

Synthesis, Characterization and Biological Activity of Mn(II), Ni(II), Cu(II) and Zn(II) Complexes of Schiff Base Ligand

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The Schiff base has been prepared by refluxing S-benzyl dithiocarbamate with *o*-chloro benzaldehyde in ethanolic media and form coordination compounds of Mn(II), Ni(II), Cu(II) and Zn(II) metal ions. These complexes were characterized by elemental analysis, molar conductance, infrared, NMR and electronic spectra. Infrared spectral data of the complexes have revealed bidentate complexing nature of the Schiff base through thioketo sulphur and azomethine nitrogen atoms. The possible structures for all the metal complexes are reported here. The antibacterial and antifungal activity of the Schiff base and their complexes have also been screened.

Key Words: Schiff base, Complexes, Antibacterial, Antifungal.

INTRODUCTION

Dithiocarbamate are now well established as an important class of nitrogen and sulphur donor ligands^{1,2}. This is due to the remarkable biological activities observed for these compounds, which have since been shown to be related to their metal complexing ability. Metal complexes of dithiocarbamate have recently drawn special attention due to their activity against cancer^{3,4} tumour⁵, tuberculosis⁶, bacteria⁷, fungus⁸ and as antipyretic agents⁹. The biological activities of these compounds is due to the presence of the toxophorically important (-N-C=S) moiety¹⁰. The number and diversity of nitrogen and sulphur donor chelating agents used to prepare new coordination and organometallic compounds has increased rapidly during the past few years¹¹. Studies on metal complexes of dithiocarbamate have been thoroughly studied and reported by earlier workers¹²⁻¹⁴. In view of the importance of coordination compounds in medicinal chemistry¹⁵, we report here the Mn(II), Ni(II), Cu(II) and Zn(II) complexes of the *o*-chlorobenzaldehyde Schiff bases of S-benzyl esters of the dithiocarbamic acid.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. The purity of the compounds have been checked by TLC using silica gel-G. Analytical reagents grade chemicals were used. The IR spectra of ligand and its complexes

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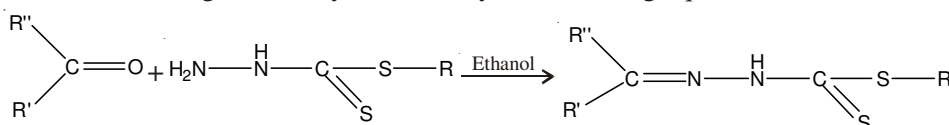
were recorded on a Perkin-Elmer 283 spectrophotometer in the 4000-400 cm^{-1} region. Electronic absorption spectra were obtained on a Spectrascan UV-2700, using a prepared dimethyl sulphoxide solution in the 200-1100 nm region. The ^1H NMR spectral analysis were performed on a Bruker advance 400 spectrophotometer using TMS as an internal standard.

Elemental analysis (N and S) of the ligand and its metal complexes were carried out in microanalytical laboratory, CDRI Lucknow on Elemental Vario EL III Carlo Erba 1108 elemental analyzer. Molar conductance measurements were carried out in 10^{-3} M solution of the complexes in DMF solvent at 298K using Decibel DB1011.

Preparation of S-aryl dithiocarbamate: S-Benzyl dithiocarbamate have been prepared by reported method¹⁶.

Preparation of Schiff base (Hocbsbz): A solution of S-benzyl dithiocarbamate (0.01 mol) in ethanol (50 mL) was added to a solution of *o*-chloro benzaldehyde (0.01 mol). The mixture was refluxed for 1 h and cooled, the yellow crystals had formed, were filtered off and recrystallized from ethanol. Yield; 2.3 g (71.6 %); m.p. 180 °C; anal. (%); found: N, 8.6; S, 19.4 %; calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{S}_2\text{Cl}$: N, 8.7; S, 20 %.

Schiff base ligand was synthesized by the following equation:



where $\text{R} = \text{C}_6\text{H}_4\text{Cl}$; $\text{R}' = \text{H}$, $\text{R}'' = \text{CH}_2\text{C}_6\text{H}_5$.

