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RESEARCH ARTICLE

SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL SCREENING OF Mn (II), co (II), Ni(II) and Zn(II) COMPLEXES OF SCHIFF BASE LIGAND (e)-2-methoxy-6-((p-tolylimino) methyl) phenol

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ABSTRACT

New Schiff base derived from p-toludine and 2-hydroxy-3-methoxy benzaldehyde in ethanolic media and its complexes with Mn(II), Co(II), Ni(II) and Zn(II) have been prepared. These complexes are characterised by molar conductance, magnetic susceptibility measurement, elemental analysis, IR, UV, ^{1}H and ^{13}C-NMR and cyclic voltammetry. From the analytical and spectral data, the stoichiometry has been found to be 1:2 for all the complexes. The Schiff base ligand and the complexes have been screened for antimicrobial activity by disc diffusion technique. The activity data showed that the m*et al.,* complexes have more antifungal and antibacterial activity than the parent ligand.

INTRODUCTION

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields eg., biological, inorganic and analytical chemistry (Singh *et al.,* ,1975). They are known to exhibit potent antibacterial, anticonvulsant, anti inflammatory activities (Robin R Coombs et al, 2005). In addition some Schiff bases show pharmacologically useful activities like anticancer, anti-hypertensive and hypnotic activities (Walcourt *et al.,* 2004) (Gomathi *et al.,* 2013) (Shivakumar K *et al.,* 2008). Schiff bases are important class of compounds due to their flexibility, structural similarities with natural biological substances and also due to presence of imine (-N=CH-) which imparts in elucidating the mechanism of transformation and rasemination reaction in biological system. These novel compounds could also act as valuable ligands whose biological activity has been shown to increase on complexation. Schiff bases of isatin derivatives have been reported to demonstrate a variety of biological activities, such as anti-inflammatory anti HIV and anti-depressant activities (Rajesh D Hunsahal *et al.,* 2012) (Tarafder *et al.,* 2000) (Hahn *et al.,*2003) (Zahid H chohan *et al.,*2007).

The present paper describes the synthesis and characterization of Co(II), Mn(II) Ni(II) and Zn(II) complexes derived from p-toludine and 2-hydroxy-3-methoxy benzaldehyde. The ligand and its Metal *et al.,* complexes are characterized by molar conductance, magnetic susceptibility measurement,elemental analysis, IR, UV, ^{1}H and ^{13}C-NMR and cyclic voltammetry. The biological activities are also studied against gram positive and gram negative bacterial and fungi organisms for Schiff base ligand and their complexes. The structure of Schiff base ligand is given in Figure 1.

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EXPERIMENTAL

All chemicals used were of analytical reagent grade (AR) and of highest purity available. Solvents were purified and dried according to the standard procedures. All Metal *et al.,* (II) compounds were used as acetate salts. IR spectra of the complexes were recorded in KBr pellets with a Perkin Elmer RX1 FT-IR Spectrophotometer in the 4000-400cm^{-1} range. The electronic spectra were recorded in DMF on a Perkin Elmer Lambda 35 spectrophotometer in the 190-1100 nm range. The ^{1}H NMR spectra were recorded on a Bruker 400MHz FT-PMR spectrometer (DMSO-d_6). Elemental analysis of the ligand and complexes were obtained using Elementar Vario EL CHN rapid analyser. Cyclic Voltammetric measurements for the complexes were measured using Princeton applied Research –Multichannel VersaSTAT-II. Melting points were determined using melting point apparatus (Elico) and were uncorrected. Conductivity measurements for the complexes were carried out on Elico Conductivity Bridge and a dip conducitivity cell using dimethyl formamide as solvent.

Synthesis of Schiff base ligand (L)

(L) The Schiff base was prepared by the condensation of equimolar amounts of p-toludine (0.002mol) and 2-hydroxy-3-methoxy benzaldehyde (0.002mol) in minimum quantity of ethanol. The resulting mixture was then refluxed on a water bath for 4 hours. An pale orange coloured solid mass separated out on cooling was filtered, washed and dried.The purity of the ligand was checked by melting point, TLC and spectral data. The ligand is insoluble in some common organic solvents viz.acetone, benzene and soluble in polar solvents viz.DMF, DMSO.

