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Synthesis, Spectral Characterization and Antibacterial Study of a Schiff Base Metal Complexes Derived from N-[(E)-(5-Bromo-2-Hydroxyphenyl) Methylidene]-4-Nitrobenzenesulfonamide

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Abstract: Metal complexes of Cu (II), Co (II), Ni (II) and Zn (II) of Schiff based derived from 5-bromo-2-hydroxybenzaldehyde and 4-nitobenzenesulfonamide have been prepared and characterized on the basis of physical characteristics, micro-analytical data, ^{1}H NMR, FTIR spectrum and electronic data. The spectrum data exhibit coordination of Schiff base with metal through imine nitrogen and oxygen atom and prove the bidentate nature of ligand. The biological screening effect of Schiff base and their metal complexes are studied against gram positive and gram negative bacteria. The biological activity show that complex exhibit higher antibacterial activity than that of Schiff base.

Key words: Schiff Base · Metal Complexes · Spectroscopic Study · Antibacterial Activity

INTRODUCTION

Schiff base compounds which contain azomethine group >-C=N are usually prepared by the condensation of primary amines and active carbonyl compounds [1]. Schiff bases derived from aromatic amines and aromatic carbonyl compounds have wide range of applications in many fields as sulfonamide Schiff bases have been reported to posses' antimicrobial, anti-inflammatory and antitumor activities [2-4]. Sulfonamides compounds are important class of therapeutic agents used for the treatment of various bacterial infections. Study of the coordination behavior of sulfonamides is acquired interest due to their biological activity. The metal complexes of Schiff bases derived from sulfonamides drug has gain interest due to enhance biological activity. Compounds containing sulfonamide group have been used as drug for diseases [5, 6]. Sulfonamide coordination compounds are important components in view of biological system [7].

In this research work, Schiff base N-[(E)-(5-bromo-2-hydroxyphenyl) methylidene]-4-nitrobenzenesulfonamide and its metal complexes with Cu (II), Co (II), Ni (II) and Zn (II) were synthesized. The structure of ligand and metal complexes had been characterized by FTIR, ^{1}H NMR and UV spectroscopy. The biological activity also studied against Gram-positive and Gram-negative bacteria for ligand and metal complexes. The structure of the Schiff base ligand in present work is shown in Fig 1.

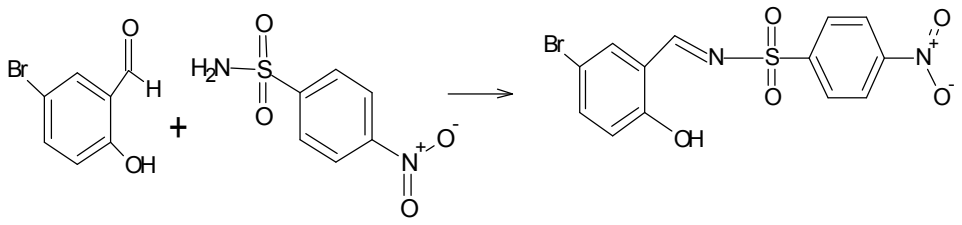

Fig. I: structure of ligand

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MATERIAL AND METHODS

Experimental Work: All chemical used were of analytical grade and of highest purity available. 4-nitobenzenesulfonamide and 5-bromo-2-hydroxybenzaldehyde were obtained from Sigma-aldrich. Metal (II) chloride and acetate salts were obtained from Merck. Solvents used were distilled and purified before used.

Synthesis of Schiff Base Ligand: 0.1M solution of 4-nitobenzenesulfonamide was added to 0.1M solution of 5-bromo-2-hydroxybenzaldehyde in methanol, after addition reaction mixture is heated under reflux for about 6-7 hours at 70°C. After completion of reaction precipitate of ligand are formed out as yellow to brown solids. The product filtered after cooling and purified with methanol. The purity of ligand was checked by M. P. and TLC. The ligand is soluble in methanol, ethanol, DMF and DMSO.

Synthesis of Metal Complexes: Metal complexes of Schiff base ligand were prepared by mixing 0.2M of Schiff base with 0.1M of Cu, Co, Ni and Zn salts keeping ligand-metal ratio 2:1. The resultant mixture was than refluxed for 2-3 hours. The complex obtained in each time was cooled, filtered and washed with the ethanol many times to purify and removed the excess of ligand. Finally complexes were places in desiccators for drying.

