed against bacteria. The comparative study of MIC values of the Schiff's base and its metal complexes indicate that the metal complexes exhibit greater antibacterial activity than the free ligand.

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INTRODUCTION

Metal complexes with a variety of Schiff base ligands have been studied for their application in

biological, clinical, analytical and pharmacological areas. Studies of new kinds of Schiff's bases and their functions are now attracting the attention to

biochemists (Zehiha Hayvali, 2005; Hitoshi *et al.*, 1997) Earlier work reported that some drugs showed greater activity, as metal complexes when compared to the organic compounds.⁴ The coordinating properties of 4-aminoantipyrene have been modified to give new ligands formed by the reaction with aldehydes, ketones, thiocarbazides and carbazides etc., (Raman *et al.*, 2007; Agarwal *et al.*, 1997). Several works have been reported with 4-aminoantipyrene as a ligand and its coordinating abilities to metals. But its Schiff's bases are not well studied. It is found from literature that very less work was done with Schiff base derived from 4-aminoantipyrene (Raman *et al.*, 2008). As a continuation of our work on the synthesis of Schiff base from vanillin and various carbonyl compounds, efforts were taken for the synthesis, characterization and antimicrobial studies of transition metal complexes containing a new tetra dentate Schiff's base derived from vanillin, 4-aminoantipyrene and o-phenylenediamine. We are reporting a new versatile tetra dentate Schiff base ligand capable of binding with the metals through two different types of azomethine group in the same ligand and its characterization using various spectroscopic and analytical methods.

MATERIAL AND METHODS

All the reagents, 4-aminoantipyrene, vanillin, o-phenylenediamine and the metal salts were purchased from Merck and Loba chemie Mumbai, India are used as supplied. The solvents like ethanol, methanol, DMSO etc are purified and dried by the standard procedures (Raman *et al.*, 2007). The micro analytical data of complexes were recorded at Central Electro chemical Research Institute (CECRI) India using vario EL elemental analyzer. IR spectroscopy analyses were recorded on Shimadzu FTIR 8400S spectrometer in 4000-200cm⁻¹ range using KBr pellet. The UV-Visible spectra were recorded on a Shimadzu UV spectrometer in the wave length range 200-800nm. The thermal analyses were recorded on Universal V4.3A TA Instrument from CECRI, India, with heating rate of 20deg C/min in static air. The ESR spectral analyses were recorded on Bruker instrument at 300 and 77 K from CECRI. The ¹H-

NMR and ¹³C-NMR were recorded on a Bruker DPX-300 spectrometer using EtOD as solvent and TMS as internal standard. The molar conductance was measured on ELICO-CM180 using DMSO as the solvent at room temperature. The antibacterial activity was determined with the Disc Diffusion method. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the Minimum Inhibition Concentration (MIC).

Synthesis of Schiff's base

An ethanolic solution (20ml) of 1-phenyl 2, 3-dimethyl-4-aminopyrazol-5-one (2.03gm, 0.01 mol) (4-aminoantipyrene) was added to an ethanolic solution of vanillin (1.52gm, 0.01mol) and the solution was refluxed for ca 5 hours with vigorous stirring and allowed to cool then it was poured in crushed ice when crystals formed. The yellow crystals were filtered and recrystallized from ethanol (I). The solid intermediate (3.373g, 0.01mol) was added to an ethanolic solution (20ml) of o-phenylenediamine (0.541g, 0.005mol). The mixture was refluxed for about 30 hours. The reaction was followed using TLC. The contents were poured in to crushed ice. The brown solid (L) product was separated, filtered and re crystallized from ethanol. The scheme of the experiment is given in the Figure-1. Yield: 72%; m.p: 210 °C. (Fig 1).