Synthesis of Metal et al., complexes

Metal *et al.,* complexes were synthesized by mixing the hot solution of ligand (0.004 mol) in minimum quantity of dimethyl formamide and ethanolic solution of Metal *et al.,* acetates (0.002 mol) (2:1). The resulting mixture was then refluxed in a water bath for 6 hours. The complexes obtained in each case were cooled, filtered and washed with ethanol several times to remove any excess of the ligand. Finally complexes were washed with anhydrous diethylether and dried in a desiccator.

RESULTS AND DISCUSSION

The Schiff base ligand is synthesized by using equimolar quantities of p-toludine and 2-hydroxy-3-methoxy benzaldehyde and the complexes using Metal *et al.,* acetates. according to following equation

$$M(CH_3COO)_{2.nH2O} + 2L \xrightarrow[\text{reflux}]{\text{ethanol\DMF}} ML_{2\text{-}2H}(H_2O)_2 + 2CH_3COOH + nH_2O$$

The Metal *et al.,* complexes derived vary in their colour. All the complexes are stable, non-hygroscopic and coloured solids. The Physical Characteristics and micro analytical data of the ligand and Metal *et al.,* complexes are given in Table 1 and Table 2

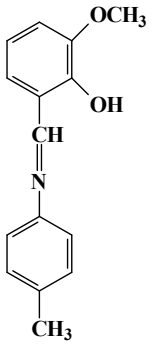

Figure 1 Structure of the ligand

Molar Conductance and Magnetic Susceptibility Measurements

The observed molar conductances of all the complexes in 10^{-3} M DMF solution are found within the range of 2.6-4.4 $ohm^{-1}cm^2mol^{-1}$ showing their non-electrolytic nature. The magnetic moment for Co^{II} and Ni^{II} complexes is consistent with octahedral geometry around the Metal *et al.,* ion for both complexes. Zn (II) complex are found to be diamagnetic as expected. The observed magnetic moment value of 6.1 BM for the Mn (II) complex suggests the octahedral geometry (Valarmathy *et al.,* 2013). The probable structure of complexes proposed in the present work is given in Figure 2.

hydrogen bonded ν(O-H) stretching vibration (Maurya *et al.,* 2003) . The azomethine ν(>C=N) band at 1616 cm^{-1} in Schiff base is shifted to lower frequency in Mn(II), Co(II), Ni(II), and Zn(II) by 4,40,5and 9cm^{-1} respectively which indicated the co-ordination of azomethine nitrogen on complexation (Gomathi *et al.,* , 2013) . The disappearance of phenolic (OH) at 3448 cm^{-1} in all the complexes suggests the coordination of phenolic oxygen after deprotonation. The linkage with oxygen atom is further supported by the appearance of a band in the region around 450 cm^{-1} which may be assigned to ν (M-O) (Maurya *et al.,* 1996). A further evidence of the coordination of the Schiff base with the Metal *et al.,* atom was shown by the appearance of a new weak frequency band at 550-600cm^{-1} assigned to the m*et al.,* nitrogen ν(M-N) (Ramakrishna Reddy *et al.,* 2005). These new bands were observed only in the spectra of the Metal *et al.,* complexes and not in Schiff base which confirmed the participation of the donor groups.

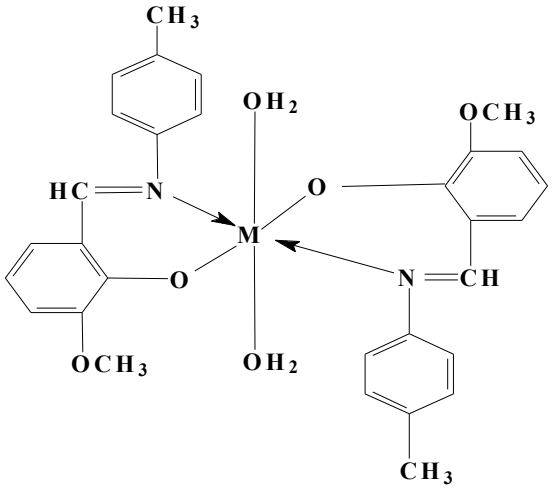

Figure 2 Structure of the complex M=Co(II), Mn(II), Ni(II) and Zn(II)

