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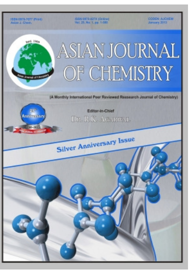

Synthesis, Characterization and Antimicrobial Screening of Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) Complexes with Schiff Base Derived from 2-Sulphanilamidopyridine and 2-Hydroxy-3-methoxybenzaldehyde

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The Schiff base derived from 2-sulphanilamidopyridine and 2-hydroxy-3-methoxy benzaldehyde and its metal complexes have been synthesized and characterised by IR, ^{1}H NMR, UV, elemental analysis, molar conductance and magnetic susceptibility. The Schiff base ligand and the metal complexes were screened for antimicrobial activity by disc diffusion technique. From the analytical and spectral data, the stoichiometry has been found to be 1:2 for all the metal complexes. An octahedral structure has been proposed. All these metal complexes were found to be active against bacteria and fungi.

Key Words: Schiff base, 2-Sulphanilamidopyridine, 2-Hydroxy-3-methoxybenzaldehyde, Metal complexes, Biological activity.

INTRODUCTION

Sulpha drugs are chemotherapeutic agents whose molecular structures contain a sulfanilamide (4-amino benzenesulfonamide) moiety. The antibacterial activity of these drugs is believed from the structural resemblance between sulfanilamide group and *p*-aminobenzoic acid where the sulpha drug mimics this metabolite and blocks folic acid synthesis in bacteria, there by causing cell death[1]. The direct use of transition metal salts as antimicrobial agents cannot be recommended as they are very toxic to host animals. It has been reported that the biologically active compounds show greater activity when administered as metal complexes than as free organic compound[2]. Transition metal complexes containing oxygen and nitrogen donor Schiff base ligands have been of research interest for many years[3] because of the versatility of their steric and electronic properties. Schiff bases and their metal complexes exhibited biological activity as antibiotics[4], antiviral[5] and antitumour agents[6] because of their specific moiety[7]. The presence of -SO_2NH moiety in sulpha drugs has toxophoric function[8]. Sulphur containing Schiff base ligands are the important components of biological transition metal complexes which are used in the preparations of diuretic, antiglaucoma or antiepileptic drugs[9]. The azomethine (>C=N) linkage in Schiff bases imparts an idea in elucidating the mechanism of transamination and resamination reactions in biological system[10]. Schiff bases can accomodate different metal centers involving various co-ordination modes allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry[11].

The present paper records the synthesis and characterization of Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) complexes of Schiff base (Fig. 1) derived from 2-sulphanilamidopyridine and 2-hydroxy-3-methoxy benzaldehyde. The structures of the ligand and its metal complexes were characterized by elemental analysis, IR, ^{1}H NMR, UV, molar conductance and magnetic susceptibility measurements.

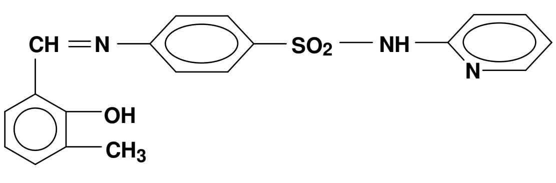

Fig. 1. Structure of the ligand

EXPERIMENTAL

All the 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 (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 4000-400 cm^{-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 400

MHz FT-PMR spectrometer (DMSO-d_6) at the microanalytical centre, Bharathidasan University. The analysis of carbon, hydrogen and nitrogen were performed at the Indian Institute of Technology, Chennai, India. Magnetic susceptibilities were measured on a Automagnetic Susceptibility meter (MSB-Auto) at room temperature. Melting points were determined using melting point apparatus (Elico) and are uncorrected. Conductivity measurements for the complexes were carried out on Elico conductivity bridge and a dip conducicitivity cell using dimethyl formamide as solvent.

Synthesis of Schiff base ligand: (L) The Schiff base was prepared by the condensation of equimolar amounts of 2-sulphanilamidopyridine and 2-hydroxy-3-methoxy benzaldehyde in minimum quantity of ethanol. The resulting mixture was then refluxed on a water bath for 5 h. An orange coloured solid mass separated out on cooling was filtered , washed and dried over anhydrous $CaCl_2$ in a desiccator. 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 complexes: Metal complexes were synthesized by mixing the hot solution of ligand (0.004 mol) in minimum quantity of dimethyl formamide and ethanolic solution of corresponding metal acetates (0.002 mol). The resulting mixture was then refluxed in a water bath for 6 h. 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.

