ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Preparation Characterization, ^{1}H, ^{13}C NMR Study and Antibacterial Studies of Schiff Bases and Their Zn (II) Chelates

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ABSTRACT

In this paper we have tried to synthesize, characterize and study theantibacterial property of four schiff bases and their Zn(II) complexes. A new series of transition metal complexes of Zinc (II) with two bidentate and two tetradentate Schiff base ligands were prepared. Several tools like elemental analysis, molar conductance methods, infrared, electronic (UV-vis), Proton Nuclear Magnetic Resonance (NMR) spectroscopic techniques, ^{13}C NMR spectroscopic techniques and thermogravimetric analysis were used to investigate the chemical structure of the prepared ligands and zinc (II) complexes. The infrared spectral studies reveal the involvement of azomethine nitrogen (-C=N) coordination/ carbonyl (-C=O) coordination / carboxylate (-COO-) coordination with the zinc (II) ion in the four complexes. The NMR spectral data of the free ligand and its zinc (II) complexes were also studied. The thermal decomposition of the zinc (II) complexes was studied in static air with a heating rate of 20ºC per minute. The antibacterial screening against bacteria such as *S.aureus, E.coli, B.subtilis, P.aeruginosa*was performed. The comparative study of MIC values of the Schiff base and its metal complexes indicate that the metal Zinc (II) complexes exhibit greater antibacterial activity than the free ligand. The Zn (II) complexes were powdery in nature hence their XRD was not recorded.

Keywords: Schiff base, anthranilic acid, 4-aminoantipyrine, vanillin, furfural, antibacterial activity, metal complexes.

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ISSN: 0975-8585

INTRODUCTION

Schiff base and its metal complexes have varied applications in biological[1-3], clinical, analytical, corrosion science and pharmacological areas.[4-6]Schiff bases are used as catalysts for certain chemical reactions. Aromatic Schiff bases and their complexes catalyze reactions on oxygenation [7-8] hydrolysis [9], electro-reduction [10], and decomposition [11]. Schiff bases appear to be important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate [12]. Earlier works done by biochemists[13-14], reported that some drugs showed greater activity, as metal complexes when compared to the organic compounds.[15] The coordinating properties of 4-aminoantipyrine have been modified to give new ligands formed by the reaction with aldehydes, ketones, thiocarbazides and carbazides etc.,[16] A continuation of our work on the synthesis of Schiff bases using vanillin, 4-aminoantipyrine, anthranilic acid, o-phenylenediamine and furfural, we have synthesized the zinc (II) complexes with the Schiff base ligands prepared. We are reporting four complexes of zinc (II) with four different Schiff base ligands, their characterization and antibacterial activity.

MATERIAL AND METHODS

All the reagents vanillin, anthranilic acid, 4-aminoantipyrine, o-phenylenediamine, furfural and the metal salts were purchased from Merck and Lobachemie Mumbai, India are used as supplied. The solvents like ethanol, methanol, DMSO etc are purified and dried by standard procedures.[17-18] The microanalytical data of complexes were recorded at Central Electrochemical Research Institute (CECRI) India using vario EL elemental analyzer. IR spectroscopy analyses were recorded on anIR spectroscopy analyses were recorded on Schimadzu FTIR 8400S spectrometer in 4000-200cm^{-1} range using KBr pellet. The UV-Visible spectra were recorded on a Schimadzu 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 ^{1}H-NMR and ^{13}C-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 DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the Minimum Inhibition Concentration (MIC).

Synthesis of Schiff's bases

Synthesis of the Schiffs base VA

The schiffs base from vanillin and anthranilic acid was prepared by dissolving 4.278 gm (0.02 mol) of vanillin in 25 ml ethanol, this solution is then added to 3.856 gm (0.02 mol) of anthranilic acid in 25 ml ethanol with constant stirring for ten minutes. The contents were refluxed on a water bath for 4-5 hrs, then cooled and poured in to crushed ice. The oily liquid

over the water is allowed to stay aside for some time [17], crystals of the schiffs base starts to appear. The crystals were washed with a pinch of sodium bisulphate to remove unreacted aldehyde [17-18]. The crystallization was enhanced by agitating the solution with a glass rod, the resulting solid product is then washed with distilled water and ethanol several times. It was then recrystallized with THF/benzene mixture.

Synthesis of Schiff base AV

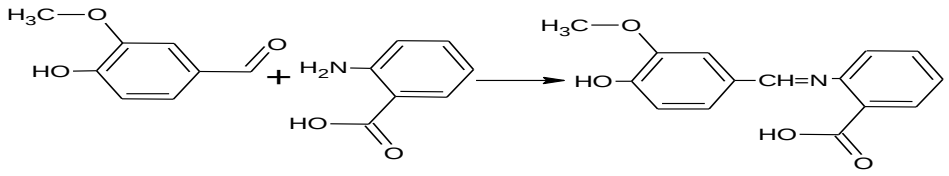
An ethanolic solution (20ml) of 1-phenyl-2, 3-dimethyl-4-aminopyrazol-5-one (2.03gm, 0.01mol) (4-aminoantipyrene) was added to an ethanolic solution of vanillin (1.52gm, 0.01). A yellow colored solid formed on stirring solution vigorously. The mixture was refluxed for 5 hrs and allowed to cool. Yellow colored crystals formed on pouring the mixture in crushed ice. The crystals are separated from the mixture by filtration. The crystals were washed with a pinch of sodium bisulphate to remove unreacted aldehyde [17-18]. Ethanol was used to recrytallize the Schiff base.