Electronic Spectra Electronic spectrum of the ligand shows band at 24346cm^{-1} is due to $\pi \longrightarrow \pi^*$ transitions respectively of the ligand moiety (Gomathi *et al.,* 2013). The electronic spectra of Co(II) complex displays band at 31666 cm^{-1}. This band corresponds to 4T1g (F) $\longrightarrow {}^4A_{2g}$ (F) transition suggesting octahedral geometry of this complex (Zahid H Chohan *et al.,* 2009). Ni(II) complex shows absorption bands at 39797,35229 and 31259 cm^{-1}.

The high intensity bands at 39798, 35229 cm^{-1} are relatively attributed to L$\longrightarrow$ M charge transfer transitions whereas the band at 31259 cm^{-1} may be due ${}^4T_{1g} \longrightarrow {}^4T_{2g}(P)$ transition (Aboaly M Metal *et al.,* , 2001).

Table 1 Physical Characteristics of Schiff base ligand and their complexes

S.No	Ligand/ Complexes	Colour	Molecular Formula	M.P °C	Yield %	μ_{eff}(BM)	CN
1	L	Orange	$C_{15}H_{15}NO_2$	90	75	-	-
2	$[ML_{2\text{-}2H}(H_2O)_2]$	Pale yellow	$C_{30}H_{32}N_2O_6Mn$	140	60	6.1	6
3	$[CoL_{2\text{-}2H}(H_2O)_2]$	Brown	$C_{30}H_{32}N_2O_6Co$	208	65	2.3	6
4	$[NiL_{2\text{-}2H}(H_2O)_2]$	Dark Yellow	$C_{30}H_{32}N_2O_6Ni$	102	75	2.1	6
5	$[ZnL_{2\text{-}2H}(H_2O)_2]$	Pale yellow	$C_{30}H_{32}N_2O_6Zn$	130	65	Dia	6

Table 2 Microanalytical data of Schiff base ligand and their complexes

S.No	Ligand/ Complexes	Elemental Analysis (%)(Calcd)found				Λ_m $ohm^{-1}m^2$ mol^{-1}
		C	H	N	%M	
1	L	(74.69) 74.21	(6.22) 6.11	(5.81)5.87	-	-
2	$[MnL_{2\text{-}2H}(H_2O)_2]$	(63.05) 62.98	(5.60) 5.32	(4.90) 4.78	(10.14) 9.89	2.6
3	$[CoL_{2\text{-}2H}(H_2O)_2]$	(62.11) 62.05	(5.52) 5.48	(4.83) 4.62	(10.25) 9.54	3.2
4	$[NiL_{2\text{-}2H}(H_2O)_2]$	(62.64) 62.53	(5.57) 5.54	(4.87) 4.76	(10.21)10.16	4.4
5	$[ZnL_{2\text{-}2H}(H_2O)_2]$	(61.92) 61.87	(5.50) 5.44	(4.81) 4.60	(11.25)11.20	3.9

Table 3 IR and Electronic spectral data

Ligand/ Complexes	IR spectral data , cm^{-1}				Electronic spectral data, cm^{-1}
	γ (O-H)	**γ(C=N)**	**γ(M-N)**	**γ(M-O)**	
L	3448	1616	-	-	24346
$[MnL_{2}\text{-}_2H(H_2O)_2]$	-	1620	732	478	35494, 30024
$[CoL_{2}\text{-}_2H(H_2O)_2]$	-	1656	680	511	31666
$[NiL_{2}\text{-}_2H(H_2O)_2]$	-	1621	640	576	39797, 35229, 31259
$[ZnL_{2}\text{-}_2H(H_2O)_2]$	-	1625	734	577	30966

