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Synthesis and Characterization of a New Schiff Base and its Metal Complexes Derived from the Mannich Base, N-(1-piperidinobenzyl)acetamide

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New neutral Schiff base complexes of Cu(II), Co(II), Ni(II), and Zn(II) derived from 4-aminoantipyrine and N-(1-piperidinobenzyl) acetamide (Mannich base) have been synthesized. The structural features of the complexes have been characterized by microanalytical data, IR, UV-Vis, ¹H NMR, ESR, CV, TGA and powder XRD techniques. Electronic absorption spectra of the complexes indicate an octahedral geometry around the metal ion. The neutral nature of the complexes is characterized from their low molar conductance values. The cyclic voltammogram of copper complex in DMSO solution shows the process is a quasi-reversible one electron transfer. The ESR spectrum of copper complex in DMSO at 300 K and 77 K was recorded and its salient features are reported. The thermal analysis shows the absence of neither coordinated nor lattice water in all the complexes. The powder XRD pattern indicates the crystalline nature of the complexes. The antimicrobial activity of the ligand and its complexes has been extensively studied on microorganisms such as Staphylococcus aureus, Bacillus subtilis, Escherichia coli and Pseudomonas aeruginosa and the fungi Aspergillus niger and Rhizoctonia bataicola by well-diffusion technique using DMF as the solvent. The values of zone of inhibition were found out at 37°C for a period of 24 h. It has been found that all the complexes have higher activity than the free ligand and the standard.

Keywords antimicrobial activity, Mannich base, N-(1-piperidinobenzyl)acetamide, Schiff base complexes

INTRODUCTION

From the survey of existing literature, it appears that metal complexes of Schiff bases have played a vital role in the

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development of coordination chemistry. The coordination chemistry of Schiff bases as multidentate ligands gained much importance for more than two decades because of their use as models of biological systems (Xiu et al., 1996; Srinivasan et al., 2001; Dharmaraj et al., 2001; Sharma et al., 2001). Among the pyrazolone derivatives, 4-aminoantipyrine forms a variety of Schiff bases with aldehydes/ketones, and are reported to be superior reagents in biological, pharmacological, clinical and analytical applications (Mohamed et al., 2004; Harikumaran et al., 2005; Warad et al., 2000; Jeyasubramanian et al., 1995; Havaldar et al., 2004; Paschke et al., 2003; Raman et al., 2004; 2003; 2001). Earlier work reported that some drugs showed increased activity when administered as metal chelates rather than as organic compounds. Keeping the above facts in mind, and as part of our continuing efforts to investigate transition metal(II) complexes using 4-aminoantipyrine derivatives (Raman et al., 2001; 2002; 2003; 2004), in this article we describe the synthesis, characterisation, redox and antimicrobial studies of Cu(II), Co(II), Ni(II) and Zn(II) complexes containing tridentate Schiff base derived by condensing the biologically active 4-aminoantipyrine with N-(1-piperidinobenzyl)acetamide. This ligand system coordinates to the metal ion in a terdentate manner through the cyclic carbonyl group of the pyrazolone ring, azomethine nitrogen and the nitrogen atom of piperidine. The proposed structure of the complexes is shown below.



M = Cu(II), Co(II), Ni(II) and Zn(II)

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RESULTS AND DISCUSSION

All the metal complexes are stable at room temperature. Physical characterization, microanalytical, molar conductance and magnetic susceptibility data of the complexes are summarized in Table 1. The ligand L, on interaction with Cu(II), Co(II), Ni(II) and Zn(II) chlorides, yields complexes corresponding to the general formula [ML₂]. The analytical data show that the metal to ligand ratio is 1:2. The low molar conductance values of the complexes support their neutral nature (Geary, 1970). Their magnetic susceptibilities at room temperature (Table 1) are consistent with octahedral geometry around the central metal ion.