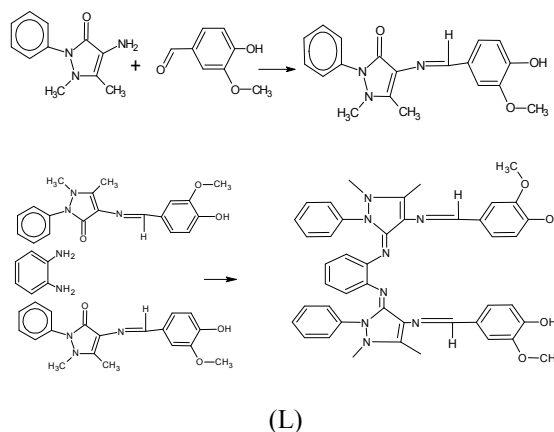


Figure 1. Formation of Schiff base ligand (L)

Synthesis of Schiff base complexes

A solution of metal salt in hot ethanol (0.002 mol) was refluxed with an ethanolic solution of Schiff base (0.002mol, 1.493g) on a water bath for 5

Antibacterial activity

The antibacterial activity was determined with the Disc Diffusion method. Stock solutions were prepared by dissolving the compounds DMSO and

Table 1. Physical characterization, analytical and molar conductance data of the complexes

| Comp. M.Formula, (Colour) | m.p (°C) | M.wt (Yield %) | Found (Calc.) (%) | | | | Λ_m ($\Omega^{-1} \text{ mol}^{-1}$) | |
|--|----------|-------------------|--------------------|------------------|--------------------|------------------|---|-----|
| | | | C | H | N | S | | |
| $\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4 = \text{L}$ (Dark Yellow) | 210 | 746.64 (72) | 70.521 (70.717) | 4.983 (5.625) | 14.997 (15.001) | 0 0 | - | |
| $[\text{Mn}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ (Brown) | 215 | 782.816 (65) | 57.934 (58.825) | 4.586 (4.679) | 12.841 (12.478) | 3.890 (3.565) | 5.963 (6.121) | 112 |
| $[\text{Co}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{Cl}_2$ (Pink) | 158 | 923.57 (68) | 59.863 (60.285) | 4.623 (4.79) | 12.541 (12.127) | 0.072 (0) | 6.728 (6.728) | 198 |
| $[\text{Ni}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ (Brown) | 165 | 789.51 (55) | 57.98 (58.62) | 4.32 (4.66) | 12.863 (12.435) | 3.632 (3.552) | 6.498 (6.516) | 78 |
| $[\text{Cu}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ (Brown) | 195 | 793 (75) | 57.937 (58.307) | 4.231 (4.638) | 11.932 (12.368) | 3.269 (3.533) | 7.264 (7.017) | 102 |
| $[\text{Zn}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ (Brown) | 175 | 796.21 (60) | 57.983 (58.188) | 4.562 (4.628) | 11.634 (12.343) | 3.603 (3.526) | 7.463 (7.206) | 102 |

Table 2. Characteristic infrared absorption frequencies in (cm^{-1}) of ligand and complexes

| Compound | Phenolic $\nu \text{O-H cm}^{-1}$ | $\nu \text{C=N cm}^{-1}$ | $\nu \text{M-N cm}^{-1}$ | Phenyl ring vibration |
|---|--------------------------------------|--------------------------|--------------------------|---|
| | | | | $1090\text{-}1100 \text{ cm}^{-1}$ & $700\text{-}750 \text{ cm}^{-1}$ |
| $\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$ | 3107.34 | 1650 | | 1032 & 763 |
| $[\text{Mn}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | 3064.97 | 1622, 1579 | 449.43 | 1037 & 750 |
| $[\text{Co}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{Cl}_2$ | 3061.99 | 1560 | 445.57 | 1031 & 748 |
| $[\text{Ni}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | 3063 | 1595, 1514 | 447.90 | 1031 & 746 |
| $[\text{Cu}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | 3063.06 | 1514 (s) | 445.57 | 1030 & 746 |
| $[\text{Zn}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | 3107.34 | 1610, 1597 | 418.57 | 1037 & 761 |

