ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.2, pp 937-943, 2015

Metal complexes of Schiff base derived from a new Mannich base

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Abstract: Novel terdentate neutral complexes of Cu(II), Co(II), Ni(II) and Zn(II) have been prepared using a Schiff base derived from biologically active 1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one (4-aminoantipyrine) and N-(1-piperidino(4-N,N-dimethylaminobenzyl) acetamide (Mannich base). The structural features of the complexes have been confirmed by microanalytical data, IR, UV-vis, EPR, Mass, CV and TGA 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 electrochemical behaviour of the copper complex in DMSO solution at 298 K was studied. The EPR spectra of copper complex in DMSO at 300 K and 77 K were recorded and its salient features are reported. The thermal analysis shows the absence of neither coordinated nor lattice water in all 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* by well-diffusion technique using DMF as solvent. The values of zone of inhibition were found out at 37^0C for a period of 24 h. It has been found that all the complexes have higher activity than the free ligand and the standard.

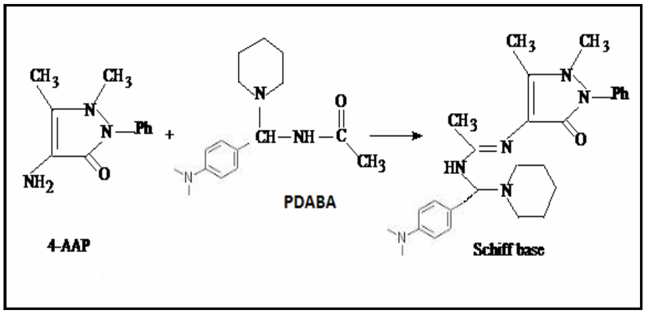
Introduction

From the survey of existing literature, it appears that metal complexes of Schiff bases have played a vital role in the development of coordination chemistry[1-4]. The coordination chemistry of Schiff bases as multi dentate ligand gained much importance for more than two decades because of their use as models of biological systems[5-8]. Transition metal complexes of pyrazolone derivatives are of great interest due to their biological activity and it has been a challenging task in most of the leading research laboratories in the world. 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. Keeping the above facts in mind and as part of our continuing efforts to investigate transition metal(II) complexes using 4-aminoantipyrine derivatives[9-15], in this paper we describe the synthesis, characterization, redox and antimicrobial studies of Cu(II), Co(II), Ni(II) and Zn(II) complexes containing terdentate Schiff base derived by condensing the biologically active 4-aminoantipyrine with N-(1-piperidino(4-N,N-dimethylamino benzyl) 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.

Experimental

Synthesis of Schiff base:

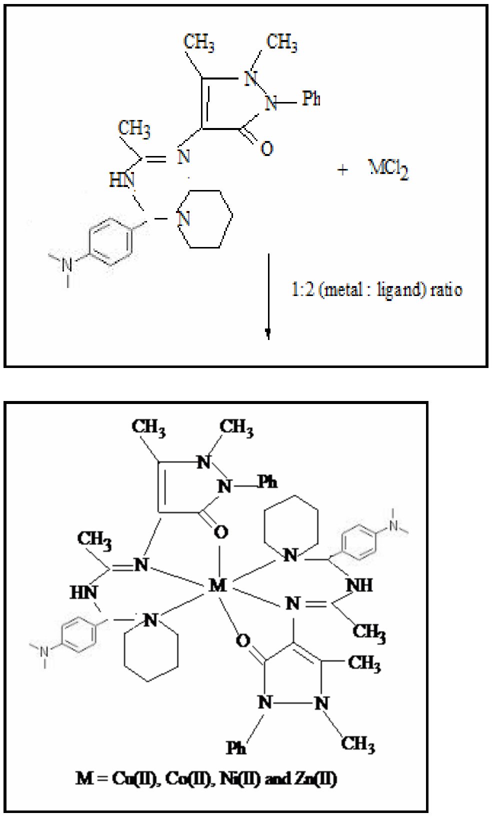
The Schiff base was synthesised by the condensation of an ethanolic solution (50 mL) of 4-aminoantipyrine (6.09 g, 30 mmol) and the Mannich base, N-(1-piperidino(4-N,N-dimethylaminobenzyl) acetamide (8.26 g, 30 mmol). The reaction mixture was boiled for *ca.* 2 h and it was then cooled at room temperature. The orange solid precipitate of Schiff base obtained was filtered, washed with distilled water, dried at room temperature and finally recrystallised from ethanol. Yield : 9.32 g (64%) ; (m.p: 178^{0}C).



Scheme 1. Formation of Schiff base

Synthesis of 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 recrystallised from ethanol.



