

Synthesis, Characterization and Antimicrobial Activity of Transition Metal Complexes of [NN] Donor Benzenesulfonamide Based Schiff Bases

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The new sulfonamide Schiff based ligands have been prepared by refluxing 7-methylquinoline-3-carbaldehyde and halo derivatives of benzenesulfonamide in methanol for 4-6 h. The complexes of Cu, Co, Ni and Zn have been synthesized and characterized on the basis of their physical characteristics, micro-analytical data, ¹H NMR, FT-IR spectrum and electronic spectrum data. The FT-IR spectrum data suggest that Schiff base ligand behaves in bidentate manner as coordinated with transition metals through nitrogen of azomethine group and nitrogen of quinolone group. ¹H NMR data confirm formation of the metal complexes. Biological screening effect of Schiff bases and their metal complexes have been studied against Gram-positive and Gram-negative bacteria by disc diffusion technique. The electronic spectrum data confirm the octahedral geometry of the complexes. Biological activities show that the metal complexes synthesized complexes exhibit higher antibacterial activity than that of Schiff base against tested bacteria.

Keywords: NN donor Schiff base, Transition metal complexes, Spectral characterization, Biological activity.

INTRODUCTION

Schiff bases are used as chelating agent in the field of coordination chemistry and therefore Schiff base metal complexes are gaining much interest for many years. It is well known that O and N atoms play an important role at the active site for metallo-biomolecules in coordination with metals [1,2]. Metal complexes of Schiff bases are extensively used and studied due to their synthetic sensitivity and flexibility towards variety of metals. A number of Schiff base compounds show biological activities including antibacterial, antifungal, antitumor, anticancer and anti-inflammatory actions [3,4]. Sulfa drugs are chemotherapeutical agents, in which molecular structures contain an aminobenzene sulfonamide moiety. Many sulfa drugs possess SO₂NH- moiety as an important toxophoric function. Sulfa drugs are also well known for their biological activities. The condensation of sulfa drug with aldehyde gives biological active Schiff base [5,6]. Schiff base ligands have been reported to show different varieties of biological actions because of their -C=N (azomethine linkage) group which is responsible for antibacterial, antifungal, clinical and analytical activities [7]. The literature survey indicates that metal complexes derived from sulfa drugs have been prepared and have been used in various physical, biological and pharmaceutical fields. Schiff base are among the most studied sulfa drug derivative which have been used for numerous biological application [8]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to possess unusual configuration [9].

In the present work, Schiff bases 4-chloro-*N*-[(7-methylquinolin-3-yl)methylene]benzenesulfonamide and 4-bromo-*N*-[(7-methylquinolin-3-yl)methylene]benzenesulfonamide were prepared by refluxing 7-methylquinoline-3-carbaldehyde with 4-chlorobenzenesulfonamide and 4-bromobenzenesulfonamide and their metal complexes were synthesized with Cu(II), Co(II), Ni(II) and Zn(II). Structure of the ligand and metal complexes were characterized by FTIR, ¹H NMR and UV spectroscopy. Biological activities were also studied against Gram-positive and Gram-negative bacteria for ligand and metal complexes.

EXPERIMENTAL

All the chemical reagents used were of analytical grade and of the highest purity available and were used without further purification. 4-Bromobenzenesulfonamide and 4chlorobenzene-sulfonamide were obtained from E.Merck. 7-Methylquinoline-3-carbaldehyde and cobalt(II), nickel(II), copper and zinc(II) acetates were obtained from Sigma-Aldrich. Solvents used were distilled and purified before used, these are obtained from Fluka and Sigma-Aldrich. Melting point of the ligands and of the transition metal complexes were determined in capillary tube using melting point apparatus. Infrared spectra were measured as KBr pellets on FT-IR spectrometer Shimadzu Japan Model IR Prestige-21 in the frequency range 4000-400 cm⁻¹. The electronic spectra were measured using DMSO as a solvent on U.V. Spectrophotometer Shimadzu Japan model Pharmaspec-1700. ¹H NMR spectrum of the ligands and of their transition metal complexes were recorded using NMR-spectrometer Bruker Germany 300 MHz. The elemental analysis was performed on Elemental Analyzer Leco USA model CHNS-932.