Table 3. Characteristic infrared absorption frequencies in $\text{nm}(\text{cm}^{-1})$ of ligand and complexes

| Compound | Absorption $\text{nm}(\text{cm}^{-1})$ | Band assignment | Geometry |
|---|---|---|---------------|
| $\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$ | 272 (36764) and 305 (32868) | $\pi \rightarrow \pi^*$, n- π^* ILCT. | |
| $[\text{Co}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{Cl}_2$ | 315 (28985), 345 (31746) and 462 (21645) | ν_1 and ν_2 are ILCT, $\nu_3 = {}^1\text{A}_1 \rightarrow {}^1\text{B}_1 \text{g}$ | Square planar |
| $[\text{Ni}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | 360 (27777), 328 (30487), 625 (16000) and 328 (31250) | ν_1 and ν_2 are ILCT $\nu_3 = {}^1\text{A}_1 \text{g} \rightarrow {}^1\text{A}_2 \text{g}^{-1}$ $\nu_4 = {}^3\text{A}_1 \text{g} \rightarrow {}^1\text{B}_1 \text{g}$ | Square planar |
| $[\text{Cu}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | 320 (31250), 352 (28409) and 660 (15151.5) | ν_1 and ν_2 are ILCT $\nu_3 = {}^2\text{B}_1 \rightarrow {}^2\text{A}_1 \text{g}$ | Square planar |

Table 4. Thermo gravimetric analyses of complexes

| S. No | Compound | Temp. Range (°C) | Stage | Weight loss (%) | |
|-------|---|------------------|-------|-----------------|------------|
| | | | | Found | Calculated |
| 1 | $[\text{Mn}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | Above 100-580 | I | 9.94 | 11.09 |
| 2 | $[\text{Ni}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | Above 100-623 | I | 9.74 | 8.262 |
| 3 | $[\text{Cu}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | Above 60-522 | I | 8.389 | 8.39 |
| 4 | $[\text{Zn}(\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4)] \text{SO}_4$ | Above 184-475 | I | 9.817 | 8.969 |

hours. Then the solution was reduced to one third of its volume on a water bath and cooled. The precipitated complex was filtered washed several times with hot ethanol and dried in vacuum.

serial dilutions of the compounds were prepared in sterile distilled water to determine the Minimum Inhibition Concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread

over the solid nutrient agar plates with the help of a spreader. Fifty microlitres of the stock solutions was applied on the 10mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature (29 \pm 2 C) for 30-36 hours. The diameter of the inhibition zones was measured in millimeters. The biological screening effects of the complexes were tested against the bacteria *S. aureus*, *E. Coli*, *B. Subtilis* and *P. aeruginosa*.

RESULTS AND DISCUSSION

The analytical data for the ligand and the complexes together with some physical properties like colour, melting point, molar conductivity etc., are summarized in Table 1. The analytical data of the complexes is in good agreement with the general molecular formula $[\text{CoL}]\text{Cl}_2$ and $[\text{ML}]\text{SO}_4$, where $\text{M}=\text{Mn}^{+2}$, Ni^{+2} , Cu^{+2} and Zn^{+2} . The high molar conductivity values 78-112 $\Omega^{-1} \text{mol}^{-1}$ corresponds to 1:1 electrolytic for $[\text{ML}]\text{SO}_4$ where $\text{M}=\text{Mn}^{+2}$, Ni^{+2} , Cu^{+2} and Zn^{+2} , but the very high value of 198 $\Omega^{-1} \text{mol}^{-1}$ for Co^{+2} complex suggests 1:2 electrolytic nature.