Synthesis of Schiff's base AVOP

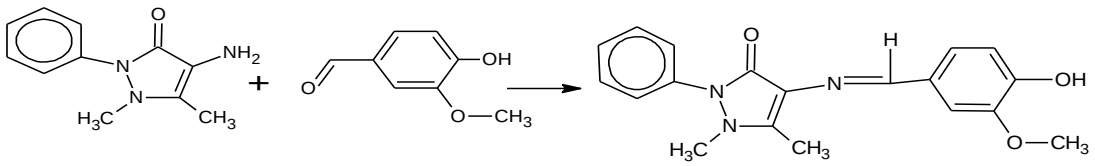
An ethanolic solution (20ml) of 1-phenyl 2, 3-dimethyl-4-aminopyrazol-5-one (2.03gm, 0.01 mol) (4-aminoantipyrine) was added to an ethanolic solution of vanillin (1.52gm, 0.01mol) and the solution was refluxed for 5hours with vigorous stirring and allowed to cool then it was poured in crushed ice when crystals formed. The yellow crystalline AV ligand was, filtered and recrystallized with ethanol. 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 crystals were washed with a pinch of sodium bisulphate to remove unreacted aldehyde [17-18]. The brown solid (L) product was, separated, filtered and re crystallized from ethanol.
Synthesis of Schiff base AFOP .

An ethanolic solution (20ml) of 1-phenyl 2, 3-dimethyl-4-aminopyrazol-5-one (2.03gm, 0.01 mol) (4-aminoantipyrine) was added to an ethanolic solution of furfural (0.96gm, 0.01mol). The solution was stirred vigorously. The solution was refluxed for ca 5hours and allowed to cool. The resulting solution was poured in crushed ice when crystals formed. The yellow crystals were filtered and re crystallized from ethanol. The solid intermediate (2.813g, 0.01mol) was added to an ethanolic solution (20ml) of o-phenylenediamine (0.541g, 0.005mol). The mixture was refluxed for calculated 30 hours. The reaction was followed using TLC. The contents were poured in to crushed ice. The brown solid (L) product was separated. The crystals were washed with a pinch of sodium bisulphate to remove unreacted aldehyde [17-18]. It was filtered and re crystallized from ethanol.

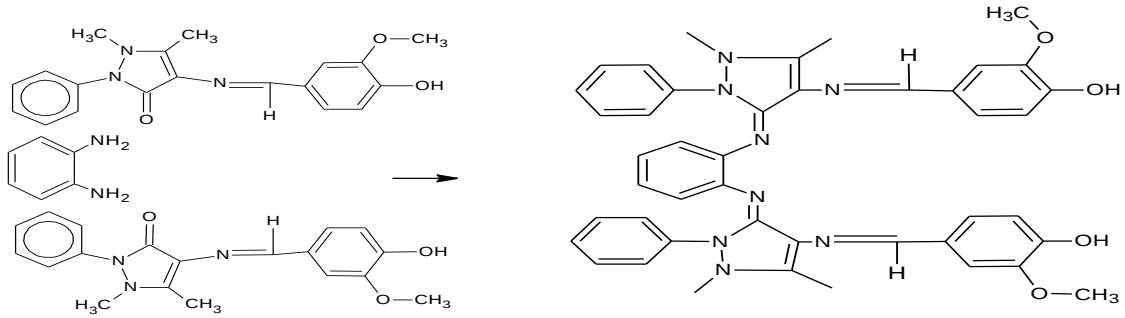
ISSN: 0975-8585



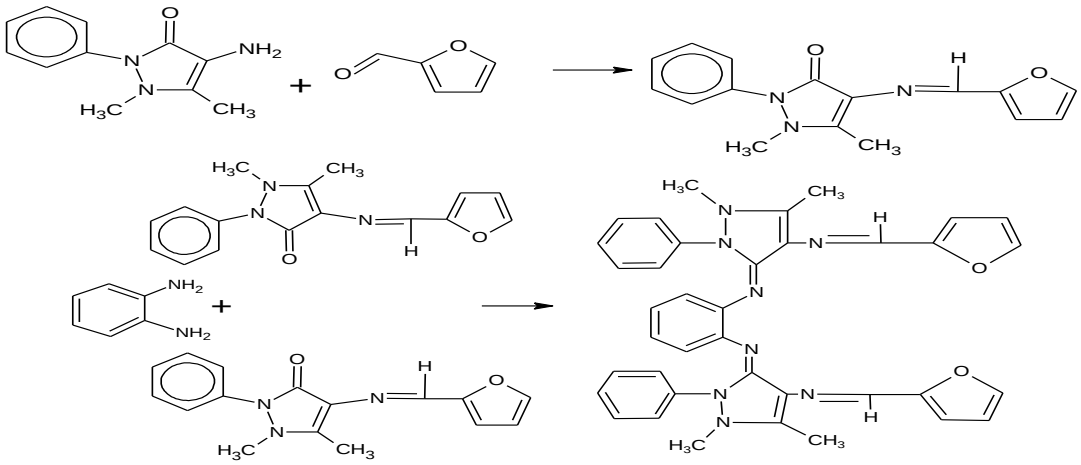
Scheme 1.1 Preparation of ligand VA (Vanillin anthranilic acid Schiff base)



Scheme 1.2 Preparation of ligand AV (4-aminoantipyrine vanillin Schiff base)



Scheme 1.3 Preparation of ligand AVOP (4-aminoantipyrine vanillin o-phenylenediamine Schiff base)



Scheme 1.4 Preparation of ligand AFOP (4-aminoantipyrine furfural o-phenylenediamine Schiff base)

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Figure-1 Preparation of ligands

***$C_{15}H_{13}NO_4$ Ligand* VA:** Yellow. Yield: 86%. M.p.: 205 ^{o}C.M.wt.:271. FT-IR (KBr, cm^{-1}): 3239ν(OH) (alcohol), 1668ν(C=O) (acid), 1585ν(C=N) (benzilidine), 1481ν(COO)..^{1}H NMR (400 MHz, DMSO-d_6): 3.85 (s, 3H, CH_3-O), 5.35 (m, 1H, O-H), 6.90, 7.54, 7.35 (m, 3H, Ar-H), 7.66, 7.80, 8.10, 8.22(m, 4H, Ar-H), 8.62 (m, HC=N), 11.08 (m, COOH). ^{13}C NMR (EtOD , TMS 150MHz): 55.97 1C -CH_3, 113.11 1C-Ar, 116.73 1C-Ar-COO, 117.42 1C-Ar, 123.68 1C Ar, 124.46 1C- Ar, 127.59 1C- Ar, 128.38 1C-Ar, 135.42 1C-Ar, 148.34 1C Ar-O- , 151.08 –Ar-N=C , 155.77 –Ar-OH, 160.47 – CH=N, 166.73 1C-COOH.