The microanalytical data, melting point, colour and other physical properties of the ligand and metal complexes are given in Table-1. The probable structure of complexes proposed in the present work is given in Fig. 2.

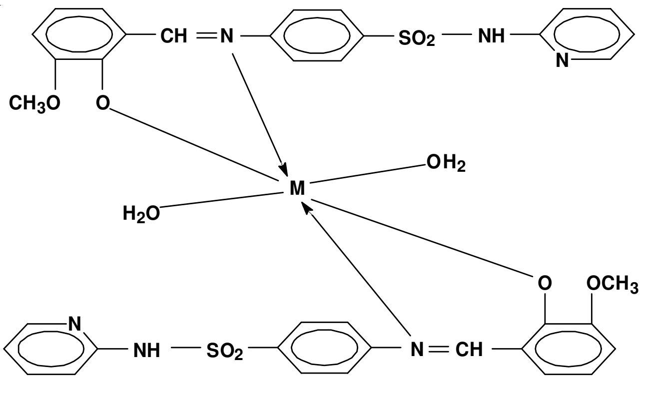

Fig. 2. Structure of the complex

RESULTS AND DISCUSSION

The Schiff base ligand is synthesized by using equimolar quantities of 2-sulphanilamidopyridine and 2-hydroxy-3-methoxy benzaldehyde and the complexes using metal acetates. The metal complexes derived vary in their colour. All the complexes are stable, non-hygroscopic and coloured solids. The low molar conductance values in the range of 2.9-16.7 ohm^{-1} cm^2 mol^{-1} in Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) chelates indicate that they are non-electrolytic in nature[12]. The low conductance values may be attributed to the large cations[13].

Infrared spectra: The infrared spectral data of the Schiff base and its metal complexes are recorded in Table-2. Schiff base showed a strong absorption band at 1618 cm^{-1} characteristic of ν(C=N) whereas the broad band at 3426 cm^{-1} is characteristic of hydrogen bonded ν(O-H) stretching vibration[14]. The azomethine ν(>C=N) band at 1618 cm^{-1} in Schiff base is shifted to lower frequency in Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) by 21, 25, 16, 07 and 26 cm^{-1}, respectively which indicated the co-ordination of azomethine nitrogen in complexation[15]. The disappearance of phenolic (OH) at 3426 cm^{-1} in all the complexes suggests the coordination of phenolic oxygen after deprotonation[16]. 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)[17]. The bands at 1374 and 1130 cm^{-1} are assigned to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, respectively in schiff base ligand. These bands also show no significant change in all the complexes and thereby indicating the non-participation of sulfonamide oxygen in the bonding. The coordination of water molecule is indicated by the presence of band in the region 3350-3200 cm^{-1} [18].

Electronic spectra: Electronic spectrum of the ligand showed two high intensity bands at 31,347 and 39,524 cm^{-1} indicates $n \rightarrow n^*$ and $\pi \rightarrow \pi^*$ transitions, respectively of the ligand moiety[19]. The electronic spectra of Co(II) complex shows bands at 35398, 32130, 27392 and 23,415 cm^{-1}. The first two high intensity peaks are due to L → M charge transfer spectra and the other two correspond to $^4T_{1g}(F) \rightarrow {}^3A_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ suggesting octahedral geometry for this complex. Ni(II) complex showed absorption bands at 39122-36626 cm^{-1}. The high intensity band at 39122 cm^{-1} is relatively attributed to L → M charge transfer transitions[20] whereas at 36626 cm^{-1} may be due to $^3A_{2g} \rightarrow {}^3T_{1g}$ transition. The Cu(II) complex displays three bands at 38022, 37460 and 36523 cm^{-1}. The first two bands are due to intraligand transitions[21]. The third band at 36, 523 cm^{-1} is due to $^2E_{(g)} \rightarrow {}^2T_{2g}$ transition. The electronic spectrum of the Mn(II) complex shows three bands at 38759, 36496 and band at 29525 cm^{-1} assignable to M → L charge transfer transitions and the 29525 cm^{-1} is due