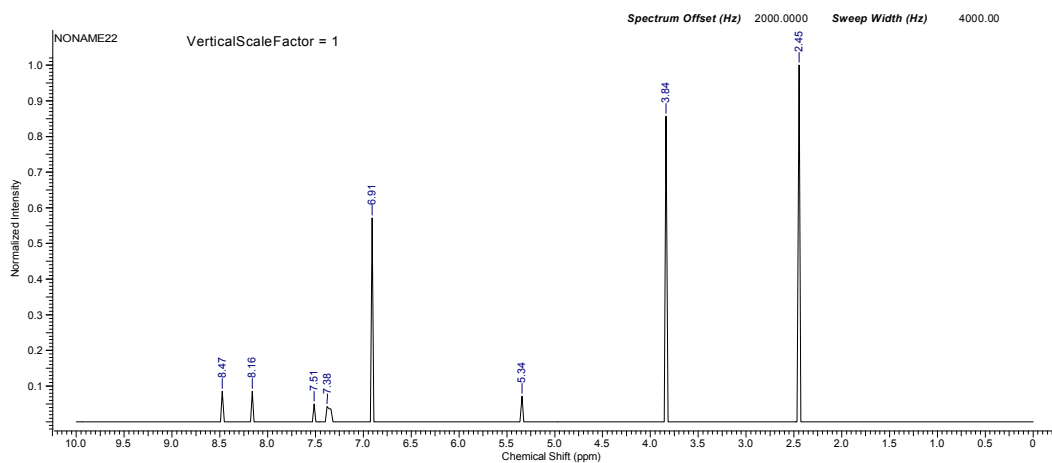


Fig. 2 ¹H-NMR spectrum of the Ligand

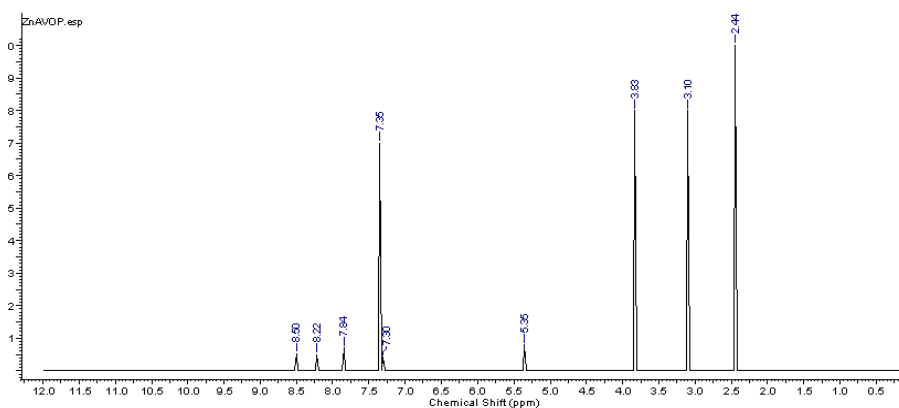


Fig. 3. ¹H-NMR spectrum of the Zn complex

IR analyses

The IR analyses provides valuable information regarding the nature of the functional group attached to the metal. The vibration frequencies of the free ligand and the metal chelates are given in Table 2. The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. The phenolic ν O-H stretching appear at 3107 cm^{-1} does not undergo any change in the spectrum suggested that phenolic O-H group does not participate in the bond formation with the metal.

Coordination to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lowers the ν C=N. The spectrum of the free Schiff base ligand shows two -C=N bands (Natarajan Raman *et al.*, 2005) in the region $1650\text{-}1565\text{ cm}^{-1}$ which is shifted to lower frequencies in the complexes showing the involvement of the coordination of C=N to make the ligand acts as a tetra dentate chelating agent, bonded to the metal ion via the four nitrogen -C=N atoms of the Schiff base reduces the electron density in the azo methine bond and lowers the ν C=N. All complexes shows band in the region $1090\text{-}1100\text{ cm}^{-1}$ and $700\text{-}750\text{ cm}^{-1}$ can be assigned to phenyl ring vibration the appearance of medium band at 450 cm^{-1} confirms the presence of M-N coordination in the complex.

