



Preparation Characterization and Antibacterial Studies of Chelates of Schiff Base Derived from 4-Aminoantipyrine, Furfural and *o*-Phenylenediamine

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Abstract: A new series of transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized from the Schiff base ligand derived from 4-aminoantipyrine, furfural and *o*-phenylenediamine. The structural features were derived from their elemental analyses, infrared, UV-visible spectroscopy, NMR spectroscopy, thermal gravimetric analyses, ESR spectral analyses and conductivity measurements. The data of the complexes suggested square planar geometry for the metals with primary valency two. 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.

Keywords: Schiff base, 4-Aminoantipyrine, Furfural, *o*-Phenylenediamine.

Introduction

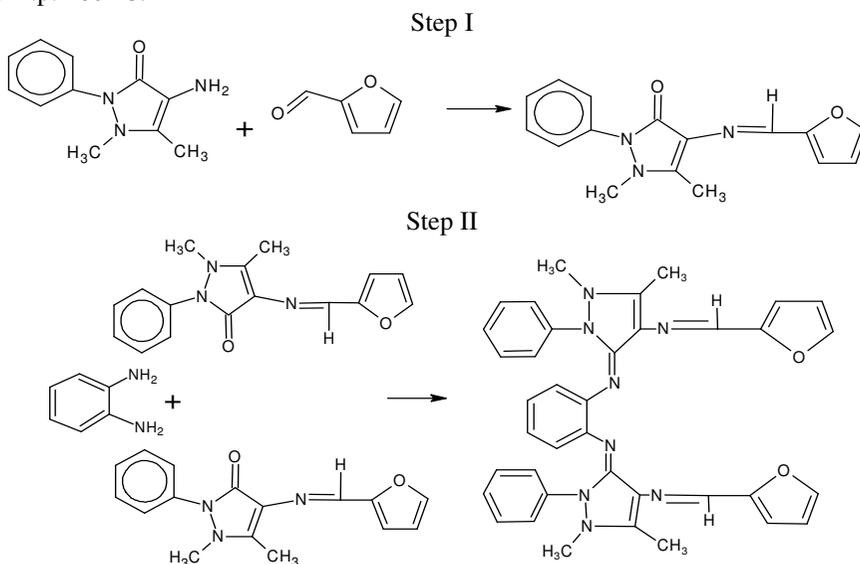
Metal complexes with Schiff base ligands have been studied for their application in biological, clinical, analytical and pharmacological areas¹. Studies of new kinds of chemotherapeutic Schiff bases are now attracting the attention of biochemists^{2,3}. Earlier work reported that some drugs showed greater activity, as metal complexes when compared to the organic compounds³. The coordinating properties of 4-aminoantipyrine have been modified to give new ligands formed by the reaction with aldehydes, ketones, thiocarbazides and carbazides *etc.*⁴. Several works have been carried out on the transition metal complexes of 4-aminoantipyrine derivatives. Very less work is done on the chemistry of transition metal complexes and biological behavior involving the amino group of 4-aminoantipyrine. It is found from literature that very less work is done on the synthesis of Schiff base and its transition metal complexes involving the carbonyl group 4-aminoantipyrine. In this paper efforts were taken for the synthesis, characterization and antimicrobial studies of transition metal complexes containing tetra dentate Schiff base derived from furfural, 4-aminoantipyrine and *o*-phenylenediamine.

Experimental

All the chemicals and solvents were of AR grade. Metal salts were purchased from Merck and Loba chemie Mumbai, India. Vanillin and anthranilic acid were purchases from Loba chemie, Mumbai, India. Ethanol, methanol and the solvents were dried by the standard procedures^{4,5}. The elemental analyses were performed at central electro chemical research institute (CECRI) India using vario EL elemental analyzer. IR spectroscopy analyses were recorded on Shimadzu FTIR 8400S spectrometer in 4000-200 cm^{-1} range using KBr pellet. The UV visible spectra were recorded on a Shimadzu UV spectrometer in the wavelength range 200-800 nm. The thermal analyses were recorded on universal V4.3A TA instrument from CECRI, India. The ESR spectral analyses were recorded on Bruker instrument at 300 and 77 K from CECRI. The ^1H 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 base