General method for preparation of metal complexes: The Schiff base metal complexes under investigation were prepared by mixing 0.001 mmol of 20 mL of ethanolic solution of the corresponding metal salts ($\text{Mn}(\text{CH}_3\text{COO})_2$, $\text{Ni}(\text{CH}_3\text{COO})_2$, $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$) with the 0.002 mmol of the Schiff base in the same amount in the same solvent, the mixture were refluxed for 3-5 h on water bath. The mixture was then cooled in an ice bath and the product were filtered with suction, washed with ethanol and dried in desiccator over anhydrous silica gel. The coloured solid are obtained and are mostly soluble in common organic solvents, DMSO and DMF.



RESULTS AND DISCUSSION

The complexes are quite stable and can be stored for a long period. The elemental analysis data of the ligand and its complexes indicates formation of 1:2 [M:L] ratio of the formulae of $[\text{M}(\text{ocbsbz})_2]$ [$\text{M} = \text{Mn}^{2+}$, Ni^{2+} , Cu^{2+} and Zn^{2+}]. The molar conductance of the complexes was determined at a concentration 1×10^{-3} M in DMF. These values reveal the presence of a non-electrolytic nature¹⁷. The non electrolytic nature of the complexes indicates that the ligand is coordinated as uninegative charged anion (Table-1).

TABLE-1
ANALYTICAL, ¹H NMR SPECTRAL DATA AND OTHER PHYSICAL PROPERTIES OF
THE SCHIFF BASES AND THEIR METAL COMPLEXES

Compd. No.	^a Ligand/ complexes	Colour	Elemental analysis found (calcd)		Molar conductance ^b	^c Chemical shifts (DMSO- <i>d</i> ₆ , δ)		
			N	S		N-H	-SCH ₂ C ₆ H ₅	Ar-H
I	Hocbsbz	Yellow	10.3 (10.8)	24.2 (24.8)	–	12.10	4.63 s	7.3-7.9 m
II	[Mn(ocbsbz) ₂]	Cream	7.8 (8.1)	18.2 (18.4)	4.8	–	4.61 s	7.4-7.8 m
III	[Ni(ocbsbz) ₂]	Brown	8.2 (8.0)	18.0 (18.3)	3.5	–	4.64 s	7.5-7.8 m
IV	[Cu(ocbsbz) ₂]	Light brown	7.8 (8.0)	18.5 (18.2)	6.6	–	4.67 s	7.6- 8.0 m
V	[Zn(ocbsbz) ₂]	Cream	8.3 (8.0)	18.5 (18.2)	3.3	–	4.62 s	7.5-7.9 m

a: Hocbsbz anionic form of the Schiff base of S-benzylthiocarbamate with *o*-chloro benzaldehyde. b: Molar conductance of approximately 10⁻³ M solutions in DMF (ohm⁻¹ cm² mol⁻¹). c: δ (ppm) relative to TMS.

Reaction of Schiff bases with metal salts (Mn²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) yields complexes depending on the nature of the anion being used. Thus in the presence of acetate anions was allowed to react with the ligand, a *bis* ligand complex of composition [M(ocbsbz)₂] always resulted¹⁸ (M = Mn²⁺, Ni²⁺, Cu²⁺, Zn²⁺).

The ¹H NMR spectra of the Schiff base in DMSO shows signal at 12.10, 4.63 and 7.3-7.9 relative to TMS may assigned to azomethine proton (NH), methylene protons of the S-benzyl moiety and aromatic protons, respectively. The above observations indicate that the ligand actually exist in thione form.

The infrared bands of Schiff base and their metal complexes are listed in Table-2. The absence of band around 2700 cm⁻¹ which would indicative of SH, indicate that in solid state the molecule remains in the thione form. The Schiff base have a broad absorption band at about 2856 cm⁻¹ which is due to the stretching vibrations of ν(N-H) group. This band is absent in the spectra of the metal complexes indicating that the ligands is convert in its thiol form through tautomerism and coordinated in its deprotonated thiol form.