4-Bromo-*N*-[(7-methylquinolin-3-yl)methylene]benzenesulfonamide (HL¹): 0.1 M Solution of 4-bromo-benzenesulfonamide (25 mL) was added to 0.1 M solution of 7-methylquinoline-3-carbaldehyde (25 mL) in ethanol: then few drops of conc. sulfuric acid (H₂SO₄) were added to the reaction mixture, and the reaction mixture was heated under reflux for about 6 h at 75 °C. The solution so obtained was further concentrated by adding distilled water on water bath. The product obtained was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled water and then with petroleum ether. The product again was recrystallized in ethanol and dried in vacuum dessicator overnight. After completion of the reaction process precipitate of the ligand were formed out as yellowish solids. Purity of the ligand was checked by m.p. and TLC. The ligand is soluble in methanol, ethanol, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) (Scheme-I) [10].

4-Chloro-N-[(7-methylquinolin-3-yl)methylene]benzenesulfonamide (HL²): 0.1 M solution of 4-chlorobenzenesulfonamide (25 mL) was added to 0.1 M solution of 7-methylquinoline-3-carbaldehyde (25 mL) in ethanol than few drops of conc. sulfuric acid (H₂SO₄) were added to the reaction mixture, and the reaction mixture was heated under reflux for about 5 h at 75 °C. The solution so obtained was further concentrated by adding distilled water on water bath. The product obtained was precipitated, cooled and collected after filtration. The precipitate was purified by washing with distilled water and then with petroleum ether. The product again was recrystallized in ethanol and was dried in vacuum dessicator overnight. After completion of the reaction process precipitate of the ligand are formed out as yellowish green solids (Scheme-I). Purity of the ligand was checked by m.p. and TLC. The ligand was soluble in methanol, ethanol, DMF and DMSO [10].

Synthesis of metal complexes: Metal complexes of the Schiff base ligand were prepared by mixing 0.2 M of HL¹ and HL² Schiff bases (25 mL) with 0.1M of Cu, Co, Ni and Zn salts (25 mL) keeping ligand-metal ratio 2:1 in ethanol. The resultant solution was further concentrated with distilled water on water bath. The resultant mixture was then refluxed for 4-6 h at 70-75 °C where solid complexes precipitate obtained. The complex obtained in each time was cooled, filtered and washed with the ethanol many times to purify and remove the excess of ligand. Finally complexes were placed in desiccators for drying [10].

RESULTS AND DISCUSSION

Schiff bases were synthesized by treating equimolar quantities of 4-bromobenzenesulfonamide and 4-chlorobenzenesulfonamide with 7-methylquinoline-3-carbaldehyde. These Schiff bases then formed complexes by mixing with transition metal acetate salts. The metal complexes so obtained were formed stable at normal temperature and were color solids. Physical characteristics and analytical data of the ligands and metal complexes are given in Tables 1 and 2.

Infrared spectroscopy: Structure of the Schiff base metal complexes were established with the help of infrared spectroscopy. IR spectra of the free ligand and its metal complexes were recorded using KBr pellets in the range 4000-400 cm⁻¹. The infrared spectral data of the Schiff base ligand and its metal complexes are listed in Table-3. Bands observed for ligand HL¹ at 3180 cm⁻¹ and for ligand HL² at 3195 cm⁻¹ were due to H-N linkage which is shifted to higher frequency when the ligand forms complexes with metal. Sharp bands observed for ligand HL^1 at 1600 cm⁻¹ and for ligand HL^2 at 1612 cm⁻¹ is due to azomethine >C=N linkage which is shifted to higher frequency on going from ligand to its metal complexes due to coordination of the azometine linkage with metal ion [11,12]. The presence of $-SO_2$ group in Schiff bases (HL¹ and HL²) is confirmed by appearance of two bands at 1144 cm⁻¹ and 1310 cm⁻¹ and at 1154 cm⁻¹ and 1321 cm⁻¹, respectively due to symmetric and asymmetric vibrations. These bands remain at the same positions in case of ligand while the complexes indicate that oxygen of -SO₂ group is not coordinated with the metal ion [13]. The strong bands of ligand HL¹ at 990 cm⁻¹ and of ligand HL^2 at 998 cm⁻¹ due to >S-N group in ligand is shifted lower frequency on chelating with metal ion indicating that S-N group can act as coordinating site in both the ligands [14]. The coordination of nitrogen of azomethine is further supported by non-ligand band >M-N which appears in the region 572-540 cm⁻¹ in all complexes of both ligands HL¹ and HL² [15]. Finally in the case of water which coordinated in all complexes under study is more complicated then ligand. All