An ethanolic solution (20 mL) of 1-phenyl 2, 3-dimethyl-4-aminopyrazol-5-one (2.03 g, 0.01 mol) (4-aminoantipyrene) was added to an ethanolic solution of furfural (1.52 g, 0.01 mol). The solution was stirred vigorously. The solution was refluxed for 5 h and allowed to cool. The resulting solution was poured in crushed ice when crystals formed. The yellow crystals were filtered and recrystallized from ethanol. The solid intermediate (3.373 g, 0.01 mol) was added to an ethanolic solution (20 mL) of *o*-phenylenediamine (0.541 g, 0.005 mol). The mixture was refluxed for calculated 30 h. The reaction was followed using TLC. The contents were poured in to crushed ice. The brown solid (L) product was separated. It was filtered and recrystallized from ethanol. The scheme of the experiment is given below. Yield: 62%; m.p: 160 $^{\circ}\text{C}$.



Scheme 1

Synthesis of Schiff base complexes

The Schiff base ligand (0.002 mol 1.493 g) is dissolved in 50 mL hot ethanol. The hot ethanolic solution of the ligand was slowly added to a hot 1:1 aqueous ethanolic solution of the metal salts. The resulting solution was refluxed on a water bath for 5 h. The solution was reduced to one third on a water bath and cooled. The (Mn⁺²-brown, Co⁺²-pink, Ni⁺²-maroon, Cu⁺²-brown, Zn⁺²-brown) colored precipitate was separated by filtration. The solid was washed several times with distilled water and hot ethanol.

Antibacterial activity

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). 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 10 mm 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.

Results and Discussion

The formation of square planar complexes with (D_{4h} symmetry) is confirmed with the help of the analyses done on the complexes. The 3d transition metals in the first row have been selected for the analyses. The ligand acts as a tetra dentate chelating agent which participates in the formation of coordinate bonding with the central metal atom. The elemental analysis confirms (Table 1) the empirical and molecular formula for the synthesized complexes. The presence of 1:1 and 1:2 electrolytic natures of complexes are confirmed by the conductivity measurements.

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

Compd. (Colour)	m.p., °C	Yield, %	Found (Calc.) %					Λ _m , Ω ⁻¹ mol ⁻¹
			C	H	N	S	M	
C ₃₈ H ₃₄ N ₈ O ₂ =L (Brown)	160	62	70.939 (71.831)	5.247 (5.356)	18.951 (17.643)	0 0	- -	
[Mn ⁺² (L)]SO ₄ (Brown)	187	72	58.426 (58.25)	4.238 (4.343)	14.268 (14.307)	3.962 (4.087)	6.782 (6.642)	108
[Co ⁺² (L)]Cl ₂ (Pink)	147	70	61.92 (62.98)	4.022 (4.188)	13.192 (13.797)	0.0 (0)	7.503 (7.259)	120
[Ni ⁺² (L)]SO ₄ (Brown)	152	50	57.082 (57.757)	4.096 (4.306)	14.083 (14.186)	3.968 (4.053)	6.498 (7.434)	92
[Cu ⁺² (L)]SO ₄ (Brown)	157	60	55.826 (56.132)	3.968 (4.432)	13.863 (13.787)	4.125 (3.939)	7.903 (7.822)	108
[Zn ⁺² (L)]SO ₄ (Brown)	151	63	59.092 (59.135)	4.208 (4.409)	14.386 (14.524)	0.03 (0)	8.853 (8.479)	108

IR analyses

The IR analyses proves the formation of bonds between the metal and the ligand through the azomethine (C=N) group. The Table 2 gives the important frequencies observed for the ligand and the complexes.

Table 2. Characteristic infrared absorption frequencies in (cm⁻¹) of ligand and complexes

No	Compound	ν C=N cm ⁻¹	ν M-N cm ⁻¹
1	C ₄₄ H ₄₂ N ₈ O ₄	1650 cm ⁻¹ to 1565 cm ⁻¹	
2	[Mn ⁺² (L)]SO ₄	1627.26 cm ⁻¹ and 1583.25 cm ⁻¹	445.57
3	[Co ⁺² (L)]Cl ₂	1620.16 cm ⁻¹ and 1582.15 cm ⁻¹	445.57
4	[Ni ⁺² (L)]SO ₄	1559.15 cm ⁻¹	505.37
5	[Cu ⁺² (L)]SO ₄	1625.16 cm ⁻¹ and 1523.15 cm ⁻¹	445.57
6	[Zn ⁺² (L)]Cl ₂	1625.16 cm ⁻¹ and 1583.20 cm ⁻¹	445.57

UV Visible analyses

The electronic spectral data was used to study the geometry of the synthesized complexes. Based on the UV Visible spectrum 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.