The ν(C=N) band observed at 1592 cm⁻¹ shifted to higher^{19,20} wavelength in the complexes indicating coordination by the azomethine nitrogen. This is further indicated by the shift of the hydrazinic ν(N-N) band of the Schiff base ligands at 1026 cm⁻¹ to lower energies. The next strong absorption at 1279 cm⁻¹ in the ligand can be assigned to ν(C=S) stretching vibration which is also absent in metal complexes indicates coordination through thioketo sulphur atom and the other band at 751 cm⁻¹ can be assigned to ν(C-Cl) group. These bands are also observed in the metal chelates nearly at the same position.

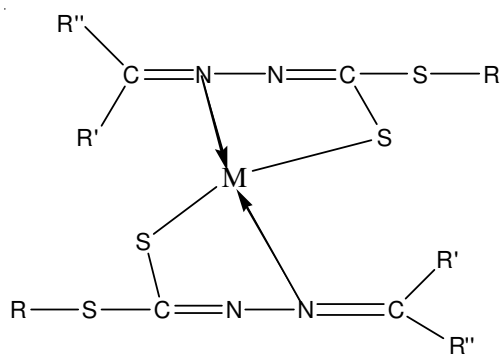
TABLE-2
INFRA RED (cm⁻¹) AND ELECTRONIC ABSORPTION SPECTRA OF
SCHIFF BASE LIGAND AND THEIR METAL COMPLEXES

Compd. No.	^a Ligand/complexes	v(C=N)	v(N-N)	v(N-H)	v(C=S)	v(C-Cl)	UV-vis (nm)
I	Hocbsbz	1592	1026	2856	1279	751	256, 310
II	[Mn(ocbsbz) ₂]	1610	1010	–	–	750	399, 321
III	[Ni(ocbsbz) ₂]	1602	1008	–	–	748	256, 312, 402
IV	[Cu(ocbsbz) ₂]	1611	1011	–	–	750	258, 338
V	[Zn(ocbsbz) ₂]	1598	1014	–	–	751	254, 356, 404

a: Hocbsbz anionic form of the Schiff base of S-benzylthiocarbazate with *o*-chloro benzaldehyde.

The electronic spectra of the Schiff base and its metal complexes were recorded in DMSO and given in Table-2. The electronic spectrum of the Mn(II) complex of Hocbsbz shows intense band at 399 nm assigned to the ⁶A_{1g} → ⁴T_{1g} transition, indicated tetrahedral geometry²¹. The electronic spectrum of nickel and copper complexes shows bands at 402, 338 nm assigned to ²B_{1g} → ²E_{1g} and ²T_{2g} → ²E_g transitions, respectively which suggest square planar geometries^{22,23}. The Zn(II) complex were suggested to be four coordinated having tetrahedral geometry based on analytical, spectral and conductance studies²⁴.

On the basis of forgoing evidences, the proposed structures for the complexes are presented in Fig. 1 analytical and spectral data the possible structure for the complexes are as follows.



where R = CH₂C₆H₅, R' = C₆H₄Cl, R'' = H, M = Mn, Ni, Cu and Zn

Fig. 1. Proposed structure of the metal complexes

Antibacterial activity: The Schiff base and its metal complexes were screened for their antibacterial activity against gram positive and gram negative bacteria like *S. aureus*, *S. albus*, *E. coli* and *Pseudomonas* species using disc diffusion method²⁵. The testing was carried out in DMSO solution at a concentration of 30 µg/mL using Muller Hinton agar media. Ampicillin and tetracycline were used as the standard drugs.

The compounds **II** and **IV** showed moderate activity against *Pseudomonas* species while compounds **I**, **III** and **V** showed very low activity against *E. coli*.

Antifungal activity: All the new metal complexes were also screened for antifungal activity against *Aspergillus niger*, *Alternaria alternata* and *Candida* species at concentration of 50 µg/mL using sabouraud's dextrose agar media disk diffusion technique. Amphotericin B disc were used as the standard drugs. Compounds **II** showed significant activity against *Aspergillus niger* while compounds **III** and **V** showed moderate activity against *Candida* species.

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