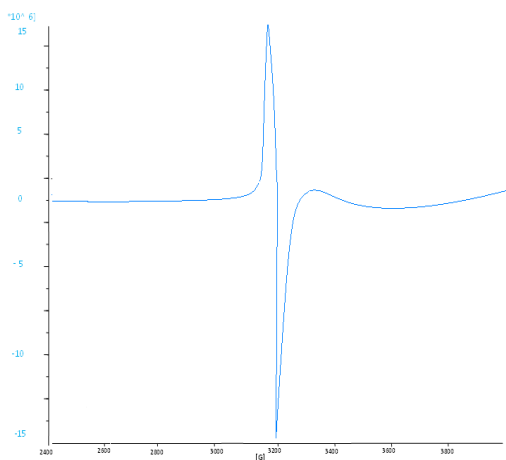


Fig.4. ESR spectrum of Cu complex at 300K

UV-visible analyses

The electronic spectral data is used to study the geometry of the synthesized complexes. Based on the UV-visible spectrum recorded in ethanol, the complexes were shown to have a square planar geometry. Table 3 gives the information on the various electronic spectral absorption regions for the ligand and their metal complexes. The UV-spectrum of Cobalt (II) complex shows three peaks

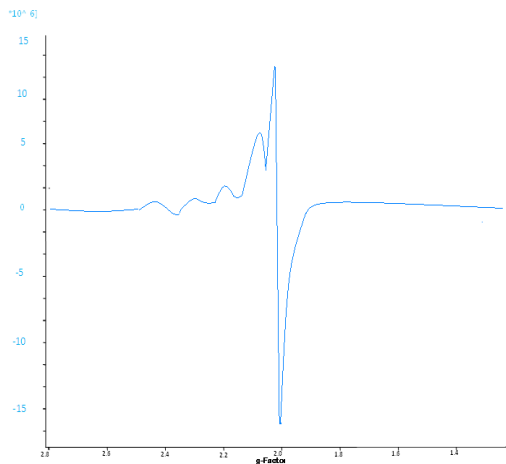


Fig.5. ESR spectrum of Cu complex at 77K

at 345 nm (28985 cm^{-1}), 315 nm (31746 cm^{-1}) and 462 nm (21645 cm^{-1}) respectively. The peak at 345 nm (28985 cm^{-1}), 315 nm (31746 cm^{-1}) are the bands corresponding to the Inter Ligand Charge Transfer band (ILCT) but the band at 462 nm (21645 cm^{-1}) is for the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition.^{1,2} The transitions suggests the presence of square planar geometry for cobalt complex. Nickel (II) has a (d^8) configuration giving peaks, found at 360 nm (27777 cm^{-1}), 328 nm (30487 cm^{-1}), 625 nm (16000 cm^{-1}) and 520 nm (31250 cm^{-1}) respectively for the nickel complex. The first and second peaks at 360 nm (27777 cm^{-1}) and 328 nm (30487 cm^{-1}) are assigned for the Inter Ligand Charge Transfer band (ILCT) but the third peak at 625 nm (16000 cm^{-1}) is assigned for the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ excitation and the fourth peak at 328 nm (31250 cm^{-1}) is assigned for the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ excitations respectively.

This confirms the presence of an square planar geometry for the Nickel complex (Raman *et al.*,

2008). Copper (II) complex also shows three peaks at 320nm (31250cm^{-1}), 352 nm (28409cm^{-1}) and 660nm (15151cm^{-1}) respectively. The first peak at 320nm (31250cm^{-1}) and second peaks at 360nm (27777cm^{-1}) are assigned for the Inter Ligand Charge Transfer band (ILCT) and the third peak at 660 nm (15151cm^{-1}) is assigned for the ${}^2\text{B}_1 \rightarrow {}^2\text{A}_1\text{g}$ excitation for the square planar geometry for the copper complex (Raman *et al.*, 2008).

