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Synthesis, Spectral Characterization and Antimicrobial Screening of Mn(II) and Zn(II) Complexes Derived from (E)-1-((p-tolylimino)methyl)naphthalene-2-ol

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ABSTRACT

The new coordination complexes of Mn(II) and Zn(II) have been synthesized from Schiff base derived from 2-hydroxy-1-naphthaldehyde and p-toluidine. The nature of bonding and the structural features of the Schiff base and its complexes have been deduced from elemental analysis, molar conductance, magnetic susceptibility measurements, IR, ^{1}H NMR, UV-Vis, and cyclic voltammetry studies. The spectral data of the complexes have revealed bidentate coordinating nature of the Schiff base through azomethine nitrogen atoms and phenolic oxygen. These Schiff base and its metal complexes were screened for their antimicrobial activity. The complexes showed enhanced antimicrobial activity as compared to uncomplexed Schiff base.

Key words: Schiff base, Metal complexes, Antibacterial, Antifungal

INTRODUCTION

The Schiff bases and their metal complexes have more importance recently because of their application as biological,biochemical, analytical, antimicrobial, anticancer, antibacterial, antifungal and anti tumor activity[1-5]. They have been studied as a class of ligands and are known to coordinate with metal ions through the azomethine nitrogen atom[6-8]. A considerable number of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds[9]. Not only have they played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials[10]. In this paper we describe the behavior of the bidentate aromatic Schiff base ligands with transition metal Mn(II) and Zn(II) ions.

EXPERIMENTAL

Materials and Methods

All the reagents used were of AR grade. Solvents were purified and dried according to the standard procedures. Conductivity measurements for the complexes were carried out using Elico conductivity bridge and dip type conductivity cell. Magnetic susceptibilities were determined using electromagnet/Gouy method-PICO make. Melting points were determined using Elico melting point apparatus. Elemental analysis (C,H,N) were performed using elemental analyser. IR spectra of the ligand and its complexes were recorded in KBr pellets with Perkin Elmer IR RXI Spectrometer in the 4000-400 cm^{-1} range. The ^1H NMR spectra was recorded on a Bruker 400 MHz FT- PMR Spectrometer (DMSO-d_6). The electronic spectra were recorded in Perkin Elmer Lambda 35 spectrometer in the 190-1100 nm range. Cyclic Voltammetric measurements for the complexes were measured using Princeton applied Research –Multichannel Versastat-II.

Synthesis of Schiff base - (E)-1-((p-tolylimino) methyl) naphthalene-2-ol(L)

The Schiff base was prepared by the condensation of equimolar amounts of p-toluidine (0.004mol) and 2-hydroxy-1-naphthaldehyde (0.004 mol) in minimum quantity of ethanol. The resulting mixture was then refluxed for 4 hours. A yellow coloured solid mass separated out on cooling is filtered, washed and dried over anhydrous $CaCl_2$ in a desiccator. The purity of the ligand was checked by TLC and spectral data.

Synthesis of complexes

Complexes of (E)-1-((p-tolylimino)methyl) naphthalene-2-ol were synthesized by mixing a hot ethanolic solution of Schiff base(L) (0.004 mol) in minimum amount of dimethylformamide, and ethanolic solution of corresponding M(II) acetate (0.002mol). The mixture was refluxed for 6 hours. The complexes obtained in each case were cooled, filtered and washed with ethanol several times to remove any excess ligand. Finally the complexes were washed with anhydrous diethylether and dried in desiccator.

RESULTS AND DISCUSSION

The physical characteristics of the Schiff base and its complexes are given in Table 1. The analytical data (Table 2) of the Schiff base and its complexes agree very well with the proposed molecular formulae and also indicates the formation of 1:2 (M:L) complexes of general formula of $[M(L-H)_2(H_2O)_2]$ [L=Mn^{2+} and Zn^{2+}].

Table 1: Physical Characteristics of the Schiff base and its complexes

S. No	Schiff base & Complexes	Molecular Formula	Colour	M.Pt (°C)	Yield %
1	L	$C_{18}H_{15}NO$	Dark yellow	115°	60
2	$Mn(L-H)_2 (H_2O)_2$	$C_{36}H_{32}N_2O_4Mn$	Brownish green	122°	59.2
3	$Zn(L-H)_2 (H_2O)_2$	$C_{36}H_{32}N_2O_4Zn$	Pale yellow	110°	65

Table 2: Analytical data of Schiff base and its complexes

S. No	Schiff base &Complexes	Λ_m (ohm^{-1} cm^{2}mol^{-1})	Elemental analysis % Found (Calcd) C	H	N	% of Metal calculated	Observed	μ_{eff}BM calculated	Observed
1	L	—	82.00 (82.76)	5.12 (5.75)	5.84 (5.36)	-	-	-	-
2	$Mn(L-H)_2 (H_2O)_2$	2.8	70.12 (70.71)	5.83 (5.24)	4.15 (4.58)	8.9	8.7	5.9	6.5
3	$Zn(L-H)_2 (H_2O)_2$	4.8	69.97 (69.41)	5.87 (5.14)	4.16 (4.50)	10.5	10.9	0	Dia