Scheme 2. Formation of metal complexes

Results and discussion

All the metal complexes are stable at room temperature. They are insoluble in water but soluble in DMF and DMSO. The ligand L, on interaction with Cu(II), Co(II), Ni(II) and Zn(II) chlorides, yields complexes corresponding to the general formula [ML_2]. 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[16]. The FAB mass spectra of the ligand and its copper complex were compared for their stoichiometric composition. The Schiff base shows a molecular ion peak at m/z = 436. The molecular ion peak for the Cu(II) complex was observed at m/z = 936 which confirms its stoichiometry as ML_2.

Their magnetic susceptibilities at room temperature are consistent with octahedral geometry around the central metal ion. The thermal analysis of metal complexes are found to be thermally stable upto 280^0C, i.e. no weight loss in TG's and no exothermic or endothermic peaks in DTA curves were observed, indicating the absence of either coordinated or lattice water. The final product of thermal decomposition was found to be the metal oxide.

IR 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 spectra of the metal complexes. The band at 1650 cm^{-1} is characteristic for the keto group in a pyrazolone ring. This band is shifted to 1600-1620 cm^{-1} region in all the complexes. Such a lowering of the frequency is due to chelation of carbonyl group to the central metal ion[17,18]. The azomethine group appears at *ca.*1600 cm^{-1} region for the free ligand. In the complexes, the C=N band was found invariably shifted 20-40 cm^{-1} towards negative side indicating the involvement of azomethine nitrogen atom on coordination to metal ion. The proof of N and O coordination is demonstrated by the bands that appeared in the spectra of complexes in the region 500-580 and 380-470 cm^{-1} assigned to M-O and M-N modes[19], respectively. The IR band observed at 1100 cm^{-1} has been assigned to C-N-C of 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. The IR spectra of the Schiff base ligand and its complexes are shown in Figure 1.

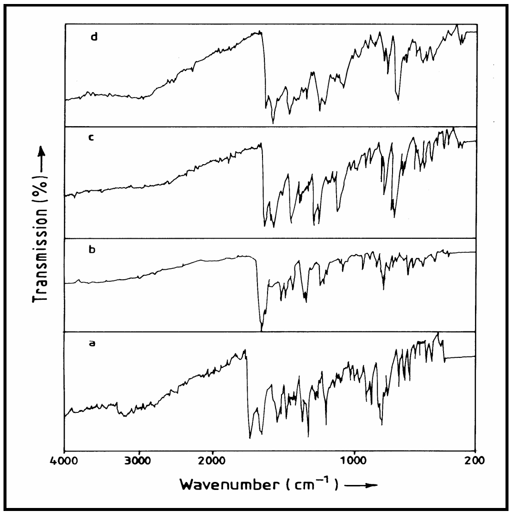


Figure 1. IR spectra of Schiff base (a), CuL_2 (b), CoL_2 (c) and NiL_2 (d) complexes

Electronic absorption spectra:

The electronic absorption spectra of the Schiff base and its Cu(II), Co(II), and Ni(II) complexes recorded at room temperature using DMSO as solvent are shown in Figure 2. Only one broad band is observed at 16650 cm^{-1} in the electronic spectrum of the Cu(II) complex assigned to $^2E_g \rightarrow ^2T_{2g}$ transition which is in conformity with octahedral geometry[20-22]. 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 spectrum of Co(II) complex showed two spin-allowed transitions at 17856 and 21740 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, are in conformity with octahedral arrangements for Co(II) ion[23-26]. The appearance of a band at 19340 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition which favours an octahedral geometry[22,27-30] for the Ni(II) complex. The absence of any band below 10000 cm^{-1} eliminates the possibility of a tetrahedral environment in this complex.

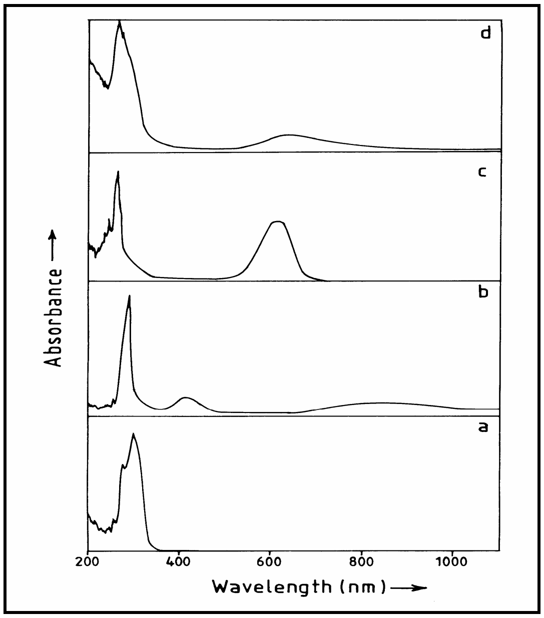


Figure 2. Electronic absorption spectra of Schiff base (a), CuL$_2$ (b), CoL$_2$ (c) and NiL$_2$ (d) complexes

Magnetic susceptibility measurements:

The magnetic moment value of Cu(II) complex is 1.9 B.M. which suggests an octahedral geometry[31] 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[32]. The Ni(II) complex has magnetic moment value of 3.8 B.M. indicating a spin free octahedral configuration[33,34]. The Zn(II) complex is found to be diamagnetic as expected for d^{10} configuration.