Thermal analyses

The thermo analytical data suggested that the compound prepared were stable only up to 80°C and above this temperature, the decomposition takes place in a single step leaving behind a stable residue may be oxides of metal. The phenomenological aspects, temperature range, residue formed etc are tabulated in Table-4. The experimental weight loss is in agreement with its calculated values.

| | |
|--|-------|
| Stage-I [Mn ($\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$) ₂] SO ₄ → MnO ₂ (Residue) | Eqn-1 |
| Stage-I [Ni ($\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$) ₂] SO ₄ → NiO (Residue) | Eqn-1 |
| Stage-I [Cu ($\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$) ₂] SO ₄ → CuO (Residue) | Eqn-1 |
| Stage-I [Zn ($\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$) ₂] SO ₄ → CuO (Residue) | Eqn-1 |

NMR studies

The spectral information is obtained from the proton NMR and ${}^{13}\text{C}$ -NMR spectrum of the ligand with respect to TMS. The proton NMR and ${}^{13}\text{C}$ NMR shows a single peak at δ 5.34 due to the aromatic O-H. Multiplet around δ 7.51 shows the presence of benzylianium CH group. The peak for the benzene appears as multiplet at δ 7.35, the peaks for O-CH₃ group, C-CH₃ and N-CH₃ appears in the region δ 3.83, 3.11, 2.44 respectively. The peaks for the benzylianium hydrogen appear at δ 8.48 and δ 8.17.

7.85 and the rest of the peaks, at δ 5.35 due to the aromatic O-H, the peak for the benzene appears as multiplet at δ 7.35, the peaks for O-CH₃ group, C-CH₃ and N-CH₃ appears in the same region δ 3.83, δ 3.11, δ 2.44 respectively. The peaks for the benzylianium hydrogen appear at low field δ 8.50 and δ 8.27. There is no appreciable change in all the signals of the complex except -CH=N-. The phenolic peak for the zinc complex is present which confirms the -OH proton free from complexation.

ESR analyses

ESR studies of paramagnetic transition metal (II) complexes yield information about the distribution of the unpaired electrons and hence about the nature of the bonding between the metal ion and its ligands. There have been many reports concerning the application of ESR to square planar or distorted octahedral complexes of Cu^{+2} and their interpretation of the ESR parameter in terms of covalence of M-L bonding. ESR spectra of [Cu($\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$)] SO₄ recorded in DMSO solution at 300 and 77 K are shown in figure -4 and figure-5. The spectrum of the Cu complex at 300 K shows one intense absorption band in the high field region and is isotropic due to the tumbling motion of the molecules. The spectrum consists of a set of four well resolved peaks in the low field region at 77K. The spin Hamiltonian parameters of the complexes were calculated. The g_{\parallel} and g_{\perp} values are computed from the spectrum. The observed g_{\parallel} (2.2312) is less than 2.3 suggesting significant covalent character of the M-L bond.

Table 5. Antibacterial activity data for the ligand and their metal complexes

| Compound | <i>S.aureus</i> | <i>E.coli</i> | <i>B.subtilis</i> | <i>P.aeruginosa</i> | Inference Anti bacterial activity |
|--|-----------------|---------------|-------------------|---------------------|-----------------------------------|
| $\text{C}_{44}\text{H}_{42}\text{N}_8\text{O}_4$ | 3 | 6 | 2 | 6 | + |
| [Mn ⁺² (L)] SO ₄ | 6 | 5 | 3 | 2 | + |
| [Co ⁺² (L)] Cl ₂ | 7 | 6 | 5 | 4 | + |
| [Ni ⁺² (L)] SO ₄ | 8 | 9 | 8 | 9 | ++ |
| [Cu ⁺² (L)] SO ₄ | 2 | 6 | 3 | 9 | + |
| [Zn ⁺² (L)] SO ₄ | 16 | 18 | 12 | 18 | +++++ |

The azomethine proton signal in the spectrum of the zinc complex is shifted downfield. Thus the peak at δ 7.52 found in the ligand is shifted to δ

The band g_{\parallel} (2.2312) > g_{\perp} . (2.0346) > g_e (2.0023) suggests that the unpaired electron is localized in dx^2-y^2 orbital for the copper complex, the four

well resolved peaks of low intensities in the low field region in the frozen state at 77K, ruled out the Cu–Cu interaction. The g tensor values of Cu (II) complex can be used to derive the ground state. In tetragonal and square planar complexes, the unpaired electron lies in the dx^2-y^2 orbital giving $2B1g$ as the ground state with the $g_{\parallel} > g_{\perp}$. From the observed values, it is clear that $g_{\parallel} > g_{\perp}$ ($2.2312 > 2.0346$), which suggests that the complex is square