***$C_{19}H_{19}N_3O_3$ Ligand* AV:** Yellow. Yield: 86%. M.p.: 167 ^{o}C.M.wt.:337. FT-IR (KBr, cm^{-1}): 3064ν(OH) (alcohol),1624ν(C=O), 1579ν(C=N) (benzilidine). ^{1}H NMR (400 MHz, DMSO-d_6): 2.44 (s, 3H, -CH_3), 3.1 (s, 3H, -CH_3)3.85 (s, 3H, CH_3-O), 5.35 (m, 1H, O-H), 7.37, 7.51 (m, 3H, Ar-H), 6.93(m, 1H, Ar-H), 9.49 (m, HC=N). ^{13}C NMR (EtOD , TMS 150MHz): 55.97 1C -CH_3, 113.11 1C-Ar, 116.73 1C-Ar-COO, 117.42 1C-Ar, 123.68 1C Ar, 124.46 1C- Ar, 127.59 1C- Ar, 128.38 1C-Ar, 135.42 1C-Ar, 148.34 1C Ar-O- , 151.08 –Ar-N=C , 155.77 –Ar-OH, 160.47 – CH=N. Anal.Calcd.for $C_{19}H_{19}N_3O_3$:. C, 67.66; H, 5.6; N, 12.45.Found:. C, 66.422; H, 5.8; N, 12.64.

$C_{44}H_{42}N_8O_4$ Ligand AVOP:Dark Yellow. Yield: 72%. M.p.: 210 ^{o}C. . M.wt.:746.64. FT-IR (KBr, cm^{-1}): 3107ν(OH) (alcohol),1650ν(C=N) (benzilidine). ^{1}H NMR (400 MHz, DMSO-d_6): 2.44 (s, 6H, -CH_3), 3.1 (s, 6H, -CH_3), 3.85 (s, 6H, CH_3-O), 5.35 (m, 2H, O-H), 7.37, 7.51 (m, 8H, Ar-H), 6.90(m, 4H, Ar-H), 8.15, 8.48 (m, 2H, HC=N). ^{13}C NMR (EtOD , TMS 150MHz): 8.61 2C- C-H, 35.23 2C-C-N, 55.97 2C -CH_3, 111.94 2C-Ar, 117.03 2C-Ar-O-CH_3, 122.90 4C Ar, 124.16 6C- Ar, 129.16 4C- Ar, 130.2 2C-Ar, 136.20 2C-Ar, 140.51 2C Ar-O- ,152.64 2C –C=N , 151.86 2C –Ar-OH, 163.6 2C – CH=N. Anal.Calcd.for $C_{44}H_{42}N_8O_4$:. C, 70.71; H, 5.6; N, 15.00.Found:. C, 70.52; H, 4.98; N, 14.99.

$C_{38}H_{34}N_8O_2$ Ligand AFOP:Brown. Yield: 62%. M.p.: 160 ^{o}C. . M.wt.:634.82. FT-IR (KBr, cm^{-1}): 3107ν(OH) (alcohol),1650ν(C=N) (benzilidine). ^{1}H NMR (400 MHz, DMSO-d_6): 2.40 (s, 6H, -CH_3), 3.19 (s, 6H, -CH_3), 6.53 (m, 8H, Furfural), 6.90 (m, 6H, Ar-H), 7.35(m, 4H, Ar-H), 7.75,7.82 (m, 2C-HC=N),7.44(m, 2C- Furfural) . ^{13}C NMR (EtOD , TMS 150MHz): 8.61 2C CH_3-C=C, 35.23 2C-CH_3, 109.98 2C –C-N=C, 112.72 2C- furfural, 118.98 2C –furfural, 122.90 2C –Ar, 124.07 6C C-N, 130.33 2C Ar-C, 136.20 2C C-Ar, 140.51 2C Ar-C-N, 149.12 2C Fur C-O, 144.42 2C Fur C-O, 152.64 2C -C=N, 163.6 2C – CH=N. Anal.Calcd.for $C_{38}H_{34}N_8O_2$:. C, 71.83; H, 5.35; N, 17.64.Found:. C, 70.93; H, 5.35; N, 17.64.

Synthesis of Schiff base complexes

Synthesis of the Zinc VA complex

The 1:2 complex of the metal and ligand is prepared by taking 0.04mol (10.18 gm) schiffs base in 50 ml of ethanol. The corresponding salt of zinc sulphate of 0.02 mol (5.7508gm) was dissolved in 50 ml hot ethanol. The hot alcoholic solution of the metal salt was slowly added to the hot alcoholic solution of the ligand. The resulting mixture was refluxed for 4-5 hrs, few drops of sodium hydroxide was added in drops to act as catalyst for the reaction. Cream

white colored complex of the respective metal starts to separate. The cream white colored precipitate was separated by filtration, washed with distilled water, hot ethanol and with ether. The product was dried and stored over calcium chloride under vacuum.

Synthesis of Zinc AV complex

The 1:2 complexes of the metal and ligand is prepared by taking 0.02mol (0.6745gm) Schiff base in 50 ml of hot ethanol. The corresponding salt of zinc sulphate of 0.001mol (0.287gm) was dissolved in 50 ml hot ethanol. The hot alcoholic solution metal was slowly added the hot alcoholic solution of the ligand. The resulting mixture was refluxed for 4-5 hrs with constant stirring. The contents were reduced to one third of the volume and allowed to crystallize. Cream colored precipitate separated. The crystals were separated by filtration, washed with distilled water, hot ethanol and with ether. The product were dried and stored over calcium chloride under vacuum.