where X = Br and Cl Scheme-I: Preparation of Ligand

TABLE-1 PHYSICAL CHARACTERISTICS OF SCHIFF BASE AND THEIR METAL COMPLEXES							
Ligand/Complexes	Colour	m.f.	Molecular mass (g mol ⁻¹)	m.p. (°C)	Yield (%)		
HL^1	Yellowish	$C_{17}H_{13}BrN_2O_2S$	389.27	150	79		
$Cu(HL^1)$	Yellowish green	$C_{34}H_{26}Br_2N_4O_4S_2Cu \cdot 2H_2O$	878.04	174	80		
$Co(HL^1)$	Golden yellow	$C_{34}H_{26}Br_2N_4O_4S_2Co\cdot 2H_2O$	873.54	185	78		
$Ni(HL^1)$	Light green	$C_{34}H_{26}Br_2N_4O_4S_2Ni{\cdot}2H_2O$	873.24	177	84		
$Zn (HL^{1})$	Orange	$C_{34}H_{26}Br_2N_4O_4S_2Zn \cdot 2H_2O$	879.93	179	82		
HL^2	Yellowish green	$C_{17}H_{13}ClN_2O_2S$	344.82	165	78		
$Cu(HL^2)$	Bright green	$C_{34}H_{26}Cl_2N_4O_4S_2Cu \cdot 2H_2O$	789.14	184	79		
$Co(HL^2)$	Light Green	$C_{34}H_{26}Cl_2N_4O_4S_2Co\cdot 2H_2O$	784.64	190	81		
Ni(HL ²)	Lime green	$C_{34}H_{26}Cl_2N_4O_4S_2Ni\cdot 2H_2O$	784.34	188	84		
$Zn (HL^2)$	Dark green	$C_{34}H_{26}Cl_2N_4O_4S_2Zn \cdot 2H_2O$	791.04	180	80		

TABLE-2

MICRO-ANALYTICAL DATA OF SCHIFF BASE AND THEIR METAL COMPLEXES

Ligand/	Elemental analysis (%): (Calcd.)/Found						
Complexes	С	Н	X (X = Br & Cl)	Ν	0	S	М
HL^1	(52.45) 52.34	(3.37) 3.26	(20.53) 20.41	(7.20) 7.10	(8.22) 8.10	(8.24) 8.11	-
$Cu(HL^1)$	(48.45) 48.34	(3.09) 2.97	(18.76) 18.66	(6.65) 6.54	(7.60) 7.50	(7.61) 7.50	(7.54) 7.45
$Co(HL^1)$	(48.71) 48.62	(3.10) 3.00	(18.86) 18.74	(6.68) 6.55	(7.64) 7.52	(7.64) 7.53	(7.04) 6.95
$Ni(HL^1)$	(48.73) 48.60	(3.11) 3.02	(18.87) 18.78	(6.69) 6.56	(7.64) 7.53	(7.64) 7.54	(7.01) 6.90
$Zn (HL^{1})$	(48.34) 48.23	(3.08) 2.97	(18.72) 18.60	(6.63) 6.53	(7.58) 7.47	(7.58) 7.47	(7.75) 7.64
HL^2	(59.21) 59.10	(3.8) 3.69	(10.28) 10.19	(8.12) 8.00	(9.28) 9.19	(9.30) 9.19	-
$Cu(HL^2)$	(54.17) 54.06	(3.45) 3.33	(9.43) 9.32	(7.43) 7.34	(8.49) 8.38	(8.50) 8.40	(8.43) 8.32
$Co(HL^2)$	(54.50) 54.38	(3.47) 3.36	(9.48) 9.37	(7.48) 7.39	(8.54) 8.42	(8.55) 8.43	(7.88) 7.76
$Ni(HL^2)$	(54.52) 54.40	(3.48) 3.38	(9.49) 9.38	(7.48) 7.38	(8.55) 8.43	(8.56) 8.44	(7.84) 7.73
Zn (HL ²)	(54.04) 53.94	(3.44) 2.35	(9.40) 9.30	(7.42) 7.30	(8.48) 8.37	(8.49) 8.37	(8.66) 8.55