TABLE 4 Antimicrobial Activity of Schiff base ligand and complexes

Antimicrobial activity of the ligand and complexes	Staphylococcus aureus	Bacillus subtilis	E.coli	Pseudomonas aeruginosa	Candida albicans	Aspergillus niger
L	++	++	++	++	++	++
$[MnL_{2\text{-}2H}(H_2O)_2]$	+++	++	+++	+++	++	+++
$[CoL_{2\text{-}2H}(H_2O)_2]$	+++	+++	+++	+++	+++	+++
$[NiL_{2\text{-}2H}(H_2O)_2]$	+++	+++	+++	++	+++	++
$[ZnL_{2\text{-}2H}(H_2O)_2]$	+++	++	+++	+++	+++	++

Standard= ciprofloxacin 5 g/ disc for bacteria ; Nystatin= 100 units/disc for fungi.
Highly active = +++ (inhibition zone > 15mm) ; Moderatively active = ++ (inhibition zone> 10mm) ; slightly active = + (inhibition zone >5mm); Inactive = -- (inhibition zone <5mm)

The electronic spectrum of the Mn(II) complex shows two bands at 35494 assignable to M ⟶ L charge transfer transitions and the band at 30024cm^{-1} is due to $^6A_{1g}$ ⟶ $^4E_{g(D)}$ transition (Suraj b. adel *et al.,* 2012). Zn(II) complex displays single absorption band at 30966cm^{-1}. This is due to Ligand Metal *et al.,* charge transfer spectra (Dhanaraj *et al.,* 2009).

***^{1}H and ^{13}C NMR Spectra*:** The ^{1}H NMR and 13 C-NMR Spectra of Schiff base are recorded in DMSO (d_6). The azomethine proton (-CH=N-) in Schiff base appeared at δ = 8.9 ppm has been shifted to downfield in Metal *et al.,* complexes. This confirms the coordination by azomethine nitrogen Farag MA Altal, *et al.,* , 2010). The multiplet which extents from δ 6.9 to 7.3 corresponds to the protons of the aromatic rings. The disappearance of phenolic –OH proton signal at δ 13.3 ppm in the complex confirms the coordination by phenolic oxygen to Metal *et al.,* ion (Lee JD, 1999). The ^{13}C-nmr spectral data (imine at δ 160.0 ppm., aromatic OH at δ 150.1 ppm) supports the proposed structure for ligand.

Cyclic Voltammetry

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 cell was charged with DMF solution of all the complexes ($1x10^{-4}$M) and tetrabutyl ammonium perchlorate (0.1M) as supporting electrolyte. Measurements were made over a potential range between -2.3 V to +1.7 V for Mn(II), Co(II) complexes and -2.2 V to +1.7 V for Ni(II) and Zn(II) complexes with a scan rate of 0.2 Vs^{-1}. Generally the electrochemical properties of the complexes depend on a number of factors such as chelate ring/size, axial ligation, degree and distribution of unsaturation and substitution pattern in the chelate ring. All the complexes undergo redox reaction involving Metal *et al.,* centered one electron quasi reversible process since the ΔEp value is greater than 100mV (Tumer, 2007).

Antimicrobial activity

Antibacterial and antifungal activity of Schiff base ligand and its cobalt, nickel, manganese and zinc complexes have been tested by disc diffusion technique (Gomathi *et al.,*2013) (Saleh *et al,* 2003). Gram negative bacteria *pseudomonas aeruginosa, E.coli,* Gram positive bacteria *staphylococcus aureu* and *Klebsiella sp* and the fungi *aspergillus niger* and *Mucor* were used to find out the antibacterial and antifungal activity (Table 4). Filter paper discs of diameter 6mm were used and the diameters of zones of inhibition formed around each disc after incubating for a period of 72 hours at 25-30 °C were recorded. Results were compared with standard drug Ciprofloxacin for bacteria and Nystatin for fungi at the same concentration. All the new complexes showed a remarkable biological activity against bacteria and fungus. From the results it is clear that the Metal *et al.,* complexes are found to have more antimicrobial activity than the parent ligand (Raman *et al,* 2003).

CONCLUSION

On the basis of these results obtained from molar conductance, magnetic susceptibility measurement, elemental analysis, IR, UV, ^{1}H and ^{13}C-NMR an octahedral structure has been proposed for all the complexes

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