Infrared Spectra

In order to study the binding mode of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with the IR spectra of the metal complexes. The band at $1650 \,\mathrm{cm}^{-1}$ is characteristic for the keto group in a pyrazolone ring. This band is shifted to ca. $1590-1575 \text{ cm}^{-1}$ region in all the complexes, which is due to enolization of the ligand, i.e., the carbonyl group is converted into the enolic C–O form. Such a lowering of the frequency is due to chelation of carbonyl group to the central metal ion (Nakamoto, 1977; Li et al., 2005) The azomethine group appears at ca. $1600 \,\mathrm{cm}^{-1}$ region for the free ligand. In the complexes, the C=N band was found invariably shifted $20-40 \text{ cm}^{-1}$ towards the negative side, indicating the involvement of azomethine nitrogen atom on coordination to metal ion, and this can be explained by the donation of electrons from nitrogen to the empty d-orbitals of the metal atom. The proof of N and O coordination is demonstrated by the bands that appeared in the far IR spectra of complexes in the regions 500-580 and $380-470 \text{ cm}^{-1}$ assigned to M-O and M-N modes (Ferraro. 1971), respectively. The IR band observed at 1100 cm^{-1} has been assigned to C-N-C of the piperidine group. In all the complexes, the C-N-C of piperidine band displayed substantial negative shifts with fairly low intensity, indicating the coordination through the nitrogen of piperidine entity present in the ligand. In the spectra of all the complexes, the N-H band remained at the same position as in the free ligand, indicating that the secondary nitrogen is not coordinated.

Electronic Absorption Spectra

The electronic absorption spectra of the Schiff base and its Cu(II), Co(II), and Ni(II) complexes were recorded at room temperature using DMSO as a solvent. Only one broad band is observed at 16638 cm^{-1} in the electronic spectrum of the Cu(II) complex assigned to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition, which is in conformity with octahedral geometry (Dunn, 1960). Though three transitions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope. The electronic spectra of Co(II) complex showed two spin-allowed transitions at 17856 and 21734 cm⁻¹ assignable to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (F) and ${}^4T_{1g}$ $(F) \rightarrow {}^{4}T_{1g}(P)$ transitions, respectively, that are in conformity with octahedral arrangements for Co(II) ion (Lever 1968). The appearance of a band at 19240 cm⁻¹ due to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transition favors an octahedral geometry (Cotton and Wilkinson, 1988) for the Ni(II) complex. The absence of any band below 10000 cm⁻¹ eliminates the possibility of a tetrahedral environment in this complex.

Magnetic Susceptibility Measurements

The magnetic moment value of Cu(II) complex is 1.9 B.M., which suggests an octahedral geometry (Dunn, 1960) around the metal ion. The magnetic moment of Co(II) complex is 4.5 B.M., which suggests the high spin six coordinated octahedral arrangement of ligand molecules around the metal ion (Lever, 1968). The Ni(II) complex has a magnetic moment value of 3.8 B.M., indicating a spin free octahedral configuration (Cotton, 1988). The Zn(II) complex is found to be diamagnetic as expected for d^{10} configuration.

¹H NMR Spectra

The ¹H NMR spectra of the Schiff base ligand exhibits a multiplet signal at 7.2–7.8 δ (m, Ar-H) and 10.1 δ (s, N-H). In Zn(II) complex, the N-H proton is shifted slightly downfield at 10.3 δ , which reveals the bonding of the azomethine nitrogen

	% Analysis, found (calcd)						
Compound	М	С	Н	N	Yield %	$\mu_{\rm eff}$ (B.M)	λm (mho cm ² mol ⁻¹)
Ligand	_	71.0 (71.9)	7.1 (7.7)	15.9 (16.8)	69	_	
$[CuL_2]$	6.7 (7.1)	66.1 (66.8)	6.2 (6.9)	15.1 (15.6)	57	1.9	2.8
$[CoL_2]$	6.2 (6.6)	66.7 (67.2)	6.3 (6.9)	15.4 (15.7)	53	4.5	4.1
[NiL ₂]	6.5 (6.6)	66.5 (67.1)	6.7 (6.9)	14.8 (15.6)	51	3.8	3.6
$[ZnL_2]$	7.0 (7.3)	66.0 (66.6)	6.1 (6.8)	15.0 (15.6)	55	—	3.8

 TABLE 1

 Analytical data of the Schiff base ligand and its metal complexes

L = Schiff base ligand.

to Zn(II) ion. The ¹H NMR spectrum of the ligand shows a signal at 2.4–2.6 δ (piperidine N-CH₂). In Zn(II) complex, the signal due to piperidine N-CH₂ protons also shifted slightly and appeared at 2.6–2.8 δ in the complex. This is an indication of the coordination of piperidine nitrogen. The ¹H NMR spectra of the Schiff base ligand exhibits a signal at 10.7 δ and is assigned to -C=C-OH, which was absent in the Zn(II) complex, suggesting that the ligand is in enol form, followed by coordination of carbonyl oxygen to the metal via deprotonation.