RESULTS AND DISCUSSION

The Schiff base is synthesized by using equimolar quantities of 4-nitobenzenesulfonamide and 5-bromo-2-hydroxybenzaldehyde. Schiff base is complexed with metal salts. The metal complexes are stable at normal temperature and are colored solids. The physical characteristics and analytical data of ligands and metal complexes are given in Table 1 and Table 2.

Infrared Spectroscopy: The infrared spectral data of Schiff base ligand and its metal complexes are listed in Table 3. A strong band observed for ligand at 1612 cm^{-1}, is characteristic of azomethine >C=N linkage [8] whereas the band at 3423cm^{-1} is characteristic of intra-molecular hydrogen bond >O-H stretching vibration [9]. A medium intensity band at 3248 cm^{-1} is due to the presence of >N-H group. The presence of -SO_2 group in Schiff base can be confirmed by appearance of two bands at 1156cm^{-1} and 1325 cm^{-1} due to symmetric and asymmetric vibrations.

Table 1: Physical characteristics of Schiff base and their metal complexes

Sr. No.	Ligand/ Complexes	Color	Molecular Formula	M. P. (°C)	Yield (%)
1	L	Yellow	$C_{13}H_9BrN_2O_5S$	178	76
2	$CuL_2(H_2O)_2$	Pale Yellow	$C_{26}H_{18}Br_2N_4O_{10}S_2Cu$	190	68
3	$CoL_2(H_2O)_2$	Brown Yellow	$C_{26}H_{18}Br_2N_4O_{10}S_2Co$	198	72
4	$NiL_2(H_2O)_2$	Orange	$C_{26}H_{18}Br_2N_4O_{10}S_2Ni$	188	68
5	Zn $L_2(H_2O)_2$	Brown	$C_{26}H_{18}Br_2N_4O_{10}S_2Zn$	196	66

Table 2: Micro-analytical data of Schiff base and their metal complexes

		Elemental analysis (%). (calculated)/ found					
Sr. No.	Ligand/ Complexes	C	H	N	S	O	%Metal (calculated)/ found
1	L	(40.54) 40.48	(2.36) 2.30	(7.27) 7.22	(8.32) 8.26	(20.77) 20.69	--
2	$CuL_2(H_2O)_2$	(37.42) 37.38	(2.16) 2.12	(6.72) 6.68	(7.67) 7.58	(19.18) 19.12	(7.61) 7.58
3	$CoL_2(H_2O)_2$	(37.62)37.58	(2.17) 2.12	(6.75) 6.68	(7.72) 7.67	(19.29) 19.20	(7.11) 7.08
4	$NiL_2(H_2O)_2$	(37.63) 37.56	(2.17) 2.11	(6.75) 6.77	(7.72) 7.66	(19.30) 19.22	(7.08) 7.04
5	Zn $L_2(H_2O)_2$	(37.33) 37.28	(2.15) 2.13	(6.70) 6.64	(7.66) 7.60	(19.14) 19.08	(7.82) 7.78

Table 3: IR spectra cm^{-1} of Schiff base and its metal complexes

			SO_2					
Compound	N-H	C=N	Sym.	Asym.	O-H	M-N	M-O	H_2O
L	3248	1612	1325	1156	3423	--	--	--
$CuL_2(H_2O)_2$	3226	1633	1315	1155	3442	558	476	3692
$CoL_2(H_2O)_2$	3256	1629	1330	1149	3452	547	467	3712
$NiL_2(H_2O)_2$	3234	1640	1329	1147	3446	550	472	3702
Zn $L_2(H_2O)_2$	3242	1648	1322	1150	3418	540	456	3714

Table 4: ^{1}H NMR data

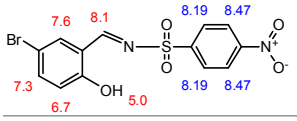
	ppm δ 6.7 to 7.6	aromatic-H
	ppm δ 5.0	
	phenolic –OH	
	ppm δ 8.1	-N=CH-
	Ppm δ 8.19 to 8.47	Heterocyclic –C-H

Table 5: Antibacterial activity of ligand and its complexes (inhibition zone mm)

	Gram +ve		Gram -ve	
Compound	*B. cereus*	*B. subtilis*	*E. coli*	*P. aeruginosa*
L	13	14	18	19
$CuL_2(H_2O)_2$	17	16	21	18
$CoL_2(H_2O)_2$	13	12	16	20
$NiL_2(H_2O)_2$	18	15	16	22
$Zn\ L_2(H_2O)_2$	15	18	19	21

