



# SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ASPECTS OF O-AND N-DONOR SCHIFF BASE LIGANDS AND THEIR Co (II) & Zn (II) COMPLEXES

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## ABSTRACT

New cobalt (II) and zinc (II) complexes of O-and N-donor Schiff bases derived from furfuraldehyde and 2-aminopyridine (SB1) or hydrazine hydrate (SB2) have been synthesized. The ligands and their metal complexes have been characterized on the basis of elemental analysis, molecular weight determinations, molar conductance measurements, IR, <sup>1</sup>H NMR and UV-vis. spectral studies. The purity of the compounds was confirmed by TLC. The Schiff base ligands act as non-functional bidentate and tetradentate donors and coordinate through furfural oxygen and azomethine nitrogen. These have also been screened for their *in vitro* antibacterial and antifungal activities against bacterial species like *escherichia coli* and *Staphylococcus aureus* as well as fungal species like *Candida albicans* and *Asper niger* by using disc diffusion method wherefrom the complexes have been found biologically more potential than the respective ligands.

**Key words:** Schiff bases, Metal complexes, Spectral studies.

## INTRODUCTION

Schiff bases and their transition metal complexes, containing nitrogen and oxygen donor atoms, play an important role in biological and inorganic research and have been studied extensively due to their unique coordination and biological properties<sup>1,2</sup>. Transition metal Schiff base complexes have found applications in various fields such as medicine, agriculture, industries<sup>3</sup> etc. Furfuraldehyde is well known as an analytical reagent<sup>4,5</sup>. Its various derivatives<sup>6</sup> are also useful.

Cobalt forms very stable complexes with nitrogen donor ligands, both in the di- and tri-valent states, and both are thought to be implicated in the catalytic cation of the vitamin.

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Zinc forms stable complexes in its invariable +2 oxidation state with ligands such as halides,  $\text{CN}^-$  and those containing O, N and S donor atoms.

Keeping all these facts into consideration, We have synthesized and characterized four new complexes of Co (II) and Zn (II) with O- and N- donor Schiff bases derived from furfuraldehyde and 2-aminopyridine (SB1) or hydrazine hydrate (SB2). In order to establish the biological role of metals, the Schiff bases and their Co (II) & Zn(II) complexes have been screened for their antimicrobial activity against some bacterial species like *E. Coli*, *S. Aureus* and fungal strains like *A. Niger* and *C. Albicans*.

## EXPERIMENTAL

All the chemicals and solvents used were of analytical grade. The metal salts  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnCl}_2$  (Qualigens) available in pure state have been used as such. Furfuraldehyde obtained from Qualigens fine chemicals was distilled before use, whereas hydrazine hydrate and 2-aminopyridine were used as received.

### Synthesis of the ligands

The ligands were synthesized by the reaction of furfuraldehyde with 2-aminopyridine or hydrazine hydrate in 1 : 1 or 2 : 1 molar ratio respectively in ethanol. The reaction mixtures were refluxed on a water bath for 3-4 hrs. The precipitates thereby obtained were separated and washed with ethanol and dried in vacuo in desiccator over anhydrous  $\text{CaCl}_2$ .

### Synthesis of the Co (II) complexes

To the hot ethanolic solution (25 mL) of the ligand SB1 (0.002 mol) or SB2 (0.001 mol) was added the hot ethanolic solution (15 mL) of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.001 mol) and the reaction mixture was refluxed on a water bath for 4-5 hrs. On cooling, the resulting coloured metal complexes precipitated out. The precipitates were washed with ethanol and finally purified by recrystallization from absolute alcohol.

### Synthesis of the Zn (II) complexes

The hot ethanolic solutions of  $\text{ZnCl}_2$  (0.001 mol) and SB1 (0.002 mol) or SB2 (0.001 mol) were mixed and the mixture was refluxed on a water bath for 4-5 hrs. The precipitates of the resulting metal complexes were filtered, washed with ethanol and dried over anhydrous  $\text{CaCl}_2$  in vacuo.