Synthesis of zinc AVOP complex

The Schiff base ligand (0.002mol 1.493g) is dissolved in 50ml hot ethanol. The hot ethanolic solution of the ligand was slowly added to a hot 1:1aqueous ethanolic solution of zinc sulphate (0.002mol 0.338gm). The resulting solution was refluxed on a water bath for 5 hrs. The solution was reduced to one third on a water bath and cooled. The brown colored precipitate is separated by filtration. The solid was washed several times with distilled water and hot ethanol.
Synthesis of zinc AFOP complex

The Schiff base ligand (0.002mol 1.269g) is dissolved in 50ml hot ethanol. The hot ethanolic solution of the ligand was slowly added to a hot 1:1aqueous ethanolic solution of zinc sulphate (0.002mol 0.5751gm). The resulting solution was refluxed on a water bath for 5 hrs. The solution was reduced to one third on a water bath and cooled. The brown colored precipitate is separated by filtration. The solid was washed several times with distilled water and hot ethanol.

[Zn($C_{15}H_{13}NO_4$)$_2$(H_2O)$_2$]Complex:Cream. Yield: 80%. M.p.: 205 ^{o}C.M.wt.:642.39. FT-IR (KBr, cm^{-1}): 3299ν(OH) (water),3131ν(OH) (alcohol),1594ν(C=O) (acid), 1585ν(C=N) (benzilidine), 1457ν(COO). ^{1}H NMR (400 MHz, DMSO-d_6): 3.85 (s, 3H, CH_3-O), 5.35 (m, 1H, O-H), 6.90, 7.54, 7.35 (m, 3H, Ar-H), 7.66, 7.80, 8.10, 8.22(m, 4H, Ar-H), 8.38 (m, HC=N), 11.08 (m, COOH). ^{13}C NMR (EtOD , TMS 150MHz): 55.97 1C -CH_3, 113.11 1C-Ar, 116.73 1C-Ar-COO, 117.42 1C-Ar, 123.68 1C Ar, 124.46 1C- Ar, 127.59 1C- Ar, 128.38 1C-Ar, 135.42 1C-Ar, 148.34 1C Ar-O- , 153.82 –Ar-C-N=C , 155.77 –Ar-OH, 160.47 – CH=N, 170.25 1C-COOH. Anal.Calcd.for[Zn($C_{15}H_{13}NO_4$)$_2$(H_2O)$_2$]Complex: C, 56.13; H, 4.366; N, 4.366. Found: C, 55.18; H, 4.281; N, 4.262. Molar conductance.: 1.56 Λm (Ω^{-1} mol^{-1})

[Zn($C_{19}H_{19}N_3O_3$)$_2$(H_2O)$_2$]SO_4Complex: Cream. Yield: 54%. M.p.: 166 ^{o}C. . M.wt.:871.39. FT-IR (KBr, cm^{-1}): 3130ν(OH) (water), 2993ν(OH) (alcohol), 1607ν(C=O), 1559ν(C=N) (benzilidine). ^{1}H NMR (400 MHz, DMSO-d_6): 2.44 (s, 3H, -CH_3), 3.1 (s, 3H, -CH_3)3.85 (s, 3H, CH_3-O), 5.35 (m, 1H,

O-H), 7.37, 7.51 (m, 3H, Ar-H), 6.93(m, 1H, Ar-H), 9.79 (m, HC=N). ^{13}C NMR (EtOD , TMS 150MHz): 55.97 1C -CH_3, 113.11 1C-Ar, 116.73 1C-Ar-COO, 117.42 1C-Ar, 123.68 1C Ar, 124.46 1C- Ar, 127.59 1C- Ar, 128.38 1C-Ar, 135.42 1C-Ar, 148.34 1C Ar-O- , 151.08 –Ar-N=C , 155.77 – Ar-OH, 160.47 – CH=N. Anal.Calcd.for[Zn($C_{19}H_{19}N_3O_3$)$_2$(H_2O)$_2$]SO_4 Complex :. C, 52.33; H, 4.819; N, 9.639;S, 7.504.Found:. C, 51.892; H, 4.642; N, 9.581; S, 7.461. Molar conductance.:96Λm (Ω^{-1} mol^{-1}).

[Zn($C_{44}H_{42}N_8O_4$)]SO_4 Complex:Dark Yellow. Yield: 60%. M.p.: 210 ^{o}C. . M.wt.: 907.39. FT-IR (KBr, cm^{-1}): 3107ν(OH) (alcohol),1610,1597ν(C=N) (benzilidine), 418 ν(M-N) . ^{1}H NMR (400 MHz, DMSO-d_6): 2.44 (s, 3H, -CH_3), 3.1 (s, 3H, -CH_3), 3.85 (s, 3H, CH_3-O), 5.34 (m, 1H, O-H), 7.37, 7.51 (m, 8H, Ar-H), 6.90(m, 2H, Ar-H), 8.22, 8.50 (m, 2H, HC=N). ^{13}C NMR (EtOD , TMS 150MHz): 8.61 2C- C-H, 35.23 2C-C-N, 55.97 2C -CH_3,108.81 2C, Ar-C-N-,111.94 2C-Ar, 117.03 2C-Ar-O-CH_3, 110.37 2C, Ar-C-N-,122.90 4C Ar, 124.16 6C- Ar, 129.16 4C- Ar, 130.2 2C-Ar, 136.20 2C-Ar, 140.51 2C Ar-O- ,152.64 2C –C=N , 151.86 2C –Ar-OH, 165.56 2C – CH=N. Anal.Calcd.for[Zn($C_{44}H_{42}N_8O_4$)]SO_4 Complex:. C, 58.188; H, 4.628; N, 12.343; S, 3.526 .Found:. C, 57.983; H, 4.562; N, 11.634; S, 7.463. Molar conductance.: 102Λm (Ω^{-1} mol^{-1}).