ESR Spectra

The ESR spectrum of copper complex provides information that is important in studying the metal ion environment. The ESR spectra of the Cu(II) complex were recorded (Figure 1) in DMSO at 77 K and at 300 K. The spectrum of the copper 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 at 77 K shows four well resolved peaks with low field region. The copper complex exhibits the g_{\parallel} value of 2.31 and g_{\perp} value of 2.16. These values indicate that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital (Dutta and Syamal, 1992). The spin-orbit coupling constant, λ value (-488 cm⁻¹) calculated using the relations, $g_{av} = 1/3[g_{\parallel} + 2g_{\perp}]$ and $g_{av} = 2(1-2\lambda/10Dq)$, is less than the free Cu(II) ion (-832 cm⁻¹), which also supports covalent character (Yen, 1969) of M-L bond in the complex.



FIG. 1. The X-band ESR spectrum of the copper complex in DMSO at (a) 300 K and (b) 77 K.

The G value of 3.82 indicates negligible exchange interaction of Cu-Cu in the complex. The covalency parameter α^2 is calculated ($\alpha^2 = 0.82$) using the following equation:

$$\alpha_{cu}^{2} = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

If the value of $\alpha^2 = 0.5$, it indicates a complete covalent bonding, while the value of $\alpha^2 = 1.0$ suggests a complete ionic bonding. The observed value of α^2 (0.82) of the complex is less than unity, which indicates that the complex has some covalent character in the ligand environment (Dutta and Syamal, 1992).

Cyclic Voltammetric Study

The cyclic voltammogram of Cu(II) complex (0.01 M) in DMSO solution at room temperature in 0.8 to -1.0 V potential range at scan rate 50 mVs⁻¹ indicating quasi-reversible oneelectron process (Tumer et al., 2001). A noteworthy feature has been observed in the cyclic voltammogram of Cu(II) complex (Figure 2). During the forward scan, it shows two cathodic reduction peaks, one at +0.23 V and another at -0.82 V, which are attributed to reduction of Cu(II) \rightarrow Cu(I) and Cu(I) \rightarrow Cu(0), respectively. During the reverse scan, it shows two anodic oxidation peaks, one at -0.61 V and another at +0.28 V which are attributed to oxidation of Cu(0) \rightarrow Cu(I) and Cu(I) \rightarrow Cu(II), respectively.

Thermal Study

The thermal decomposition studies of Cu(II), Co(II), Ni(II) and Zn(II) complexes show no appreciable change at about 170° C when heated. The thermal analytical data of the Cu(II) complex shows a 7.0% loss in weight (theor. 7.1%), Co(II) complex shows a 6.5% loss in weight (theor. 6.6%), Ni(II) complex shows a 6.4% loss in weight (theor. 6.6%) and Zn(II) complex shows a 7.1% loss in weight (theor.



FIG. 2. Cyclic voltammogram of copper complex in DMSO.

7.3%), indicating the absence of either coordinated or lattice water molecules in these complexes.

FAB Mass Spectra

The FAB mass spectra of the Schiff base ligand and its copper complex (Figure 3) are used to compare their stoichiometric composition. The Schiff base ligand shows a molecular ion peak M^+ at m/z = 417. The molecular ion peak for the copper complex was observed at m/z = 898, which confirms the stoichiometry of metal chelates as ML₂.

Powder XRD Pattern

Due to practical difficulties in obtaining good crystals, single crystal XRD could not be employed to ultimately confirm the structure. However, powder X-ray diffractogram is some consolation to us. The X-ray diffraction pattern of copper complex is in the 2θ range from 3 to 65° C, which corresponds to inter-planar distance d = 7.824. The pattern was found to be similar with a sharp peak clearly indicating the crystalline nature of the copper complex.



FIG. 3. The FAB mass spectrum of (a) the Schiff base and (b) its copper complex.