### Anti-microbial studies

The Schiff bases as well as their complexes were screened for their *in vitro* antibacterial and antifungal activities against some pathogenic bacterial species like *E. coli* and *S. aureus* or fungal species like *C. albicans* and *A. niger*. The paper disc diffusion method was adopted for the determination of such activities<sup>7</sup>. The compounds were tested at two different concentrations of 50 ppm and 100 ppm in their DMF solutions. Standard drugs such as Ciprofloxacin for bacterial and Fluconazol for fungus species were used as reference. The susceptibility zones measured in diameter (mm) were the zones around the disc killing the active bacteria and fungi.

### Physical measurements and analytical methods

The carbon, hydrogen and nitrogen analyses were performed by VarioEL (III) Carlo Erba 1108 Elemental analyser. The IR spectra of the ligands and their complexes were scanned as KBr pellets on a Perkin-Elmer 575 spectrophotometer. The <sup>1</sup>H NMR spectra of the ligands were recorded on Bruker -300 FT NMR spectrometer in DMSO-d<sub>6</sub> using TMS as an internal standard. The molar conductances of the complexes were determined by a conductivity meter with a dip type cell and platinized electrode. UV-Vis. Spectra of the complexes were recorded on Helios-alpha Spectrophotometer. Melting points were measured in open capillaries and are uncorrected. Molecular weights of the complexes were determined by Rast method using camphor as a solvent. Metal contents of the complexes were determined by the atomic absorption technique. Chloride was determined by the standard procedure reported in the literature<sup>8</sup>.

## RESULTS AND DISCUSSION

The reactions of CoCl<sub>2</sub>.6H<sub>2</sub>O or ZnCl<sub>2</sub> with the Schiff bases have been carried out in unimolar and bimolar ratios in ethanol. The analytical results and molecular weights of the compounds support the formulations represented in Table 1. All the complexes are coloured, crystalline powders and are soluble in acetone and DMF but sparingly soluble in DMSO.

### IR Spectral studies

The IR spectra of the ligands showed (Table 2) a band in the range 1647-1635 cm<sup>-1</sup>, which is due to ν(C=N). This band shifts to lower frequency 1640-1620 cm<sup>-1</sup> in all the Co (II) and Zn (II) complexes possibly indicating the coordination to metal ions through the azomethine nitrogen<sup>9, 10</sup>. The C-O-C band appeared at 1150 or 1148 cm<sup>-1</sup> in the spectra of SB1 or SB2, respectively, shifted to 1140-1120 cm<sup>-1</sup> in the spectra of the complexes. Such a

shifting is probably due to the involvement of furfural ring oxygen in coordination<sup>11</sup>. Two distinct bands appeared in the region 468-434  $\text{cm}^{-1}$  and 592-548  $\text{cm}^{-1}$  in the spectra of complexes are due to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$ , respectively and these further provide evidence for the coordinated metal ion in the ligand framework<sup>12,13</sup>.

**Table 1: Physical characteristics and analytical data of the Schiff bases and their metal complexes**

Compound	Colour	M.P. (°C)	Molar cond. ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )	Mol. wt. found/(calcd.)	Elemental analysis % found/(calcd.)				
					C	H	N	Cl	M
SB1	Dark brown	65	-	170 (172)	69.60 (69.76)	4.57 (4.65)	16.25 (16.27)	-	-
SB2	Yellow	92	-	185 (188)	63.00 (63.83)	4.83 (4.25)	14.31 (14.89)	-	-
[Co(SB1) <sub>2</sub> .Cl <sub>2</sub> ]	Dirty green	120	14	471.5 (474)	50.09 (50.63)	3.39 (3.37)	11.07 (11.81)	14.05 (14.97)	11.51 (12.44)
[Co(SB2).Cl <sub>2</sub> ]	Reddish brown	115	18	316.5 (318)	36.91 (37.73)	2.52 (2.51)	8.74 (8.80)	22.43 (22.32)	18.64 (18.55)
[Zn(SB1) <sub>2</sub> ].Cl <sub>2</sub>	Dirty white	102	180	477.5 (480)	50.06 (50.00)	3.35 (3.33)	10.72 (11.66)	14.08 (14.79)	12.61 (13.54)
[Zn(SB2)].Cl <sub>2</sub>	Yellow	180	170	322 (324)	36.73 (36.03)	2.48 (2.46)	8.69 (8.64)	21.04 (21.91)	20.18 (20.44)