EPR spectra:

The EPR spectrum of copper complex often provides useful and reliable informations which are important in studying the metal ion environment. The EPR spectra of the Cu(II) complex recorded in DMSO at 77 and at 300 K are shown in Figure 3. The spectrum of the copper complex at RT 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 LNT shows four well resolved peaks with low field region. The copper complex exhibits the $g_{||}$ 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[35]. The spin-orbit coupling constant, λ value (-488 cm^{-1}) calculated using the relations, $g_{av} = 1/3[g_{||}+2g_{\perp}]$ and $g_{av} = 2(1-2\lambda\ /10Dq)$, is less than the free Cu(II) ion (-832 cm^{-1}) which also supports covalent character[36] of M-L bond in the complex. 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:

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

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[37].

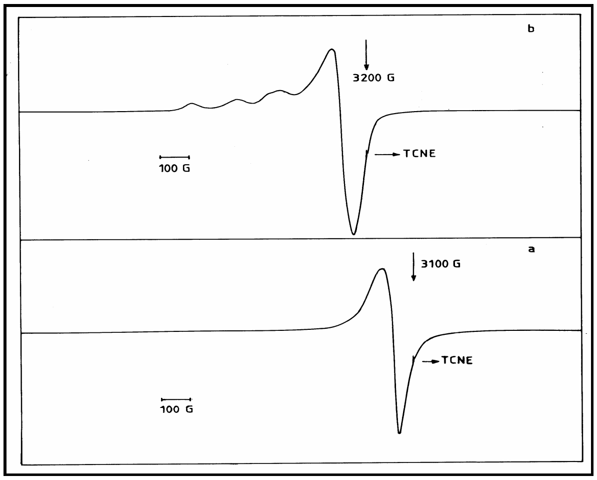


Figure 3. EPR spectrum of CuL_2 complex in DMSO at 300 (a) and 77 K (b)

Cyclic voltammetric study:

The cyclic voltammogram of Cu(II) complex (0.01 M) in DMSO solution in the absence of molecular oxygen at room temperature in 0.8 to –1.0 V potential range at scan rate 50 mVs^{-1} indicates quasi-reversible one-electron process[38]. A noteworthy feature has been observed in the cyclic voltammogram of Cu(II) complex (Figure 4). During the forward scan it shows two cathodic reduction peaks, one at +0.22 V and another at –0.82 V which are attributed to reduction of Cu(II)→Cu(I) and Cu(I)→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)→Cu(I) and Cu(I)→Cu(II) respectively.

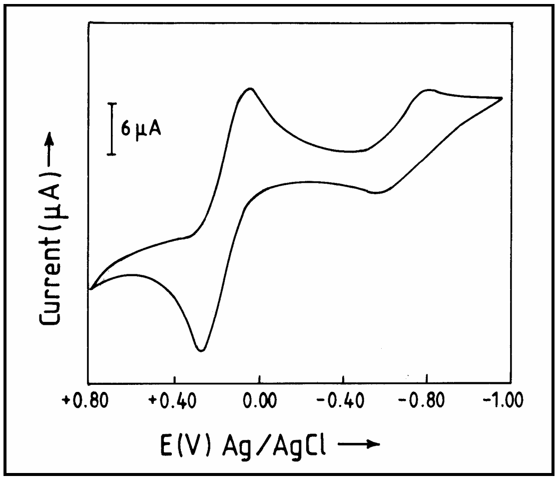


Figure 4. Cyclic voltammogram of CuL_2 complex in MeCN at 300 K (0.1 TMAP); scan rate 50 mVs^{-1}.

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. auroginosa* using Mueller-Hinton agar by well-diffusion method[39,40] using DMF as solvent. Ampicillin was used as the standard for comparing the results. The zone of inhibition values were determined at the end of an incubation period of 24 h at 35^0C. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. It has been observed from the results (Table 1) that the metal complexes have higher activity than that of the free ligand and the standard.

Table 1. Antibacterial activity of the ligand and its metal complexes

No.	Compound	Inhibition zone (mm)			
		S.aureus	E.coli	P.auroginosa	B.subtilis
1	Ligand	10	12	12	11
2	CuL_2 complex	17	23	20	20
3	CoL_2 complex	19	20	19	17
4	NiL_2 complex	19	21	20	18
5	ZnL_2 complex	18	20	21	22
6	Ampicillin	9	11	10	10

Acknowledgements

The author **Dr.SR** thanks the Managing Board of Veltech University, Chennai for their encouragement. **CM** grateful to the Principal of Jaya College of Engineering, Chennai. The authors also thank the RSIC, CDRI, Lucknow and RSIC, IIT, Chennai and Mumbai for the use of their instrumentation facilities.

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