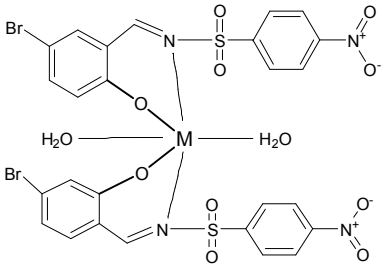


Fig. 2: Probable structure of metal complexes

These bands remain unchanged in ligand and complexes indicate that $–SO_2$ group not coordinated with the metal [10]. Infrared spectra of Schiff base metal complexes provided information about coordination. The band of azomethine appears at 1612 cm^{-1} in ligand is shifted to higher frequency 1633 cm^{-1} to 1648 cm^{-1} after the complex formation. This shifting of band indicates that nitrogen of azomethine group is coordinated with metal ion [11]. The strong band at 3248 cm^{-1} due to >N-H group in ligand shifted to lower frequency on coordination with metal ion [12]. The coordination of azomethine nitrogen with metal >M-N is also supported by appearing band in region of 540-558 cm^{-1} in all complexes [13]. The shifting of phenolic >O-H at 3423cm^{-1} in all complexes indicates the coordination of phenolic oxygen after deprotonation [14]. Linkage of oxygen with metal ion is further supported by the appearance of band in the region of 456-476 cm^{-1} which is due to >M-O [15]. All the metal complexes of Schiff base shows bands in the region of 3692-3714 cm^{-1} which indicates the presence of coordinated water molecules with the metal ion [16].

Electronic Spectra: Electronic spectra of ligand shows absorption two high intensity bands at 42275 cm^{-1} and 38550 cm^{-1} which indicate n → n* and □ → □* transition of the ligand. The electronic spectra of Co (II) complex shows two energy bands at 38252 cm^{-1} and 36865 cm^{-1} this is due to $^4T_{1g}$ (F) → $^4T_{1g}$ (P) transition respectively [17]. The Cu (II) complex shows three energy bands at 33944 cm^{-1}, 33075 cm^{-1} and 25873 cm^{-1} is due to $^2B_{1g}$ → ^2E_g. The Ni (II) shows absorption band at 39270 cm^{-1} is due to the $^3A_{2g}$ → $^3T_{2g}$ [18]. The Zn (II) complex shows high energy band at 36345 cm^{-1} and 35020 cm^{-1} due to ligand → metal charge transfer [19].

^{1}H NMR Spectra: ^{1}H NMR Spectra of Schiff base and their complexes were recorded in DMSO solution and TMS used as internal standard. The azomethine proton appears at ppm δ 8.1, it has been shifted to downfield in metal complexes which show coordination of ligand with metal by azomethine group [20]. The aromatic proton in Schiff base appears at ppm δ 6.7 to 7.6 and in their metal complex in the range of ppm δ 6.4 to 7.3. The disappearance of phenolic –OH confirmed the coordination of phenolic oxygen to metal ion [21].

On the basis of above given data the probable structure of metal complex of Schiff base is given in Fig. 2

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

Antibacterial Activity: The antibacterial activity data is presented in Table 4. The antibacterial activity of ligand and their metal complexes were screened on Gram-positive bacteria: *bacillus cereus* & *bacillus subtilis* and Gram-negative bacteria: *Escherichia coli* & *Pseudomonas aeruginosa* by disc diffusion technique [22]. Filter paper disc were used for the incubation period of 72 hours at 25°C and results were recorded. The antibacterial activity of ligand and their complexes were tested by measuring

inhibition zone observed around material. Ligand showed significant range of activity on growth of all selected bacterial stain. The results suggest that complexes increase the antibacterial activity [23].

CONCLUSION

A new Schiff base has been prepared by the condensation of 5-bromo-2-hydroxybenzaldehyde and 4-nitobenzenesulfonamide. The coordination ability of Schiff base has been reported by physical characteristics, micro-analytical data, ^{1}H NMR, FTIR and UV spectrum data and it confirm the suggested co-ordination of ligand which is bidentate and linked through azomethine group and phenolato oxygen forming stable chelate. The metal chelate of ligand has been structurally characterized and it is concluded that metal complexes show coordinated octahedral geometry. Biological study shows significant activity of metal complexes as compared to that of ligand.

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