Biological Activity

Antibacterial activity of the ligand and its complexes have been carried out against the Gram positive bacteria like S. aureus, B. subtilis and Gram negative bacteria such as E. coli, P. aeruginosa using Muller-Hinton agar by welldiffusion method (Chakrawarti, 2001) using DMF as solvent. Ampicillin was used as the standard for comparing the results. Antifungal activity of the ligand and its complexes has been carried out using the fungi such as A. niger and R. bataicola by well-diffusion technique using DMF as solvent. For the antifungal activity, potato dextrose agar (PDA) medium was used. Amphotericin was used as the standard. The zone of inhibition values were determined at the end of an incubation period of 24 h at 35°C. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. It has been observed from the results (Tables 2 and 3) that the metal complexes have a higher activity than that of the free ligand and the standard. This may be 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 only lipid soluble materials due to which liposolubility is an important factor that 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 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.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. The solvents were dried and distilled before use according to standard

 TABLE 2

 Antibacterial activity of the Schiff base ligand and its metal complexes

			-			
		Inhibition zone (mm)				
No.	Compound	S.aureus	E.coli	P.auroginosa	B.subtilis	
1.	Ligand	11	13	12	12	
2.	$[CuL_2]$	18	24	21	20	
3.	$[CoL_2]$	16	20	19	17	
4.	[NiL ₂]	17	22	20	18	
5.	$[ZnL_2]$	18	23	25	21	
6.	Ampicillin	10	12	11	11	

L = Schiff base ligand.

TABLE 3 Antifungal activity of the Schiff base ligand and its metal complexes

		Inhibition zone (mm)		
No.	Compound	A.niger	R.bataicola	
1.	Ligand	7	9	
2.	$[CuL_2]$	10	13	
3.	$[CoL_2]$	13	17	
4.	[NiL ₂]	11	14	
5.	$[ZnL_2]$	14	15	
6.	Amphotericin	9	11	

L =Schiff base ligand.

procedures. The supporting electrolyte, tetramethylammoniamperchlorate, Me₄NClO₄ (TMAP) used in the voltammetric experiment was purchased from Sigma. IR spectra were recorded at Pondicherry University on a Jasco FT-IR-5300 instrument (KBr pellet technique). The ¹H NMR spectra were recorded in DMSO-d₆ on a Brucker instrument using tetramethylsilane (TMS) as internal standard. The UV-Vis spectra of all the complexes were recorded in DMSO on a Shimadzu UV 1601 spectrophotometer. Microanalytical data were performed at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. Magnetic susceptibility measurements of the complexes in the solid state were determined by Gouy balance using CuSO₄ as the calibrant. Molar conductance of the complexes were measured in DMSO at room temperature using Systronic conductivity bridge type 305. Electrochemical measurements were carried out in electrochemical analyzer model BAS-50 voltammograph. The three-electrode cell contained a reference Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode. E.p.r. spectra of the copper complex were recorded on a Varian E112 X-band spectrometer at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, using tetracyanoethylene (TCNE) as the internal standard. The thermogravimetric analysis of copper complex was carried out in nitrogen atmosphere on a STA 409C instrument at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai. The computer controlled X-ray diffractometer system JEOL JDX 8030 was used to record the data for powder copper complex, recorded at Central Electrochemical Research Institute, Karaikudi. Muller-Hinton agar was used for testing the susceptibility of microorganisms to antibacterial agents using the well-diffusion technique. Ampicillin was used as the standard. For the antifungal activity, potato dextrose agar (PDA) medium was used. Amphotericin was used as the standard.

Synthesis of Schiff Base

The Schiff base was synthesized by the condensation of an ethanolic solution (50 mL) of 4-aminoantipyrene (6.09 g, 30 mmol) and the Mannich base, N-(1-piperidinobenzyl)acetamide (6.96 g, 30 mmol). The reaction mixture was boiled for ca. 2 h and it was then cooled at room temperature. The orange solid precipitate of Schiff base obtained was filtered, washed with distilled water, dried at room temperature and finally recrystallized from ethanol. Yield: 8.75 g (69%); (m.p: 148°C).

Synthesis of Metal Complexes

An ethanolic solution of Schiff base (5 mmol) was mixed with metal(II) chloride (2.5 mmol) in ethanol (25 mL) solution keeping ligand-metal ratio 2:1. The reaction mixture was then refluxed for ca. 1 h on a water bath till the complex precipitated out. The solid complex obtained was removed by filtration, successively washed with water, dried at room temperature and recrystallized from ethanol.

CONCLUSIONS

The Schiff base and its complexes have been synthesized using the Mannich base and characterized on the basis of analytical and spectral data. All the complexes exhibit octahedral geometry. The antimicrobial activity of the complexes is higher than the ligand and the standard. The synthesized metal complexes may serve as a vehicle for activation of ligand as the principle cytotoxic species.

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