TABLE-1
PHYSICAL CHARACTERISTICS AND MICROANALYTICAL DATA OF SCHIFF BASE LIGAND AND THEIR COMPLEXES

Ligand/ complexes	Colour	m.f.	m.p. (ºC)	Yield (%)	Elemental analysis (%) calcd. (found.)			CN	μ_{Eff} (BM)	Λ_m (ohm^{-1} m^2 mol^{-1})
					C	H	N			
L	Red orange	$C_{19}H_{17}O_4N_3S$	180	80	59.38 (59.48)	4.42 (4.01)	10.93 (10.94)	–	–	–
$[CoL_2(H_2O)_2]$	Dark green	$C_{38}H_{36}N_6O_{10}S_2Co$	235	60	53.08 53.20)	4.19 (4.01)	9.77 (9.55)	6	4.45	16.7
$[NiL_2(H_2O)_2]$	Green	$C_{38}H_{36}N_6O_{10}S_2Ni$	220	65	53.10 (53.30)	4.19 (4.07)	9.78 (9.62)	6	3.4	3.44
$[CuL_2(H_2O)_2]$	Yellow brown	$C_{38}H_{36}N_6O_{10}S_2Cu$	221	70	52.80 (52.62)	4.16 (4.15)	9.72 (9.22)	6	1.96	6.0
$[MnL_2(H_2O)_2]$	Yellow orange	$C_{38}H_{36}N_6O_{10}S_2Mn$	160	55	53.33 (53.41)	4.21 (4.09)	9.82 (9.86)	6	5.2	7.86
$[ZnL_2(H_2O)_2]$	Pale yellow	$C_{38}H_{36}N_6O_{10}S_2Zn$	150	55	52.69 (52.51)	4.15 (4.10)	9.70 (9.63)	6	Dia	2.9

TABLE -2
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	3426	1618	–	–	31347, 39, 524
$[CoL_2(H_2O)_2]$	3420	1597	568	460	35398, 32130, 27392, 23, 415
$[NiL_2(H_2O)_2]$	3416	1593	554	480	39122, 36626
$[CuL_2(H_2O)_2]$	3436	1602	574	440	38022, 37460, 36523
$[MnL_2(H_2O)_2]$	3411	1594	560	460	38759, 36496, 29525
$[ZnL_2(H_2O)_2]$	3409	1611	564	450	38461, 35211

TABLE-3
ANTIMICROBIAL ACTIVITY OF SCHIFF BASE LIGAND AND COMPLEXES

Antimicrobial activity of the ligand and complexes	*Staphylococcus aureus*	*Pseudomonas aeruginosa*	*Candida albicans*	*Aspergillus niger*
Ligand (L)	++	++	++	++
$[CoL_2(H_2O)_2]$	++	+++	+++	+++
$[NiL_2(H_2O)_2]$	++	+++	+++	+++
$[CuL_2(H_2O)_2]$	+++	+++	+++	+++
$[MnL_2(H_2O)_2]$	+++	+++	+++	+++
$[ZnL_2(H_2O)_2]$	++	+++	+++	+++

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

to $^6A_{1g} \rightarrow {}^4E_{g(D)}$[22]. Zn(II) complex displays absorption bands at 38461 and 35211 cm^{-1}. This is due to ligand metal charge transfer transition. The magnetic moment value of 1.96BM measured for the copper complex lies in the range expected for d^9 system.The presence of two unpaired electrons in Ni(II) complex is confirmed from the value of magnetic moment of 3.4 BM. The Zn(II) complex is found to be diamagnetic as expected.

^{1}H NMR spectra: The ^{1}H NMR spectra of Schiff base and its complexes were recorded in DMSO (d_6). The azomethine proton (-CH=N-) in Schiff base appeared at $\delta = 8.94$ ppm has been shifted to downfield in metal complexes. This confirms the coordination by azomethine nitrogen[23]. The aromatic protons in Schiff base appeared in the range at δ 6.93-8.0 ppm and metal complexes in the range δ 6.54-8.75 ppm[24]. The disappearance of phenolic -OH proton signal at 12.65 ppm confirms the coordination by phenolic oxygen to metal ion.

Antimicrobial activity: Antibacterial and antifungal activity of Schiff base ligand and its cobalt, nickel, copper, manganese and zinc complexes have been tested by disc diffusion technique[25]. The various gram positive and gram negative bacterial organisms such as gram negative bacteria *Pseudomonas aeruginosa*, gram positive bacteria *Staphylococcus aureus* and fungi *Aspergillus niger* and *Candida albicans* are used to find out the antimicrobial activity (Table-3). Filter paper discs of diameter 6 mm were used and the diameters of zones of inhibition formed around each disc after incubating for a period of 72 h at 25-30 ºC 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 complexes are found to have more antimicrobial activity than the parent ligand.

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