Molar Conductance

The molar conductance of metal complexes are measured using 10^{-3}M DMF solutions and are found within the range 2.8 and 4.8 ohm^{-1} cm^2 mol^{-1} suggesting the non-electrolytic nature[11] and indicate that no anions are present outside the coordination sphere. (Table 2)

Table 3: Antimicrobial activity of Schiff base and its complexes

S. No.	Schiff base and its complexes	L	$Mn(L\text{-}H)\text{-}_2\ (H_2O)_2$	$Zn(L\text{-}H)\text{-}_2\ (H_2O)_2$
1	*Staphylococcus aureus*	++	+++	+++
2	*E.coli*	+++	+++	+++
3	*Pseudomonas aeruginosa*	+++	+++	+++
4	*Klebsiella sp.*	+++	+++	++
5	*Aspergillus Niger*	+++	+++	+++
6	*Mucor*	+++	++	+++

Standard-Ciprofloxacin 5mg/disc for bacteria; Nystatin 100 units / disc for fungi.

High active = +++ (inhibition zone > 15mm), moderatively active=++ (inhibition zone > 10mm), slightly active = + (inhibition zone > 5mm), inactive = – (inhibition zone < 5mm).

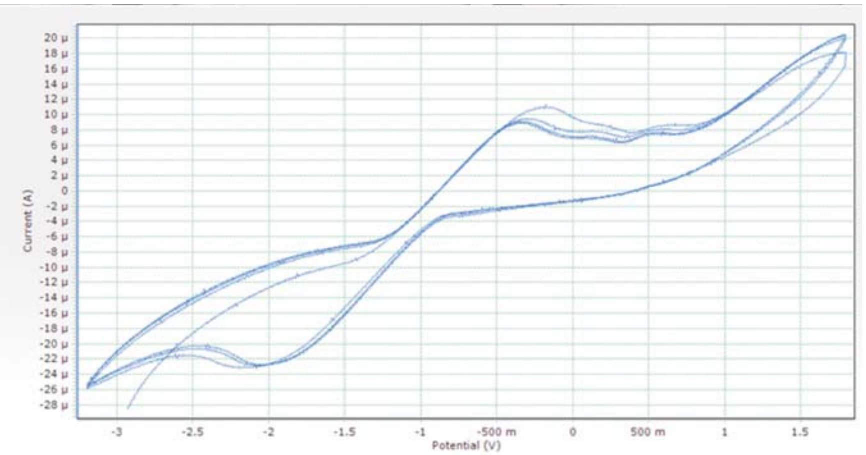


Fig. 1: Cyclic voltammagram of $Mn(L\text{-}H)\text{-}_2\ (H_2O)_2$

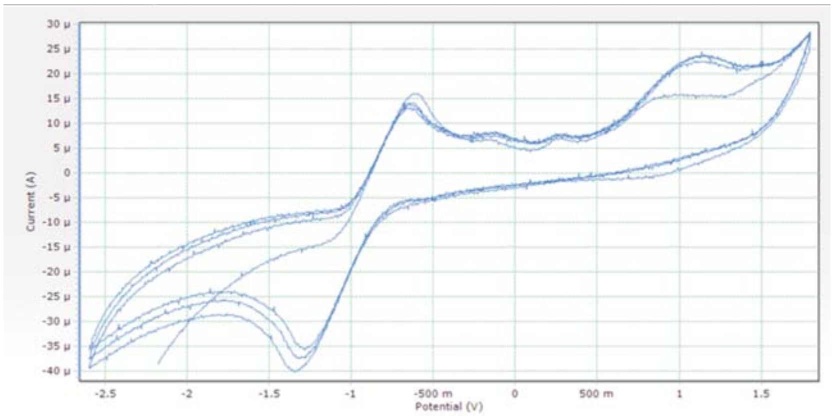


Fig. 2: Cyclic voltammagram of $Zn(L\text{-}H)_2\ (H_2O)_2$

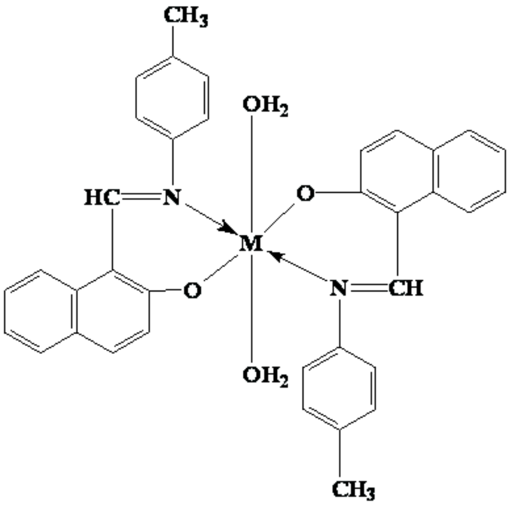
IR Spectra

The Schiff base shows a strong absorption band at 1627cm^{-1} characteristic of $\nu_{(>C=N-)}$ [12] whereas the broad band at 3448cm^{-1} is characteristic of hydrogen bonded $\nu_{(O-H)}$ [13] stretching vibration. The azomethine peak in the ligand at 1627cm^{-1} is shifted to 1615cm^{-1} in Co(II) complex and 1614 cm^{-1} in Zn(II) complex suggest the coordination through >C=N– group. The disappearance of phenolic (OH) at 3448cm^{-1} in both the complexes suggest that the coordination of phenolic oxygen to metal atom after deprotonation. The linkage with oxygen atom is further supported by the appearance of a band in the region at 659cm^{-1} and 650 cm^{-1} may be assigned to $\nu_{(M-O)}$ and the appearance of a band in the region at 499 cm^{-1} and 449cm^{-1} may be assigned to $\nu_{(M-N}$. The band in the region 3400-3600cm^{-1} indicates the presence of water molecule[14].

Electronic spectra and magnetic susceptibility measurements

The ligand is yellow in colour and shows three absorption bands at 347.02nm (28816 cm^{-1}), 417.2nm (23968 cm^{-1}), 478.80nm (20885 cm^{-1}) accounts for n→n* and $\pi \rightarrow \pi^*$ transitions. The Mn(II) complex is dark brownish green in colour and it shows absorption band around 320.11, 336.11, 373.27, 384.33, 439.88nm (31,239, 29752, 26,790, 26,019, 22,7334cm^{-1}). The band at 22,733cm^{-1} may be due to the transition from $^6A_{1g} \rightarrow {}^4E_g(D)$ and 31,239cm^{-1} band is assignable to M → L charge transfer spectra. The Mn(II) complex is dark brown in colour exhibits three absorption bands at 271.23nm (36869cm^{-1}), 322.22nm (31034cm^{-1}), 394.13nm (25372 cm^{-1}). The first two bands may be attributed to L à M charge transfer transitions[15]. The band in the region 25372cm^{-1} can be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ d-d transition[16] and the magnetic moment of 2.3 BM confirms the octahedral geometry. The Zn(II) complex is pale yellow in colour and it shows absorption bands around 267.24, 320.28, 382.88nm (37.419, 31.222, 26,117 cm^{-1}), these transitions may be due to MàL charge transfer spectra[15].