Table 3. Characteristic infrared absorption frequencies in (cm⁻¹) of ligand and complexes

Compound	Solvent	Absorption, cm ⁻¹	Band assignment	Geometry
C ₄₄ H ₄₂ N ₈ O ₄ =L	Ethanol	262 and 319	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions.	
[Co ⁺² (L)]Cl ₂	Ethanol	28735, 31646 and 21367	ν_1 and ν_2 are INCT, $\nu_3 = {}^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar
[Ni ⁺² (L)]SO ₄	Ethanol	28169, 31645, 15873 and 19417	ν_1 and ν_2 are INCT $\nu_3 = {}^1A_{1g} \rightarrow {}^1A_{2g}$ ¹ $\nu_4 = {}^3A_{1g} \rightarrow {}^1B_{1g}$	Square planar
[Cu ⁺² (L)]SO ₄	Ethanol	30303, 27932 and 15797	ν_1 and ν_2 are INCT $\nu_3 = {}^2B_1 \rightarrow {}^2A_{1g}$	Square planar

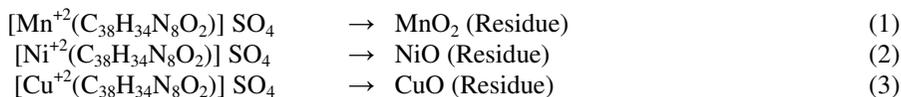
Thermal analyses

The thermal analyses data provides the information on the number of water molecules coordinated to the metal in the coordination sphere, the water of hydration and the residue gives information on the type of molecular formula. Based on the TGA it is confirmed that there are no water molecules present in the coordination sphere. Table 4 gives the data on the TGA for the complexes. The complexes of manganese and zinc donot give absorptions in the UV- visible region.

Table 4. Thermogravimetric analyses of complexes

S. No	Compound	Temp. Range, °C	Stage	Weight loss, %	
				Found	Calculated
1	[Mn ⁺² (L)]SO ₄	Above 614	I	10.16	11.09
2	[Ni ⁺² (L)]SO ₄	Above 598	I	9.262	8.262
3	[Cu ⁺² (L)]SO ₄	Above 579	I	8.389	8.39

Stage-I

*NMR analyses*

The spectral information (Figure 1) was obtained from the proton NMR and ¹³C NMR spectrum of the ligand (Figure 2) with respect to TMS. Multiplet around δ 7.52 shows the presence of benzyldonium CH group. The peak for the benzene appears as multiplet at δ 7.44, the peaks for C-CH₃ and N-CH₃

appears in the region δ 3.11 and δ 2.44 respectively. The peaks for the benzyldienium hydrogen appear at δ 7.82 and δ 7.75. The C^{13} NMR spectral analyses shows corresponding peaks at δ 152.6 for imines, the peak at δ 140.5 corresponds to $-N=C$ bonded to benzene ring through nitrogen. The peak at δ 129.2 corresponds to the benzene carbon atoms. The peak at δ 56.1 and δ 35.2 corresponds to the $-CH_3$ group present in the ring.

