

Synthesis, Spectral Characterization and Antibacterial Study of a Schiff Base Metal Complexes Derived from N-[(E)-(5-Chloro-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-chloro-2-hydroxybenzaldehyde and 4-nitrobenzenesulfonamide have been prepared and characterized on the basis of physical characteristics, micro-analytical data, ¹H NMR, FTIR and UV spectrum data. The spectrum data confirm coordination of Schiff base with metal through imine nitrogen and oxygen atom. These metal complexes are screened against Gram positive and Gram negative bacteria for their biological activity. These complexes shows enhance biological activity as compare to ligand base.

Key words: Schiff Base • Metal Complexes • Spectroscopic Study • Biological Activity

INTRODUCTION

Schiff bases and their metal complexes have gained much importance recently due to their chelating ability. They play important rule in synthetic research because of their structural diversity. Metal complex of Schiff bases show application as biological, antimicrobial, antiviral, antitumor and antifungal activity [1-3]. Schiff bases have been studied as a class of ligands contain azomethine (Imine) group (-RC=N-) are usually prepared by condensation of primary amines with carbonyl compounds and coordinate with the metal ion through azomethine nitrogen atom [4]. Schiff bases derived from sulfonamides drug have been acquired interest due to their biological system. Compounds containing sulfonamide group have been used as drug for diseases

[5]. Sulfonamide coordination compounds and their derivatives are widely used as antifungal, anti-inflammatory and hypoglycemic agents. Ligands based on sulfonamides are used as asymmetric catalyst. Metal complexes modify the pharmacology and toxicology of the sulfonamide base ligands [6, 7].

In this research work, Schiff base N-[(E)-(5-chloro-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 was 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. The structure of the Schiff base ligand in present work is shown in Fig. 1.

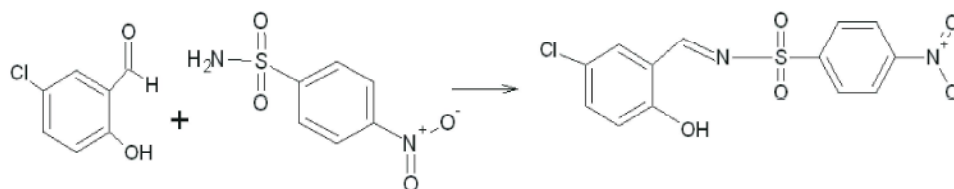


Fig. 1: Structure of ligand

MATERIALS AND METHODS

All chemical used were of analytical grade and of highest purity available. 4-nitobenzenesulfonamide and 5-chloro-2-hydroxybenzaldehyde were obtained from Sigma-aldrich. Metal (II) chloride and acetate 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-chloro-2-hydroxybenzaldehyde in methanol, after addition reaction mixture is heated under reflux for about 5-6 hours at 70°C. After completion of reaction precipitate of ligand are formed out as yellow to orange 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 then 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 placed in desiccators for drying.

RESULTS AND DISCUSSION

The Schiff base is synthesized by using equimolar quantities of 4-nitobenzenesulfonamide and 5-chloro-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 1622 cm⁻¹, is characteristic of azomethine >C=N linkage [8] whereas the band at 3432 cm⁻¹ is characteristic of hydrogen bond >O-H stretching vibration [9]. A medium intensity band at 3280 cm⁻¹ is due to the presence of >N-H group. The presence of -SO₂ group in Schiff base can be confirmed by appearance of two bands at 1168 cm⁻¹ and 1320 cm⁻¹ due to symmetric and asymmetric vibrations [10]. Infrared spectra of Schiff base metal complexes provided

information about coordination. The band of azomethine appears at 1622 cm⁻¹ in ligand is shifted to higher frequency after the complex formation. This shifting of band indicates that nitrogen of azomethine group is coordinated with metal ion [11]. The coordination of azomethine nitrogen is also supported by appearing band in region of 440-452 cm⁻¹ due to >M-N in all complexes [12]. The shifting of phenolic >O-H at 3432 cm⁻¹ in all complexes indicates the coordination of phenolic oxygen after deprotonation [13]. Linkage of oxygen with metal ion is further supported by the appearance of band in the region of 531-565 cm⁻¹ which is due to >M-O [14]. The bands of -SO₂ group almost remain unchanged which indicates that -SO₂ group not participate in coordination with metal ions [15]. All the metal complexes of Schiff base shows bands in the region of 3521-3529 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 energy bands at 32573 cm⁻¹ and 29725 cm⁻¹ which indicate n → n* and π → π* transition of the ligand [17]. The electronic spectra of Cu (II) complex shows two energy bands at 35852 cm⁻¹ and 31653 cm⁻¹ this is due to ²B_{1g} → ²E_g transition respectively. The Co (II) complex shows three energy bands at 37644 cm⁻¹, 34755 cm⁻¹ and 25873 cm⁻¹ is due to ⁴T_{1g} (F) → ⁴T_{1g} (P). The Ni (II) shows absorption band at 63927 cm⁻¹ is due to the ³A_{2g} → ³T_{2g}. The Zn (II) complex show high energy band at 35632 cm⁻¹ and 34916 cm⁻¹ due to ligand → metal charge transfer [18].

