



Synthesis, Spectral Characterization and Antibacterial Study of Schiff Base Metal Complexes Derived from 4-Bromo-N-[(E)-(5-chloro-2-hydroxyphenyl)methylidene]benzenesulfonamide

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A new sulfonamide Schiff based 4-bromo-N-[(E)-(5-chloro-2-hydroxyphenyl)methylidene]benzenesulfonamide prepared by refluxing 5-chloro-2-hydroxybenzaldehyde and 4-bromobenzenesulfonamide. The Schiff base was used as a complexing agent for the Cu, Co, Ni and Zn complexes. All the metal complexes were characterized by micro-analytical data, ¹H NMR, FT-IR and electronic spectra. The spectral data suggest coordination of Schiff base ligand with metal through nitrogen and oxygen atom and proves the bidentate nature of ligand. The biological screening effect of Schiff base and their metal complexes were studied against Gram-positive and Gram-negative bacteria by disc-diffusion technique. The biological activity shows that complex exhibit higher antibacterial activity than that of Schiff base against tested bacteria.

Keywords: Schiff base, Metal complexes, Spectroscopic study, Biological activity.

INTRODUCTION

Schiff bases are an important class of ligand, which coordinated with transition metal ions *via* azomethine nitrogen and have been studied extensively [1]. Schiff base ligands and their metal complexes have expanded enormously and included vast area of organometallic compounds and various aspects of bioinorganic chemistry. The coordination chemistry of Schiff base as bidentate ligand gains much importance due to their biological and industrial applications [2]. Sulfonamides compounds were the first drug found to act selectively and used as preventative and therapeutic agent against various diseases. The presence of sulfonamide functional group is responsible for antimicrobial activity, which can be altered depending upon the type of substituent present on the aromatic rings [3,4]. Schiff bases derived from sulfa drugs acquired interest due to their useful application in biological system. The condensation product of sulfa drugs with aldehydes and ketones are biologically active and also have good complexing ability, their activity increases a complexation with metal ions [5]. Schiff base ligands have been reported to show different variety of biological action because of their -C=N (azomethine linkage) group which is responsible for antibacterial, antifungal, clinical and analytical activities [6]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to possess unusual configuration [7].

In present research work, Schiff base 4-bromo-N-[(E)-(5-chloro-2-hydroxyphenyl)methylidene]benzenesulfonamide (Fig. 1) prepared by refluxing 5-chloro-2-hydroxybenzaldehyde and 4-bromobenzenesulfonamide 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, ¹H NMR and UV spectroscopy. The biological activity also studied against Gram-positive and Gram-negative bacteria for ligand and metal complexes.

EXPERIMENTAL

All the chemicals used were of analytical grade and of highest purity available and used without further purification. 4-Bromobenzenesulfonamide and 5-chloro-2-hydroxybenzaldehyde were obtained from Sigma-Aldrich. Metal(II) chlorides, sulphates and acetate salts were also obtained from Sigma-Aldrich. Solvents used were distilled and purified before used.

Schiff base ligand: 0.1 M solution of 4-bromobenzenesulfonamide was added to 0.1 M solution of 5-chloro-2-hydroxybenzaldehyde in ethanol, after addition reaction mixture is heated under reflux for about 5 h at 78 °C. The product was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled water and then with ethanol. The product were recrystallized in ethanol and dried in vacuum desiccator overnight. After completion of reaction process precipitate of ligand are formed out as yellowish to orange brown solids.

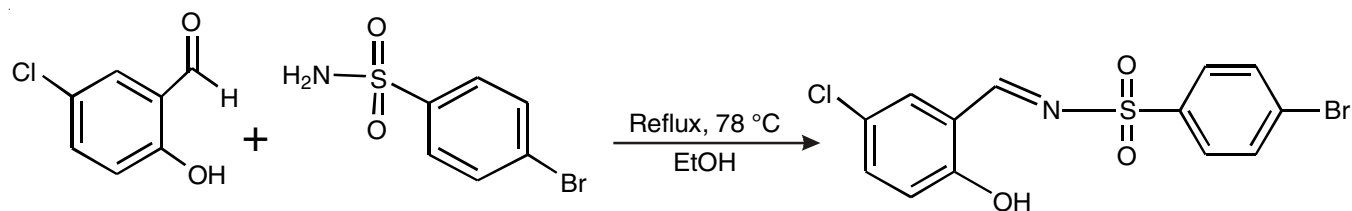


Fig. 1. Structure of ligand

Synthesis of metal complexes: Metal complexes of Schiff base ligand were prepared by mixing 0.2 M of Schiff base with 0.1 M of transition metal salts keeping ligand-metal ratio 2:1 in ethanol. The resultant mixture was then refluxed for 2 h where solid complexes precipitate obtained. The complex obtained in each time was cooled, filtered and washed with ethanol several times to removed the excess of ligand. Finally complexes were placed in desiccators for drying.

RESULTS AND DISCUSSION

The Schiff base is synthesized by using equimolar quantities of 4-bromobenzenesulfonamide and 5-chloro-2-hydroxybenzaldehyde. The physical characteristics and analytical data of ligand and its metal complexes are given in Tables 1 and 2.