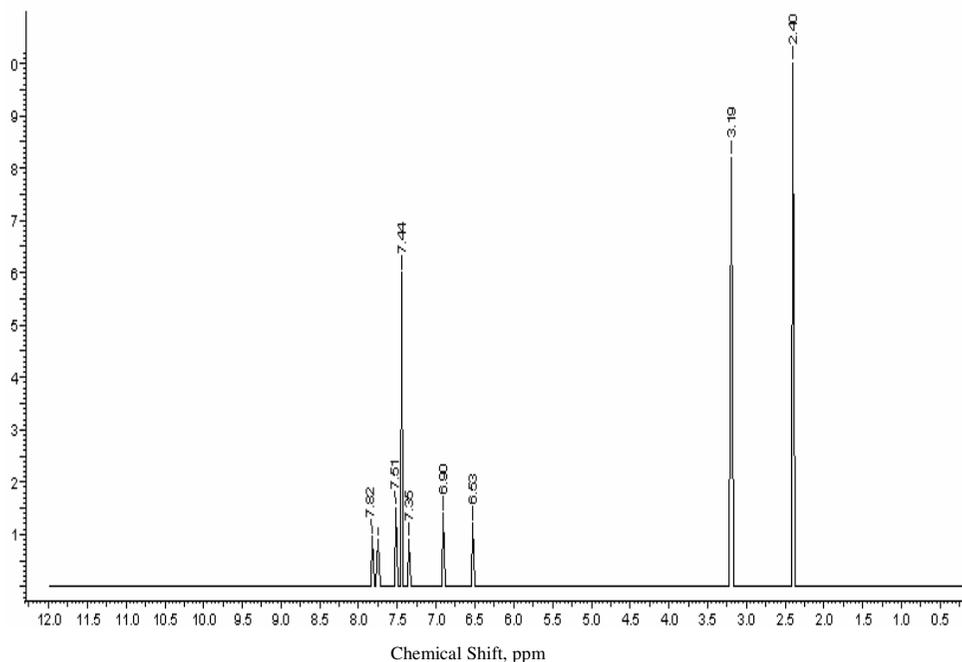


Figure 1. 1H NMR spectrum of the ligand

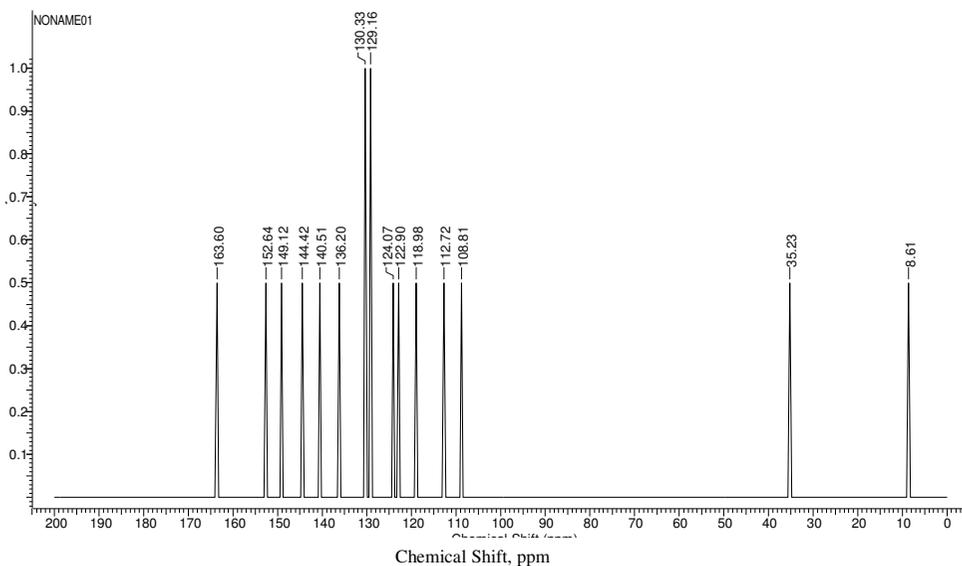


Figure 2. ^{13}C NMR spectrum of the ligand

NMR studies of zinc complex

The azomethine proton signal in the spectrum (Figure 3) of the zinc complex is shifted downfield. Thus the peak at δ 7.52 found in the ligand is shifted to δ 7.84 and the rest of the peaks, C-CH₃ and N-CH₃ appear in the same region δ 3.11, δ 2.44 respectively. The peaks for the benzylidene hydrogen appear at low field δ 8.68 and δ 8.27. There is no appreciable change in all the signals of the complex except -CH=N. This shows the formation of coordinate bond between the Zn⁺² metal and the four azomethine groups.