¹H NMR Spectra: ¹H NMR Spectra of Schiff base and their complexes were recorded in DMSO solution. The azomethine proton appear at 8.1 ppm, it has been shifted to downfield in metal complexes [19]. The aromatic proton in Schiff base appear between 6.7 to 7.5 ppm and in their metal complex in the range of 6.4 to 7.2 ppm. The disappearance of phenolic -OH confirmed the coordination of phenolic oxygen to metal ion [20].

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

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: *staphylococcus aureus* and *bacillus subtilis* and Gram negative bacteria: *Escherihia coli* and *klebsiella pneumonia*. The antibacterial activity of ligand and their

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

Sr. No.	Ligand/ Complexes	Color	Molecular Formula	Molecular Mass (gmol ⁻¹)	M. P. (°C)	Yield (%)
1	L	Pale Yellow	C ₁₃ H ₉ ClN ₂ O ₅ S	340.7	184	72
2	CuL ₂ (H ₂ O) ₂	Brown Yellow	C ₂₆ H ₁₈ Cl ₂ N ₄ O ₁₀ S ₂ Cu	744.9	210	64
3	CoL ₂ (H ₂ O) ₂	Greenish Yellow	C ₂₆ H ₁₈ Cl ₂ N ₄ O ₁₀ S ₂ Co	740.4	205	70
4	NiL ₂ (H ₂ O) ₂	Light Orange	C ₂₆ H ₁₈ Cl ₂ N ₄ O ₁₀ S ₂ Ni	740.1	195	65
5	Zn L ₂ (H ₂ O) ₂	Orange Yellow	C ₂₆ H ₁₈ Cl ₂ N ₄ O ₁₀ S ₂ Zn	746.8	190	68

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

Sr. No.	Ligand/ Complexes	Elemental analysis (%). (calculated)/ found						%Metal (calculated)/ found
		C	H	N	S	O		
1	L	(45.78) 44.46	(2.64) 2.42	(8.22) 8.02	(9.39) 9.24	(23.48) 23.18	--	
2	CuL ₂ (H ₂ O) ₂	(41.88) 41.80	(2.42) 2.32	(7.52) 7.40	(8.59) 8.40	(21.48) 21.38	(11.73) 11.67	
3	CoL ₂ (H ₂ O) ₂	(42.14) 42.06	(2.43) 2.34	(7.56) 7.48	(8.64) 8.52	(21.61) 21.54	(7.96) 7.90	
4	NiL ₂ (H ₂ O) ₂	(42.16) 42.04	(2.43) 2.35	(7.57) 7.49	(8.64) 8.54	(21.62) 21.54	(7.93) 7.86	
5	Zn L ₂ (H ₂ O) ₂	(41.78) 41.64	(2.41) 2.32	(7.50) 7.42	(8.57) 8.45	(21.42) 21.35	(8.76) 8.70	

Table 3: IR spectra cm⁻¹ of Schiff base and its metal complexes

Compound	N-H	C=N	SO ₂		O-H	M-N	M-O	H ₂ O
			Sym.	Asym.				
L	3280	1622	1320	1168	3432	--	--	--
CuL ₂ (H ₂ O) ₂	3290	1635	1320	1148	3423	448	554	3529
CoL ₂ (H ₂ O) ₂	3295	1648	1318	1152	3440	452	565	3539
NiL ₂ (H ₂ O) ₂	3295	1643	1316	1155	3434	450	542	3521
Zn L ₂ (H ₂ O) ₂	3300	1655	1322	1158	3415	440	532	3527

Table 4: ¹H NMR data of Schiff base in ppm

Schiff Base	Chemical Shift in ppm	
	6.7 to 7.5 ppm	aromatic-H
	5.0 ppm	phenolic -OH
	8.1 ppm	-N=CH-
	8.19 to 8.47 ppm	Homocyclic -C-H

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

Compound	Gram +ve		Gram -ve	
	<i>s. aureus</i>	<i>b. subtilis</i>	<i>E. coli</i>	<i>k. pneumonia</i>
L	12	15	16	18
CuL ₂ (H ₂ O) ₂	15	18	20	19
CoL ₂ (H ₂ O) ₂	12	14	15	16
NiL ₂ (H ₂ O) ₂	16	17	18	17
Zn L ₂ (H ₂ O) ₂	14	16	18	18

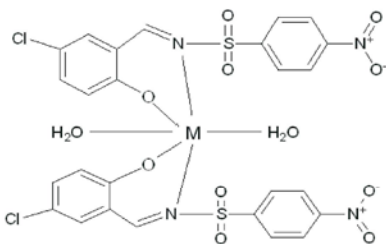


Fig. 2: Probable structure of metal complexes where M = Cu (II), Co (II), Ni (II) and Zn (II)

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 [21].

CONCLUSION

A new Schiff based has been prepared by the condensation of 5-chloro-2-hydroxybenzaldehyde and 4-nitrobenzenesulfonamide. The coordination ability of Schiff base has been reported by physical characteristics, micro-analytical data, ¹H NMR, FTIR and UV spectrum data confirm the suggested coordination of ligand 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 compare to that of ligand.

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