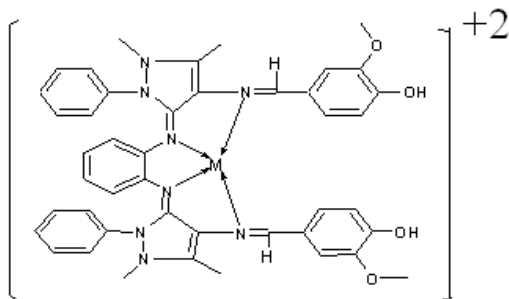


Fig. 6. Structure of Complex

planar¹⁹⁻²¹. Also it is supported by the fact that the unpaired electron lies predominantly in the dx^2-y^2 orbital for the copper complex, $g_{\parallel} = 2.2312$, which is between 2.3–2.4 and thus in conformity with the presence of copper–nitrogen bonds in these chelates. Molecular orbital coefficients, α^2 (covalent in-plane s -Bonding) and β^2 (covalent in-plane p -bonding), were calculated by using the following equations.

$$\alpha^2 Cu = -(A/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04 \quad (1)$$

$$\beta^2 Cu = (g_{\parallel} - 2.0023) E / -8\lambda \alpha^2 \quad (2)$$

Where E is the electronic transition energy of $2B1g \rightarrow 2A1g$

The α^2 (0.721) and $\beta^2 = 0.7262$, value for the complex supports its covalent nature of the bonding. Hathway²⁰ pointed out that for the pure σ – bonding $K_{\parallel} > K_{\perp} \approx 0.77$ and for in-plane π - bonding $K_{\parallel} < K_{\perp}$, while for the out-of-plane π - bonding $K_{\perp} < K_{\parallel}$ the following simplified expressions were used to calculate K_{\parallel} and K_{\perp} .

$$K_{\parallel} = (g_{\parallel} - 2.0023 / 8 \times \lambda_0) \times d - d \text{ transition} \quad (3)$$

$$K_{\perp} = (g_{\perp} - 2.0023 / 2 \times \lambda_0) \times d - d \text{ transition} \quad (4)$$

The observed K_{\parallel} (0.5236) $>$ K_{\perp} (0.2955) relation indicates the absence of significant in-plane π - bonding. The molar conductance of the complexes reveals the presence of chloride ions outside the coordination sphere in chromium and iron complexes. In the complexes of Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} the primary valency of the metals are satisfied by the ions chloride ions for cobalt and sulphate ions for manganese, nickel, copper and zinc complexes.

Antibacterial activity

The antibacterial study for the complexes was performed on staphylococcus aureus, Escherichia coli, Bacillus subtilis and *Pseudomonas aeruginosa*. The toxicity of the complexes was found to be better than the ligand owing to the theory of Tweedy²². This is probably due to the greater lipophilic nature of the complexes. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and chelation theory. According to Overtone's concept of cell permeability the lipid membrane that surrounds the cell favors the passage of lipid soluble materials due to which liposolubility is an important factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of microorganisms.

Conclusion

In this work the synthesis and characterization of a tetradentate Schiff base ligand derived from vanillin, 4-aminoantipyrine and *o*-phenylenediamine and its interaction with transition metals like Mn (II), Co (II), Ni (II) Cu (II) and Zn(II) is reported. The metal complexes formed were 1:1 electrolytes except Co(II) complexes which is 1:2. The synthesized $[MN_4]$ chromophore systems were characterized by microanalysis, molar conductance values, IR, ESR, electronic & NMR spectroscopic techniques. These Analytical and spectral data suggests that

azomethine N atoms of 2 different types are coordinated around the metal ions generate a square planar environment around the metal ion. Based on the above results the structure of coordination compounds under investigation can be formulated in figure-6. The antibacterial studies are also reported.

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