Proposed structure of the complexes



M=Mn(II) & Zn(II)

Fig. 3:

^{1}H NMR

^{1}H NMR Spectra of free ligand and its Zn(II) complex were recorded in DMSO-δ_6. The multiplet which extents from δ 7.2 to d 8.4 corresponds to the 10 protons of the aromatic rings[17]. The ligand NMR spectrum has a singlet peak at δ 9.6 ppm suggest the presence of -CH = N- linkage. The peak at δ15.9 ppm confirms the presence of hydroxyl proton in the ligand[18]. The CH_3 protons appear at δ 2.3 ppm.

Cyclic voltammetry measurements

Electrochemical cyclic voltammetry measurements were performed at room temperature in an airtight three electrode cell by using glassy carbon electrode with 0.071 cm^2 surface area as a working electrode, a platinum wire served as the counter electrode and a Ag/AgCl in a saturated KCl solution as reference electrode. The electrochemical reaction was charged with 10 ml DMF solution of all the complexes (1x10^{-4}M) and n-Bu4NClO4 [19] (0.1M) as supporting electrolyte. From the cyclic voltammogram obtained for Mn(II) complex (Figure 1) it is inferred that the redox potential value is metal centered, one electron quasireversible, since the ΔEp value is greater than 100mV (160mV). The cyclic voltammogram obtained for Zn(II) complex (Figure 2), it is inferred that the redox potential value is metal centered, one electron reversible. Since the ΔEp value is 60mV

Antimicrobial activities of the complexes

Antibacterial and antifungal activity of Schiff base and its complexes (Table 3) have been tested by disc diffusion technique[20,21]. The various gram positive and gram negative bacterial organisms such as gram positive bacteria (*Staphylococcus aureus* & *Klebsiella* Sp.), gram negative bacteria (*E.coli* & *Pseudomonas aeruginosa*) and fungi (*Aspergillus Niger* & Mucor Sp.) are used to find out the antimicrobial activity. The results were compared with standard drug ciprofloxcin 5mg/disc for bacteria and Nystatin 100 mg/disc for fungi. Here it is evident that overall potency of the ligand is enhanced on coordination with metal ion. All the new complexes showed a remarkable biological activity against bacteria and fungus

CONCLUSION

Two new complexes of Mn(II) and Zn(II) with (E)-1-((p-tolylimino)methyl)naphthalene-2-ol have been synthesized. On the basis of the spectral data obtained it is found that there is a formation of 1:2 (metal : ligand) complex and also indicates an octahedral environment around the metal ion and the probable structure of the complexes proposed in the present work is given in Fig. 4.The complexes have been screened against gram positive and gram negative bacteria and found to have considerable therapeutic activity compared to the ligand.

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