**Table 2: IR spectral data of Schiff base and their metal complexes**

Compound	$\nu(\text{CH=N})$ (Azomethine)	$\nu(\text{C-O-C})$ (Furfural)	$\nu(\text{C-N})$ Pyridine	$\nu(\text{N-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
SB1	1647	1150	1495	-	-	-
SB2	1635	1148	-	1017	-	-
[Co(SB1) <sub>2</sub> .Cl <sub>2</sub> ]	1640	1135	1493	-	592	468
[Co(SB2).Cl <sub>2</sub> ]	1620	1120	-	1022	580	460
[Zn(SB1) <sub>2</sub> ].Cl <sub>2</sub>	1636	1140	1497	-	585	434
Zn(SB2)].Cl <sub>2</sub>	1625	1130	-	1022	548	454

## NMR spectral studies

The  $^1\text{H}$  NMR spectral data of the Schiff bases are summarized in Table 3. The multiplet appeared at 6.31-8.48  $\delta$  or 6.69-7.10  $\delta$  in the spectrum of SB1 or SB2, respectively corresponds to the aromatic ring protons. The singlet centered at 9.03 or 8.49  $\delta$  in the case of SB1 or SB2 is due to the azomethine (-CH = N-) proton<sup>14</sup>.

**Table 3:  $^1\text{H}$  NMR spectral data of Schiff base ligands**

Compound	$^1\text{H}$ signal $\delta$ (ppm)	Assignment
SB1	6.31-8.48 (7H,m)	Ring protons
	9.03 (1H,s)	Azomethine proton
SB2	6.69-7.10 (6H,m)	Ring protons
	8.49 (2H,s)	Azomethine proton