[Zn($C_{38}H_{34}N_8O_2$)]SO_4 Complex:Brown. Yield: 63%. M.p.: 151^{o}C. . M.wt.:796.21. FT-IR (KBr, cm^{-1}): 3107ν(OH) (alcohol),1650ν(C=N) (benzilidine). ^{1}H NMR (400 MHz, DMSO-d_6): 2.40 (s, 6H, -CH_3), 3.19 (s, 6H, -CH_3), 6.53 (m, 8H, Furfural), 6.90 (m, 6H, Ar-H), 7.35(m, 4H, Ar-H), 7.70,7.84 (m, 2C-HC=N),7.44(m, 2C- Furfural) . ^{13}C NMR (EtOD , TMS 150MHz): 8.61 2C CH_3-C=C, 35.23 2C-CH_3, 108.81 2C –C-N=C, 112.72 2C- furfural, 118.98 2C –furfural, 122.90 2C –Ar, 124.07 6C C-N, 130.33 2C Ar-C, 136.20 2C C-Ar, 140.51 2C Ar-C-N, 149.12 2C Fur C-O, 144.42 2C Fur C-O, 152.64 2C -C=N, 166.38 2C – CH=N. Anal.Calcd.for$C_{38}H_{34}N_8O_2$:. C, 59.13; H, 4.409; N, 14.524; S, 4.002.Found:.C, 59.09; H, 4.208; N, 14.386; S, 4.019. Molar conductance.: 119Λm (Ω^{-1} mol^{-1}).

Antibacterial activity

The antibacterial activity was determined by the Disc Diffusion method. [26-27] Stock solutions were prepared by dissolving the compounds in dimethyl sulphoxide (DMSO).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+/- 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 Staphylococcus aureus, Escherichia coli, Bacillus subtilis and Pseudomonas aeruginosa.

ISSN: 0975-8585

RESULTS AND DISCUSSION

The analytical data for the ligand and the complexes together with physical properties is given below. The analytical data of the ZnVA complex is in agreement with the general formula $[Zn(VA)_2]$. The two primary valency for Zn^{+2} are satisfied by the two COO^- groups inside the coordination sphere. The absence of ions outside the coordination sphere is confirmed by the low conductance value. The analytical data of the ZnAV complex is in agreement with the general formula $[Zn(AV)_2 (H_2O)_2] SO_4$. This is shown from the Λ value 96 Ω^{-1} cm^{-1}. The analytical data and conductance measurements for ZnAVOP and ZnAFOP complexes shows that, the complex possesses the general formula $[Zn(AVOP)_2] SO_4$ and $[Zn(AFOP)] SO_4$.

Infrared spectral analyses

The IR spectra were recorded range 4000-400 cm^{-1} using KBr discs.The IR analyses helps in predicting the mode of bonding between the ligand and the central metal atom. From the IR spectrum it is found that the ligand VA participates in the formation of complex with zinc through [17-19] the COO^- and –C=N nitrogen in ZnVA complex. The zinc in ZnAV complex participates in the formation of complex through the –C=N and the –C=O group present in the five member ring of the ligand. In the remaining two complexes the zinc metal forms coordinate bond with the four –C=N azomethine group possessed by the tetra coordinated ligand. The VA, AV ligands are bidentate and AVOP,AFOP ligands are tetradentate in nature. In all the above cases, it is observed that there is a shift in the frequency of absorption of the functional groups participating in complex formation. This shows the formation of complexes between the zinc metal and the ligand.

UV-Visible spectral analyses

The electronic absorption data are provided in table-3. The electronic absorption spectrum of the zinc complexes [20-25] of VA and AV ligands shows the presence of octahedral geometry due to the ligand to metal charge transfer bands. The zinc complexes of AVOP and AFOP do not show absorption in the electronic spectrum. The zinc metal has completely filled d-level and hence the electronic absorption results in the Ligand to metal charge transfer bands. The table 1 gives the absorption regions observed for the ligands and their complexes.

NMR spectral analyses

The proton and ^{13}C NMR spectrum for the ligand and the zinc complexes were recorded in DMSO with TMS as the standard. The proton NMR spectrum of the VA ligand and the zinc VA complex [26-30] shows peaks in the region δ 3.85 and δ 5.35 due to the O-CH_3 and the OH proton respectively. The aromatic protons show peaks in the region δ 6.9, 7.35, 7.54 for the protons in the benzene ring. There is a down field shift in the benzilidene proton and the remaining regions are not affected in the zinc complexes. The benzilidene –N=CH proton shows a peak in the region δ 8.38. The –COOH proton in the ligand appears in the region δ 11.08. In the ^1H NMR spectrum of the zinc complexes (ZnVA) the –COOH peak is not found which shows

ISSN: 0975-8585

the participation of $–COO^-$ group in bond formation. The benzilidene –N=CH proton shifts to down field in the zinc complexes which is an indication that the lone pair present on the nitrogen of the benzilidene group is participating in the coordination with the zinc metal [12,26-27].

Table 1 – Electronic absorption regions for the ligands and zinc complexes.