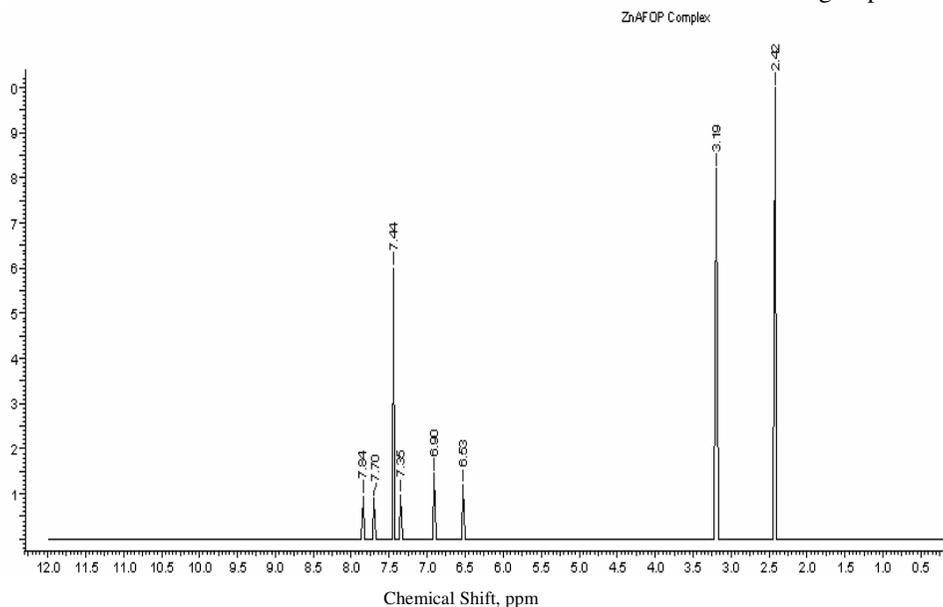


Figure 3. NMR spectrum of Zn complex

The ESR analysis was used for the study of type of bonding and geometry of the complexes. The ESR study confirms the presence of covalent character in the bond present between the ligand, azomethine (C=N) group and the central Cu⁺² metal. The presence of a square planar geometry is confirmed with the help of ESR study on Cu⁺² complex.

Antibacterial activity

The antibacterial study for the complexes was performed on *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and *Pseudomonas aeruginosa*. The results are given in the Table 5. The toxicity of the complexes was found to be better than the ligand owing to the theory of Tweedy.

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
C ₃₈ H ₃₄ N ₈ O ₂	7	6	5	4	+
[Mn ⁺² (L)]SO ₄	8	10	9	9	++
[Co ⁺² (L)]Cl ₂	7	6	5	4	+
[Ni ⁺² (L)]SO ₄	8	9	8	9	++
[Cu ⁺² (L)]SO ₄	12	13	13	14	+++
[Zn ⁺² (L)]SO ₄	13	15	12	12	+++

Elemental analyses (*cf.* Table 1) reveals the presence of 1:1 coordination of the metal with the ligands in the case of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The molar conductance of the complexes reveals the presence of chloride and sulphate ions outside the coordination sphere in the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

IR Studies

The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom⁶. The frequency corresponding to $\nu_{\text{C=N}}$ nitrogen in the complex participates in coordination to the metal ion⁷. Coordination to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lowers the $\nu_{\text{C=N}}$. The spectrum of the ligand shows two $\nu_{\text{C=N}}$ bands in the region 1650 cm^{-1} to 1565 cm^{-1} which is shifted to lower frequencies 1610 cm^{-1} and 1597 cm^{-1} in the spectrum of the complex, showing the participation of $-\text{C=N}$ nitrogen in the coordination to the metal ion⁷. The ligand acts as a tetra dentate chelating agent, bonded to the metal ion *via* the four nitrogen $-\text{C=N}$ atoms of the Schiff base. The appearance of medium band at 445.57 cm^{-1} confirms the presence of M-N coordination in the complex.

UV Studies

The UV spectrum of cobalt(II) complex shows three peaks at 348 nm (28735 cm^{-1}), 316 nm (31646 cm^{-1}) and 468 nm (21367 cm^{-1}) respectively. The peak at 348 nm (28735 cm^{-1}), 316 nm (31646 cm^{-1}) are the bands corresponding to the inter-nuclear charge transfer band. The band at 468 nm (21367 cm^{-1}) is for the $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition¹. The transitions suggests the presence of square planar geometry for cobalt complex. Nickel(II) has a (d^8) configuration giving peaks, found at 355 nm (28169 cm^{-1}), 316 nm (31645 cm^{-1}), 630 nm (15873 cm^{-1}) and 515 nm (19417 cm^{-1}) respectively for the nickel complex. The first and second peaks at 355 nm (28169 cm^{-1}) and 316 nm (31645 cm^{-1}) are assigned for the inter-nuclear charge transfer bands. The third peak at 630 nm (15873 cm^{-1}) is assigned for the $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ excitation and the fourth peak at 515 nm (19417 cm^{-1}) is assigned for the $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ excitations respectively. This confirms the presence of an square planar geometry for the nickel complex¹. Copper(II) has a (d^9) configuration giving peaks, found at 330 nm (30303 cm^{-1}), 358 nm (27932 cm^{-1}) and 633 nm (15797 cm^{-1}) respectively for the copper complex. The first peak at 330 nm (30303 cm^{-1}) and second peaks at 358 nm (27932 cm^{-1}) are assigned for the inter-nuclear charge transfer bands. The third peak at 633 nm (15797 cm^{-1}) is assigned for the $^2\text{B}_1 \rightarrow ^2\text{A}_{1g}$ excitation respectively. This confirms the presence of an square planar geometry for the copper complex¹.