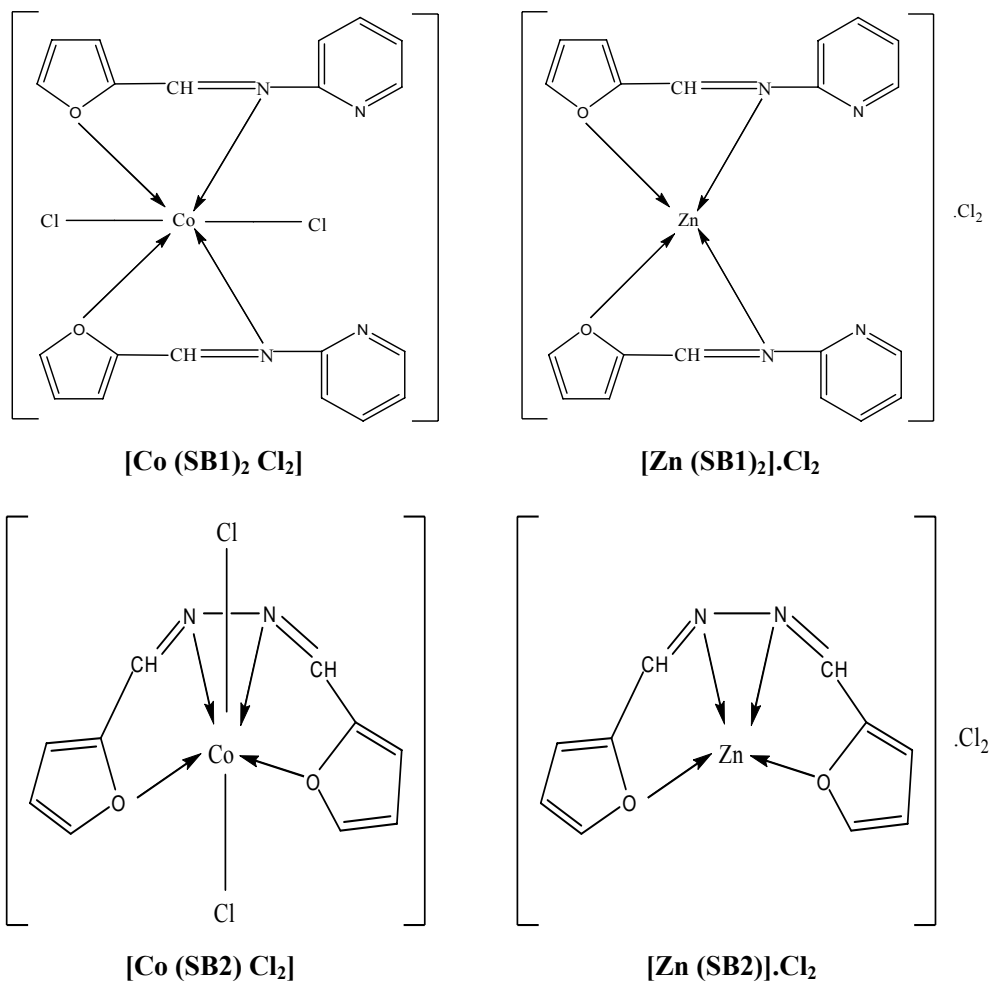
## Electronic spectra

The electronic spectra of Co (II) complexes of SB1 and SB2 have three bands each at 10627, 8220, 19325 and 17543, 23573, 20400  $\text{cm}^{-1}$  corresponding to  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ ,  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$  and  $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$  transition, respectively, which indicates the octahedral structure of the complexes<sup>15</sup>. The electronic spectra of the Zn (II) complexes give sharp bands at 29498  $\text{cm}^{-1}$  (for SB1) and 29325  $\text{cm}^{-1}$  (for SB2) due to ligand-metal charge transfer<sup>16</sup>.

Thus on the basis of above studies, the expected structures of the Schiff base complexes may be represented as shown in the Fig. 1.

## Antimicrobial activity

The Schiff bases and their Co (II) and Zn (II) complexes exhibited varying degree of inhibitory effects on the growth of the tested bacterial and fungal species (Tables 4 and 5). The antimicrobial results evidently show that the activity of the complexes is higher than that of the corresponding ligands. This indicates that chelation increases the antimicrobial activity<sup>17,18</sup>.



**Figs. 1: Proposed structures of the complexes**

**Table 4: Antibacterial activity of the Schiff base ligands and their Co (II) & Zn (II) complexes, showing diameter of inhibition zone**

Compound	Micro-organisms			
	<i>S. aureus</i> (mm)		<i>E. coli</i> (mm)	
	50 ppm	100 ppm	50 ppm	100 ppm
SB1	13	15	11	12
SB2	16	18	12	14

Cont...

Compound	Micro-organisms			
	<i>S. aureus</i> (mm)		<i>E. coli</i> (mm)	
	50 ppm	100 ppm	50 ppm	100 ppm
[Co(SB1) <sub>2</sub> Cl <sub>2</sub> ]	16	19	15	16
[Co(SB2) Cl <sub>2</sub> ]	17	19	14	14
[Zn(SB1) <sub>2</sub> ].Cl <sub>2</sub>	13	15	12	14
[Zn(SB2)].Cl <sub>2</sub>	18	19	12	12
*Ciprofloxacin	22	26	20	22

**Table 5: Antifungal activity of the Schiff base ligands and their Co (II) & Zn (II) complexes, showing diameter of inhibition zone**

Compound	Micro-organisms			
	<i>C. albicans</i> (mm)		<i>A. niger</i> (mm)	
	50 ppm	100 ppm	50 ppm	100 ppm
SB1	13	15	12	13
SB2	12	13	14	15
[Co(SB1) <sub>2</sub> Cl <sub>2</sub> ]	13	16	13	16
[Co(SB2) Cl <sub>2</sub> ]	16	17	16	18
[Zn(SB1) <sub>2</sub> ].Cl <sub>2</sub>	14	16	13	14
[Zn(SB2)].Cl <sub>2</sub>	12	14	14	16
** Fluconazole	20	24	18	21

\*Standard for bacterial strains

\*\*Standard for fungal strains

### ACKNOWLEDGEMENT

We are thankful to the Principal, St. John's College, Agra (U.P.) for providing research facilities to carry out the work.

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*Accepted : 09.05.2011*