Compound	Absorption nm(cm^{-1})	Assignment	Geometry
$C_{15}H_{13}NO_4$=VA	260 (38461) and 315 (31746)	π→π*,n-π* transitions.	
$[Zn(VA)_2(H_2O)_2]$	360(27777)	LMCT	Octahedral
$C_{19}H_{19}N_3O_3$= AV	260(38461)and 315(31746)	π→π* , n-π* transitions.	
$[Zn(AV)_2(H_2O)_2]SO_4$	360(27777)	LMCT	Octahedral
$C_{44}H_{42}N_8O_4$= AVOP	272 (36764) and 305 (32868)	π→π*, n- π* ILCT	
[Zn(AVOP)] SO_4	-	-	
$C_{38}H_{34}N_8O_2$= AFOP	262 and 319	π→π*, n- π* transitions.	
[Zn(AFOP)] SO_4	-	-	

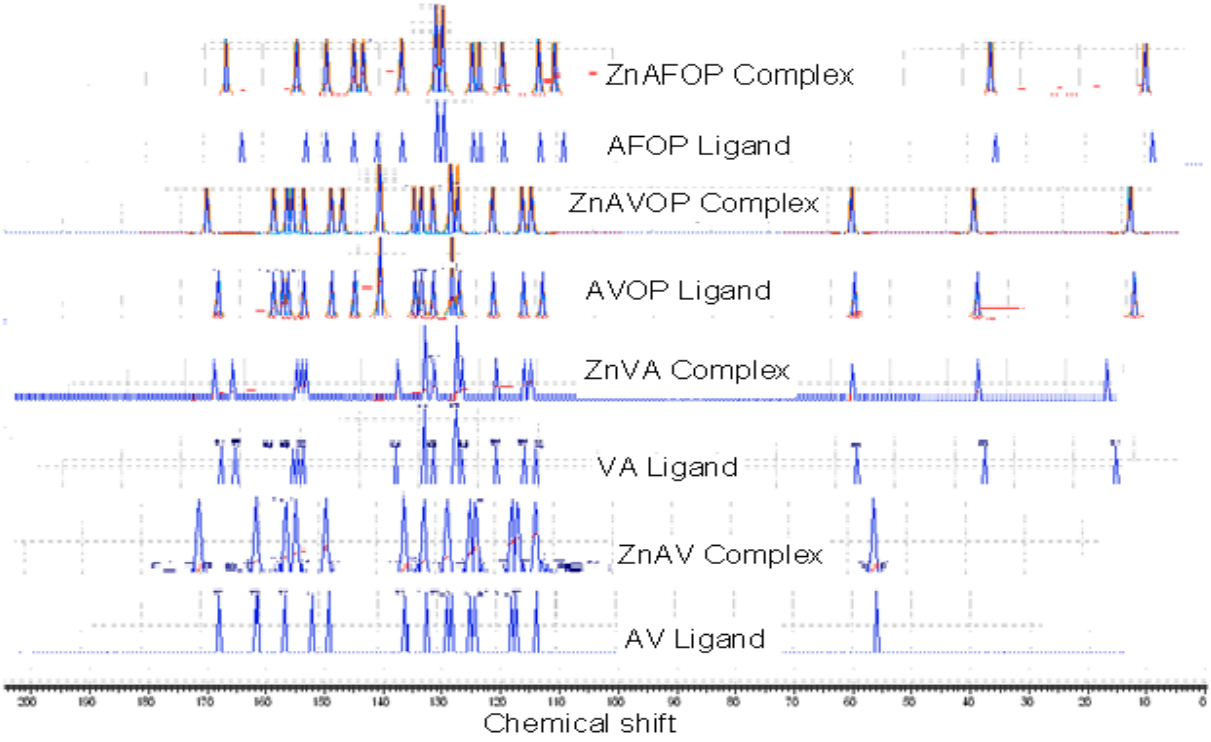

Figure-2 ^{13}C-NMR of the Schiff base and Zn complexes

The –COOH carbon in the VA ligand is shifted down field in the zinc complex when compared for the ligand. In the ^{13}C-NMR spectrum of the ligand and zinc complexes there is a down field shift in the absorption for the benzilidene –C=N carbon atom and the –C-N- carbon in the zinc complexes.The decrease in the chemical shift is attributed to the removal of electron

density around the bonded carbon atom due to coordination. This shows that the nitrogen is participating in the formation of the complex. The rest of the absorptions are not altered. [12,28-30] The various regions of ^{13}C-NMR absorptions in the ligand and the complexes are given in the figure-2. The figure shows the presence of the ligand peaks identical with the complexes except with a small shift in frequency for –C=N and –C-N- groups.

Thermal Analysis

In the thermo gravimetric analysis of the zinc complex shown in figure-3 (a), the ZnVA complex [28-30] is found to be stable till the temperature of 112.08°C. Beyond this temperature the complex loses water molecules. This is in accordance with the weight loss calculation for the loss of water molecules. The found value of weight loss for water is similar to the calculated value. The molecule decomposes from 286.13°C to the formation of a stable residue at 714.73°C. The weight of the residue 11.961% is in agreement with the calculated value of 12.69%. The decomposition of ZnVA complex is given by equations 1-3.

In the thermo gravimetric analysis of the ZnAV complex shown in figure-3 (b), it is observed that the compound is thermally stable up to 127.21 ºC. The zinc complex loses two water molecules between 127.21 ºC and 238.09ºC. The residual percentage of 9.10% after the complete decomposition of the complex is in good agreement with the theoretical value of 9.33%. On the basis of the above observation, the scheme for thermal decomposition proposed for the Schiffs base ZnAVcomplex is given by equations 4 and 5.