Thermal studies

Thermogravimetric analyses of the complex was used to get the (i) information on water of hydration if present in the coordination sphere of the central metal ion. (ii) scheme of thermal decomposition of the complexes and (iii) to find thermal stability of the complex. From the thermogram, it was observed that this compound is thermally stable up to 150-190 °C. The complexes decompose with the formation residue which is close to the theoretical value.

ESR analyses

ESR spectra of $[\text{Cu}^{+2}(\text{C}_{38}\text{H}_{34}\text{N}_8\text{O}_2)]\text{SO}_4$ recorded in DMSO solution at 300 and 77 K 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. However, this complex in the frozen state at 77 K, four well-resolved peaks of low intensities in the low field region

was observed in the spectrum ruling out any 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 $2B_1g$ as the ground state with the $g_{\parallel} > g_{\perp}$. From the observed values, it is clear that $g_{\parallel} > g_{\perp}$ ($2.2895 > 2.0478$), which suggests that the complex is square planar⁸⁻¹⁰. Also it is supported by the fact that the unpaired electron lies predominantly in the dx^2-y^2 orbital for the copper complex, $g_{\parallel} = 2.2895$, 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 π -bonding), were calculated by using the following equations.

$$\alpha^2 \text{Cu} = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04 \quad (4)$$

$$\beta^2 \text{Cu} = (g_{\parallel} - 2.0023) E / -8\lambda \alpha^2 \quad (5)$$

Where, E is the electronic transition energy of $2B_1g \rightarrow 2A_1g$. The α^2 (0.7329) and $\beta^2 = 0.9345$ value for the complex supports its covalent nature of the bonding. Hathway⁹ 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} .

$$K_{\parallel} = (g_{\parallel} - 2.0023 / 8 \times \lambda_0) \times d - d \text{ transition} \quad (6)$$

$$K_{\perp} = (g_{\perp} - 2.0023 / 2 \times \lambda_0) \times d - d \text{ transition} \quad (7)$$

The observed K_{\parallel} (0.6849) $>$ K_{\perp} (0.434) 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 within the coordination sphere due to the coordination with the carboxylate groups of the ligand.

Antibacterial activity

The antibacterial property of the ligands was compared to the complexes. The Zn^{+2} complexes show good antibacterial activity against the strain of bacteria taken under study when compared to the ligand and other metal complexes taken for study.

Conclusion

A new series of transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized from the Schiff base ligand derived from 4-aminoantipyrine, furfural and *o*-phenylenediamine. The structural features were derived from their elemental analyses, infrared, UV-visible spectroscopy, NMR spectroscopy, thermal gravimetric analyses, ESR spectral analyses and conductivity measurements. The data of the complexes suggested, square planar geometry for the metals with primary valency two. 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. The Schiff base coordinates through its four azomethine nitrogen. The Schiff base behaves as a tetra dentate ligand. The molar conductance measurements suggest the presence of anion outside the coordination sphere for Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} as shown in Figure 4. The metals, forms 1:1 complexes with the Schiff base ligand.

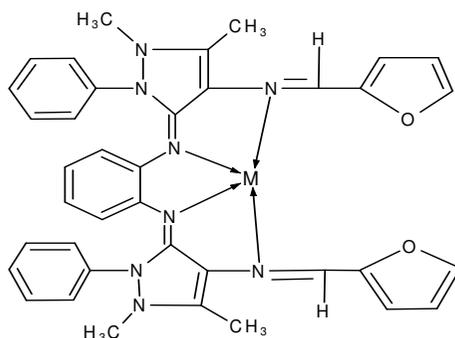


Figure 4. Structure of the metal complex

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