A sharp band observed for ligand at 1590 cm^{-1} , is characteristic of azomethine $>\text{C}=\text{N}$ linkage which is shifted to higher frequency on going from ligand to metal complexes due to coordination of imine nitrogen to metal ion [8]. Whereas the band appeared at 3384 cm^{-1} is characteristic of intramolecular hydrogen bond $>\text{O}-\text{H}$ stretching vibration (Table-3). The shifting of phenolic $-\text{OH}$ in all the complexes suggests the coordination of phenolic oxygen with the metal ion [9].

The presence of $-\text{SO}_2$ group in Schiff base can be confirmed by appearance of two bands at 1134 cm^{-1} and 1344 cm^{-1} due to symmetric and asymmetric vibrations. These bands remain at same position in ligand and complexes indicate that oxygen of $-\text{SO}_2$ group not coordinated with the metal ion [10]. Infrared spectra of Schiff base metal complexes provided information about coordination. The band of azomethine $-\text{C}=\text{N}$ appears at 1590 cm^{-1} in ligand is shifted to higher frequency 1602 to 1625 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 3310 cm^{-1} due to $>\text{N}-\text{H}$ group in free ligand shifted to lower frequency on chelating with metal ion indicating N-H group can acts as coordinating site [12]. The coordination of azomethine nitrogen further supported by non-ligand band $>\text{M}-\text{N}$ which appears in region of 548 - 562 cm^{-1} in all complexes [13]. Conclusive evidence regarding linkage of oxygen with metal ion is further supported by the appearance of band in the region of 484 - 498 cm^{-1} which is due to $>\text{M}-\text{O}$ [14]. Finally assignment of nature of molecule of water which coordinated in all complexes under study was more complicated than ligand, all the metal complexes of Schiff base shows bands in the region of 3534 - 3498 cm^{-1} which

TABLE-1
PHYSICAL CHARACTERISTICS OF SCHIFF BASE AND THEIR METAL COMPLEXES

Ligand/Complexes	Colour	m.f.	Molecular mass (g mol^{-1})	m.p. ($^{\circ}\text{C}$)	Yield (%)
L	Yellowish white	$\text{C}_{13}\text{H}_9\text{NO}_3\text{SBrCl}$	374.64	188	79
$\text{CuL}_2 \cdot (\text{H}_2\text{O})_2$	Light yellow	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_8\text{S}_2\text{Br}_2\text{Cl}_2\text{Cu}$	846.78	198	76
$\text{CoL}_2 \cdot (\text{H}_2\text{O})_2$	Orange	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_8\text{S}_2\text{Br}_2\text{Cl}_2\text{Co}$	842.28	196	75
$\text{NiL}_2 \cdot (\text{H}_2\text{O})_2$	Reddish brown	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_8\text{S}_2\text{Br}_2\text{Cl}_2\text{Ni}$	841.98	202	78
$\text{ZnL}_2 \cdot (\text{H}_2\text{O})_2$	Orange brown	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_8\text{S}_2\text{Br}_2\text{Cl}_2\text{Zn}$	848.68	206	77

TABLE-2
MICRO-ANALYTICAL DATA OF SCHIFF BASE AND THEIR METAL COMPLEXES

Ligand/Complexes	Elemental analysis (%): Calcd. (Found)						
	C	H	Br	Cl	N	S	M
L	41.64 (41.52)	2.40 (2.22)	21.74 (21.98)	9.48 (9.38)	3.37 (3.25)	8.54 (8.42)	–
$\text{CuL}_2 \cdot (\text{H}_2\text{O})_2$	37.00 (38.28)	2.36 (2.12)	18.89 (18.27)	8.26 (8.63)	3.33 (3.34)	7.55 (7.70)	7.43 (7.70)
$\text{CoL}_2 \cdot (\text{H}_2\text{O})_2$	37.04 (38.48)	2.37 (2.12)	18.99 (18.40)	8.31 (8.64)	3.32 (3.52)	7.59 (7.78)	7.00 (7.19)
$\text{NiL}_2 \cdot (\text{H}_2\text{O})_2$	37.05 (38.49)	2.37 (2.13)	19.55 (19.42)	8.31 (8.60)	3.32 (3.51)	7.60 (7.80)	6.88 (7.12)
$\text{ZnL}_2 \cdot (\text{H}_2\text{O})_2$	37.30 (38.18)	2.35 (2.14)	18.85 (19.12)	8.24 (8.58)	3.29 (3.28)	7.54 (7.76)	6.83 (7.92)

TABLE-3
IR SPECTRA (cm^{-1}) OF SCHIFF BASE AND ITS METAL COMPLEXES

Compound	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{N})$	SO_2		$\nu(\text{O}-\text{H})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{H}_2\text{O})$
			Sym.	Asym.				
L	3310	1590	1344	1134	3384	–	–	–
$\text{CuL}_2 \cdot (\text{H}_2\text{O})_2$	3266	1602	1350	1135	3398	550	486	3498
$\text{CoL}_2 \cdot (\text{H}_2\text{O})_2$	3245	1625	1342	1138	3412	548	492	3512
$\text{NiL}_2 \cdot (\text{H}_2\text{O})_2$	3270	1616	1348	1133	3424	562	484	3522
$\text{ZnL}_2 \cdot (\text{H}_2\text{O})_2$	3254	1610	1346	1130	3442	552	498	3534