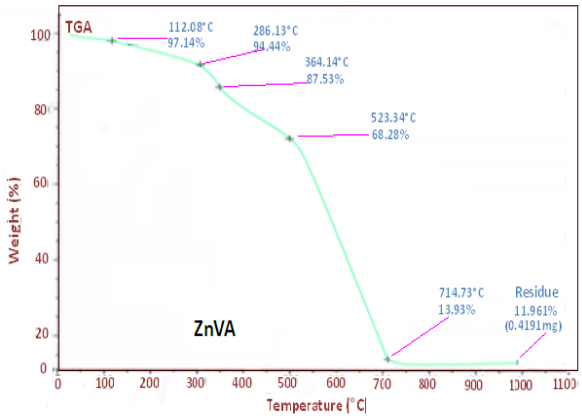

Figure-3 (a)

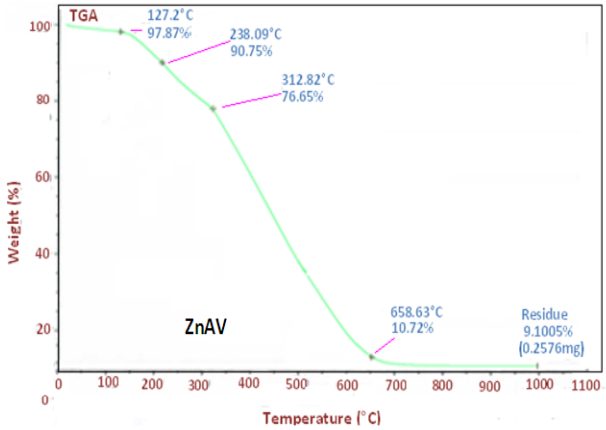

Figure-3 (b)

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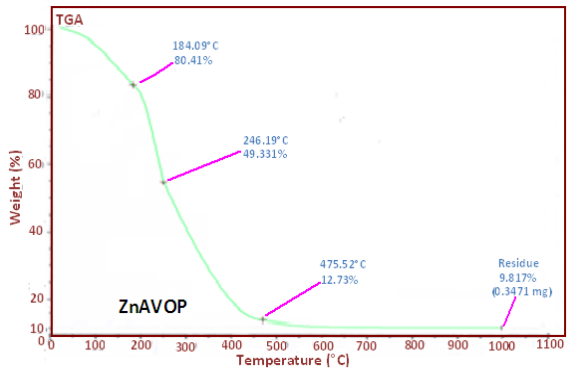

Figure-3 (c)

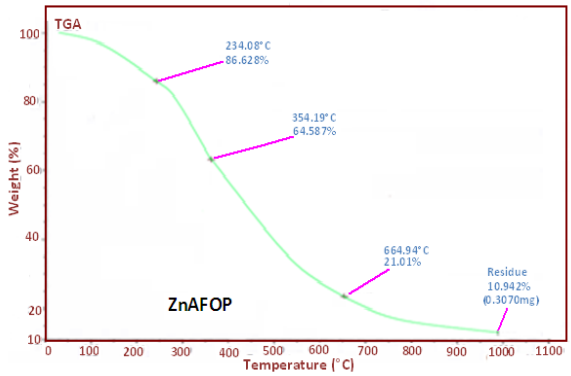

Figure-3 (d)

Stage-I

$[Zn\ (C_{15}H_{12}NO_4)_2(H_2O)_2] \rightarrow [Zn\ (C_{15}H_{12}NO_4)_2]\ H_2O + H2O$ Eqn-1

Stage-II

$[Zn(C_{15}H_{12}NO_4)_2]\ H_2O \rightarrow [Zn(C_{15}H_{12}NO_4)_2]$ Eqn-2

$[Zn(C_{15}H_{12}NO_4)_2] \rightarrow$ ZnO (Residue) Eqn-3

Stage-I

$[Zn\ (C_{19}H_{19}N_3O_3)_2(H_2O)_2]\ SO_4 \rightarrow [Zn\ (C_{19}H_{19}N_3O_3)_2]\ SO_4 + 2H_2O$ Eqn-4

Stage-II

$[Zn\ (C_{19}H_{19}N_3O_3)_2]\ SO_4 \rightarrow$ ZnO (Residue) Eqn-5

From the thermo gravimetric analyses of AVOP Zn complex shown in figure-3 (c), it was observed that the compound is thermally stable up to 184ºC. The zinc complex decomposes with the formation residue with percentage of 9.817% which is close to the theoretical value of 8.969%. The decomposition of the ZnAVOP complex occurs according to the equation 6.

Stage-I

$[Zn\ (C_{44}H_{42}N_8O_4)_2]\ SO_4 \rightarrow$ ZnO (Residue) Eqn-6

From the thermogram of Zn AFOP complex shown in figure-3 (d), it was observed that this compound is thermally stable up to 234 ºC. The zinc complex decomposes with the formation residue with percentage of 10.942% after the complete decomposition of the complex which is close to the theoretical value of 10.222%. Thus based on the thermo gravimetric analysis it is found that the zinc complexes are found to undergo decomposition with agreement to their molecular formula. The residue formed is in accordance with the molecular formula of the zinc complexes.

Stage-I

$[Zn(C_{38}H_{34}N_8O_2)]\ SO_4 \rightarrow$ ZnO (Residue) Eqn-7

ISSN: 0975-8585

Antibacterial activity

The antibacterial study for the complexes was performed on *staphylococcus aureus, Escherichia coli, Bacillus subtilis and Pseudomonosaeruginosa.* The concentration of the ligand and complexes were maintained at 1µgml^{-1} throughout the antibacterial study. The toxicity of the complexes was found to be better than the ligand owing to the theory of Tweedy [30-33]. 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 lipophilicity or liposolubility. 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. It increases the delocalization of π-electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of 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 that restricts further growth of the organisms. Further the azomethine group may involve in hydrogen bond formation with active centre of cell constituents, resulting in interference with the normal cell process. This is an important factor which controls the antimicrobial activity. Table 2 and figure 3give the antibacterial activity for the ligands and complexes.