 TABLE-3

 IR SPECTRA (cm⁻¹) OF SCHIFF BASE AND ITS METAL COMPLEXES

Compound	NU	C-N	SO ₂		C N	MAN	ПО
	IN-II	C=N	Sym.	Asym.	3-IN	IVI-IN	П ₂ О
HL^1	3180	1600	1310	1144	990	-	-
CuHL ¹	3200	1612	1315	1150	978	560	1365
CoHL ¹	3205	1635	1322	1148	982	540	1354
$NiHL^{1}$	3215	1626	1318	1143	980	572	1360
$ZnHL^{1}$	3220	1620	1326	1140	973	568	1350
HL^2	3195	1612	1318	1156	998	-	-
CuHL ²	3208	1628	1323	1154	988	555	1370
CoHL ²	3214	1633	1324	1158	992	548	1362
NiHL ²	3202	1634	1321	1159	986	554	1380
ZnHL ²	3218	1638	1322	1157	989	550	1378

the metal complexes of Schiff base show bands in the region of 1380-1350 cm⁻¹ which indicates the presence of coordinated water molecules with the metal ion [16].

Electronic spectra: Electronic spectra of the ligand HL¹ and its metal complexes displayed in DMF solution. Electronic spectra of the ligand shows absorption in UV/visible region two high intensity bands at 40421 cm⁻¹ and 42865 cm⁻¹ which indicate $n \rightarrow n^*$ and $\pi \rightarrow \pi^*$ transition respectively of azomethine group in the ligand [17]. The electronic spectra of CoHL¹ complex shows two energy bands at 10626 cm⁻¹ and 17910 cm⁻¹. This is due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition respectively which indicates the presence of octahedral geometry around CoHL¹ [18]. The electronic spectra of CuHL¹ complex shows three energy bands in 10764-14946 cm⁻¹ due to ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) and ${}^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F). The electronic spectra of CuHL¹ complex suggests an octahedral geometry [19]. The electronic spectra of NiHL¹ shows absorption bands at 15816 and 22846 cm⁻¹ assigned to ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (F) transition, indicating octahedral geometry of Ni HL¹ complex[20]. The Zn HL¹ complex shows high energy band at 32874 and 35763 cm⁻¹ due to ligand \rightarrow metal charge transfer [21].

Similarly electronic spectra of the ligand HL² and its metal complexes displayed in DMF solution. Electronic spectra of ligand shows two high intensity bands absorption in UV/ visible region at 39573 cm⁻¹ and 38252 cm⁻¹ indicating n \rightarrow n* and $\pi \rightarrow \pi^*$ transition respectively of azomethine group in the ligand. The electronic spectra of CoHL² complex shows two energy bands at 12846 and 16935 cm⁻¹ due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition, respectively, indicating presence of octahedral geometry around CoHL². The electronic spectra of CuHL² complex shows three energy bands at 11836-15282 cm⁻¹ region due to ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) and ${}^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F). The electronic spectra of CuHL² complex shows three onergy bands at 11836-15282 cm⁻¹ region due to ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) and ${}^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F). The electronic spectra of CuHL² complex shows three onergy bands at 11836-15282 cm⁻¹ region due to ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) and ${}^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F). The electronic spectra of CuHL² complex shows three onergy bands at 11836-15282 cm⁻¹ region due to ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F) and ${}^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F). The electronic spectra of CuHL² complex suggests an octahedral geometry. The electronic spectra of NiHL² shows absorption

band at 16234 and 20278 cm⁻¹ assigned to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ transition, indicating octahedral geometry of the Ni HL² complex. The Zn HL² complex shows high energy bands at 30638 cm⁻¹ and 31937 cm⁻¹ due to ligand \rightarrow metal charge transfer (Table-4).

TABLE-4 ELECTRONIC SPECTRAL DATA OF COMPLEXES						
Ligand/ Complex	Wavenumber (cm ⁻¹)	Wavelength (nm)	Band assignments			
HL^{1}	40421, 42865	303, 380	$\pi \rightarrow \pi^*$			
CuHL ¹	10764, 14946	386, 430	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$			
CoHL ¹	10626, 17910	390, 440	${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$			
NiHL ¹	15816, 22846	405, 444	${}^{^{1}\text{g}}\text{A}_{2g}(F) \rightarrow {}^{^{3}}\text{T}_{1g}(F)$ ${}^{^{3}}\text{A}_{2g}(F) \rightarrow {}^{^{3}}\text{T}_{1g}(P)$			
ZnHL ¹	32874, 35763	385, 450	Ligand \rightarrow metal charge transfer			
HL ²	39537, 38252	310, 405	$\pi \rightarrow \pi^*$ $n \rightarrow n^*$			
CuHL ²	11836, 15282	398, 434	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$			
CoHL ²	12846, 16935	380, 425	${}^{2}\mathbf{B}_{1g} \rightarrow {}^{2}\mathbf{A}_{1g}$ ${}^{2}\mathbf{B}_{2g} \rightarrow {}^{2}\mathbf{B}_{2g}$			
NiHL ²	16234, 20278	399, 430	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$			
ZnHL ²	30638, 31937	312, 415	Ligand \rightarrow Metal charge transfer			