TABLE-4
ANTIBACTERIAL ACTIVITY OF LIGAND AND ITS COMPLEXES (INHIBITION ZONE, mm)

Compound	Gram-positive						Gram-negative					
	<i>S. epidermidis</i> ATCC 14990			<i>B. subtilis</i> ATCC 33712			<i>E. coli</i> ATCC 87121			<i>P. vulgaris</i> ATCC 29905		
Ciprofloxacin/ Clarithromycin	11			12			14			10		
L	3.0	2.8	2.5	2.6	2.8	2.8	3.0	2.8	2.6	2.9	2.8	3.0
CuL ₂ ·(H ₂ O) ₂	3.4	3.8	3.2	3.6	3.2	3.4	4.0	4.0	4.2	4.6	4.2	4.9
CoL ₂ ·(H ₂ O) ₂	3.4	3.6	3.8	4.0	4.4	3.9	3.0	3.4	3.6	4.2	4.6	4.0
NiL ₂ ·(H ₂ O) ₂	2.6	3.1	2.9	2.6	2.6	2.8	3.0	3.4	3.4	3.4	3.6	3.8
ZnL ₂ ·(H ₂ O) ₂	4.6	4.0	4.8	4.0	4.4	4.6	4.6	4.8	5.0	4.2	4.6	4.9

indicates the presence of coordinated water molecules with the metal ion [15].

Electronic spectra: Electronic spectra of ligand and its metal complexes were displayed in DMF solution. Electronic spectra of ligand shows two high intensity absorption bands at 38272 and 32550 cm⁻¹ which indicate n → n* and π → π* transition of azomethine group, respectively in the ligand [16]. The electronic spectra of Co(II) complex shows energy bands at 38225, 36865 and 28658 cm⁻¹. This is due to ⁴T_{1g}(F) → ⁴T_{1g}(P) transition respectively [17] which indicates presence of octahedral geometry around Co(II). The electronic spectra of Cu(II) complex shows three energy bands at 33944, 33075 and 25873 cm⁻¹ is due to ²B_{1g} → ²E_g. This band is assigned to metal-ligand charge transfer [17]. The Ni(II) shows absorption bands at 39270, 36794 and 25652 cm⁻¹. First two bands are due to n → π* transition and third band is due to n → π* transition [17]. Zinc(II) complex shows high energy band at 36345 and 30520 cm⁻¹ due to ligand → metal charge transfer and this band is attributed to the ligand to metal charge transfer (MLCT) as electronic configuration of these complexes confirmed the absence of any d-d transition [17].

¹H NMR spectra: The azomethine proton appears at 8.1 ppm, it has been shifted to downfield in metal complexes which confirm coordination of ligand with metal by azomethine nitrogen [18]. The aromatic proton in Schiff base appears at 6.7 ppm to 7.5 ppm and in their metal complex in the range of 6.4 ppm to 7.2 ppm [19]. The -OH group appeared at 5.0 ppm in ligand but disappearance of phenolic -OH in metal complexes of ligand confirmed the coordination of phenolic oxygen to metal ion [20]. On the basis of above data, the probable structure of metal complex of Schiff base is given in Fig. 2.

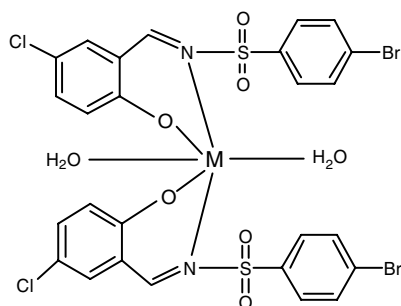


Fig. 2. Proposed structure of metal complex of Schiff base, where M = Cu(II), Co(II), Ni(II) and Zn(II)

Antibacterial activity: The antibacterial activity of ligand and their metal complexes were screened on Gram-positive bacteria: *S. epidermidis* and *B. subtilis* and Gram-negative bacteria: *E. coli* and *P. vulgaris* by disc diffusion technique

[21]. Filter paper disc were used for the incubation period of 24 h at 35 °C. The results (Table-4) suggested that complexes increased the antibacterial activity [22].

Conclusion

A new Schiff based has been prepared by the condensation of 5-chloro-2-hydroxybenzaldehyde and 4-bromobenzene-sulfonamide. The coordination ability of Schiff base has been reported by physical characteristics, micro-analytical data, ¹H NMR, FT-IR and UV spectrum data confirm the suggested coordination of ligand is bidentate and linked through azomethine group and phenol at oxygen forming stable chelate. The metal chelate of ligand has been structurally characterized and it is concluded that metal complexes show coordinated octahedral geometry. The biological study showed a significant activity of metal complexes as compared to that of ligand.

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