Table 2 - Antibacterial activity data for the ligands and their zinc metal complexes

Compound	*S.aureus*	*E.coli*	*B.subtilis*	*P.aeruginosa*	Inference Anti bacterial activity
$C_{15}H_{13}NO_4$	4	3	2	2	+
$[Zn^{+2}L_2(H_2O)_2]$	18	17	15	15	+++++
$C_{19}H_{19}N_3O_3$	4	3	3	2	+
$[Zn^{+2}(L)_2(H_2O)_2]SO_4$	16	15	14	17	++++
$C_{44}H_{42}N_8O_4$	3	6	2	6	+
$[Zn^{+2}(L)]\ SO_4$	16	18	12	18	+++++
$C_{38}H_{34}N_8O_2$	7	6	5	4	+
$[Zn^{+2}(L)]\ SO_4$	13	15	12	12	+++

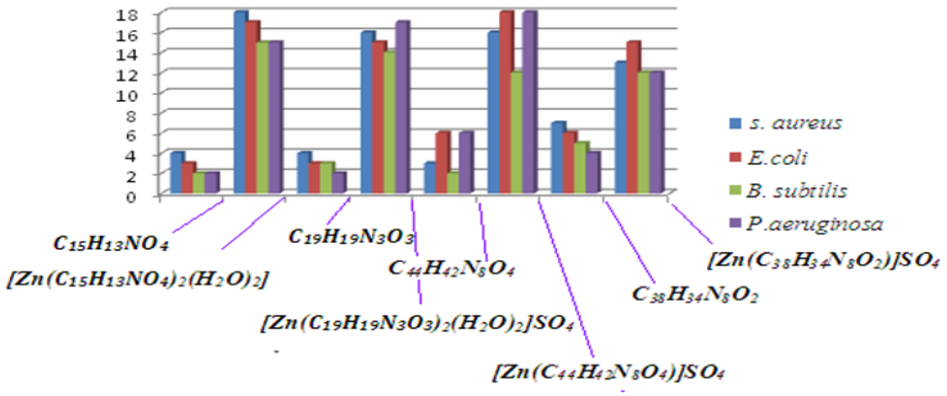

Figure-3 Antibacterial activity of the ligand and complexes

ISSN: 0975-8585

CONCLUSION

In this paper we have reported the co-ordination chemistry of a new series of transition metal complexes of Zn(II) with Schiff base ligand derived from anthranilic acid, 4-aminoantipyrine, vanillin and o-phenylenediamine and furfural. The first two ligands were bidentate and the third and fourth ligands were tetradentate ligands. The structural features were derived from their elemental analyses, infrared, UV-Visible spectroscopy, ^{1}H-NMR, ^{13}C-NMR spectroscopy, thermal gravimetric analyses and conductivity measurements. The data of the complexes suggested, octahedral structure for the ZnVA and ZnVA complexes. Square planar geometry is suggested for the ZnAVOP and ZnAFOP complexes. The Schiff base coordinates through its two and four azomethine nitrogen. The molar conductance measurements suggest the absence of charge on the coordination sphere. The valency of the Zn^{+2} ions is satisfied by the two $-COO^{-}$ anion from the VA ligand. For the ZnAV, ZnAVOP and ZnAFOP the two positive charges on the coordination sphere is satisfied by the anions present outside the coordination sphere as shown in figure 4. The zinc metals, forms 1:2 complexes with the Schiff base ligands VA and AV. The zinc metal forms 1:1 complexes with AVOP and AFOP ligands. Antimicrobial screening tests were performed against bacteria. The comparative study of the MIC values of the Schiff base and its metal complexes indicate that the metal complexes exhibit greater antibacterial activity than the free ligand.

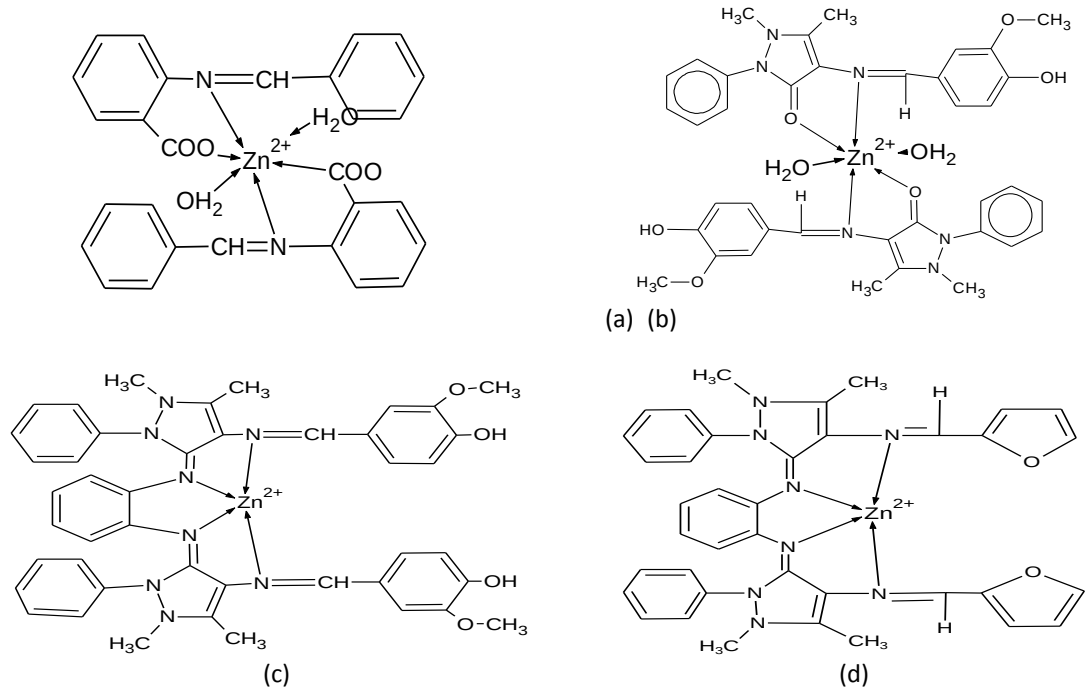

Figure-4 Structure of (a) ZnVA (b) ZnAV (c) ZnAVOP and (d) ZnAFOP complexes

ACKNOWLEDGEMENT

The authors gratefully acknowledge the Central Electrochemical research institute, Karaikudi for helping in recording TG and elemental analysis.

ISSN: 0975-8585

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