¹H NMR spectra: ¹H NMR Spectra of Schiff bases and its complexes have been recorded in DMSO solution. TMS used as internal standard. In both the ligands (HL¹ and HL²) azomethine proton appears at 9.07 ppm, but it is shifted to downfield in metal complexes which confirms coordination of ligand with metal by azomethine nitrogen [22]. The aromatic proton in Schiff base appears at 7.19 ppm to 8.93 ppm and in their metal complex in the range of 6.80 ppm to 8.53 ppm [23]. In addition, the multiple signals in the range of approximately 3.7-1.83 ppm are attributed to aliphatic protons [24].

On the basis of above given data, structure of the metal complex of Schiff base is given in **Scheme-II**.

Antibacterial activity: Antibacterial activities of the benzenesulfonamide, its Schiff base ligands and its metal



where X = Br, Cl and M = Cu(II), Co(II), Ni(II), Zn(II) Scheme-II: Structure of transition metal complexes

complexes were determined and screened on Gram-positive bacteria: S. pneumoniae and B. cereus and Gram-negative bacteria: K. pneumoniae and P. aeruginosa by disc diffusion technique [25]. Nutrient agar was used for the medium of bacterial growth. Nutrient agar is popular because it can grow variety types of bacteria and fungi and contains many nutrients needed for the bacterial growth. Nutrient agar, cotton swab, petri dishes and metallic borer were autoclaved for sterilization at 120 °C for 0.5 h. Bore of 6 mm diameter was prepared with the help of metallic borer. After solidification of the nutrient agar, bacterial stain spread over the surface of the agar with the help of cotton swab. Benzenesulfonamide, its ligands and their metal complexes were dissolved in DMSO. The sample of 1 mg/mL in DMSO was added in the wells. Benzenesulfonamide itself and ofloxacin were taken as reference antibacterial drugs. Filter paper disc were used for the incubation period of 48 h at 25-30 °C and the results were recorded. The antibacterial activities of the ligand and its complexes were tested by measuring inhibition zone observed around the material. Ligand showed significant range of activities on the growth of all the selected bacterial stain. The results suggested that complexes increased the antibacterial activity [26]. The antibacterial activity data has been presented in Table-5.

TABLE-5 ANTIBACTERIAL ACTIVITY OF LIGAND AND ITS COMPLEXES (INHIBITION ZONE, mm)					
Common 1	Gram-	positive	Gram-negative		
Compound –	SP	BC	KP	PA	
HL^1	16	17	18	19	
CuHL ¹	15	15	17	17	
CoHL ¹	14	16	19	18	
NiHL ¹	16	17	19	19	
$ZnHL^{1}$	18	19	20	19	
HL^{2}	17	18	18	16	
CuHL ²	13	17	17	14	
CoHL ²	14	15	14	13	
NiHL ²	16	17	19	15	
ZnHL ²	17	19	19	18	
Sulfonamide	19	18	20	17	
Oflocaxin	22	21	23	24	
>20: significant, 15-19: modrate, < 15: weak; SP = <i>S. pneumoniae</i> ; BC					

= B. cereus; KP = K. pneumoniae; PA = P. aeruginosa

Conclusion

New sulfonamide based Schiff bases have been prepared by the condensation of 4-bromobenzenesulfonamide and 4-chlorobenzenesulfonamide with 7-methylquinoline-3-carbaldehyde. The transition metal complexes have been prepared by reacting them with metal acetate salts. The coordination ability of the Schiff base has been reported by physical characteristics, micro-analytical data ¹H NMR, FTIR and UV spectrum data confirm suggested coordination of the ligands which is bidentate and is linked through azomethine group and nitrogen of pyridine ring forming stable chelate. The metal chelate of ligand has been structurally characterized and it has been concluded that metal complexes show coordinated octahedral geometry. Biological study shows significant activity of the metal complexes as compare to that of the ligands.

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