



# SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF TRANSITION METAL COMPLEXES DERIVED FROM S-ALKYL DITHIOCARBAZATE

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## Abstract

The Coordination compounds of Schiff base derived from S-alkyl dithiocarbazate with transition metal ions, viz, Cu(II), Mn(II) and Zn(II) have been prepared and characterized by infrared, <sup>1</sup>H NMR, UV-Vis, elemental analysis and conductivity measurement. The ligand S-methyl-β-N-(2-chlorobenzalidine) dithiocarbazate behaves as a mono and bidentate chelating agent and bonded to the metal ion through azomethine nitrogen and thiol sulphur atom of dithiocarbazate moiety. Electronic spectra and elemental analysis measurement reveal found to be non-electrolyte in nature on the basis of low value of molar conductance. All of the synthesized compounds are biologically active and screened for their antibacterial and antifungal activities which are found to exhibit moderate to significant biological activities.

**Keywords:** Synthesis, Schiff base, Complexes, Antibacterial and antifungal activity.

## Introduction

Metal dithiocarbazate complexes involving nitrogen-sulphur donor ligands are of considerable interest due to their potential biological activity<sup>1</sup> and practical applications in the fields of pharmaceutical and agricultural industries<sup>2,3</sup>, in addition to the general considerations of metal-nitrogen and metal-sulphur bonding and electron delocalisation in transition metal complexes. Dithiocarbazates exhibit significant anti-fungal, anti-protozoal, anti-bacterial and anti-cancer activity<sup>4-6</sup>.

Recently, as in vitro insulinomimetic potential of these compounds has been established<sup>7</sup>. We report herein the synthesis and characterization of a new ligand having NS donor atoms and its complexes with Cu(II), Mn(II) and Zn(II) ions and describe their potential as anti-bacterial and anti-fungal agents.

## Experimental

All the chemical and reagent used were of reagent grade and used with out any further purification. The IR spectra of ligand and its complexes in DMSO were recorded on a Perkin-Elmer 283 spectrophotometer in the 4000-400cm<sup>-1</sup> region. Electronic absorption spectra were obtained on a Spectrascan UV-2700, using a prepared dimethyl sulphoxide solution in the 200-1100 nm region. The <sup>1</sup>H NMR spectral analysis were performed on a Bruker advance 400 spectrophotometer using TMS as an internal standard.

Elemental analysis (N, S and Cl) of the ligand and 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 for the 10<sup>-3</sup>M solution of the complexes in DMF solvent at 298K using Decibel DB1011. Purity of the compounds was checked on TLC using silica gel-G. Melting points were determined in open capillaries and are uncorrected.

## Synthesis of Ligand

A solution of s-methyl dithiocarbazate (0.1mol) in absolute ethanol (40cm<sup>3</sup>) was added to an equimolar solution of 2-chlorobenzaldehyde in

50 cm<sup>3</sup> of the same solvent. The solution was heated on a steam bath for 2-3hrs and then cooled to 0°C in an ice bath. Precipitated Schiff base were filtered, washed and recrystallized with ethanol and dried at room temperature.

M.P. 143°C. Yield 70%.

Anal.(%) Found: N,11.3; S, 26.0 %,

Calc for C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>ClS<sub>2</sub>: N,11.5; S, 26.2 %.

### General method for synthesis of Metal Complexes

The Schiff base (0.002mmol) and metal salt (0.001) Cu(OAc)<sub>2</sub>.H<sub>2</sub>O, CuCl<sub>2</sub>, Mn(oAc)<sub>2</sub> and Zn(OAc)<sub>2</sub>. was dissolved in ethanol (20 ml) and content were refluxed for 3-5hrs 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.

The physical properties, analytical and spectral data of ligand and their complexes are shown in Table 1 and 2.

### Results and Discussion

The elemental analysis data of the ligand and its complexes are given in Table-1. The data indicates the formation of 1:1 [M:L] ratio of the formulae of [M(2cbsme)<sub>2</sub>] [M = Cu<sup>2+</sup>] and 1:2 [M:L] ratio of the formulae of [M(pmame)<sub>2</sub>]

[M = Cu<sup>2+</sup>, Mn<sup>2+</sup> and Zn<sup>2+</sup>]. The molar conductances of the complexes in DMF indicate that they are essentially non-electrolyte in this solvent. The non-electrolytic nature of the complexes indicates that the ligand is coordinated as a uninegatively charged anion that the chloride anions are also coordinated to copper (II) ions<sup>6</sup> in formation of [M(L)Cl] whereas in case of [M(L)<sub>2</sub>] anion being used (OAC)<sub>2</sub> is not coordinated with metal ions<sup>7</sup>.

The 2-cholorobenzaldehyde Schiff base of S-methyl dithiocarbazate has the -N(H)C(S) (thioamide) function and therefore, in principle, it can exhibit thione (Fig.1a) and thiol (Fig.1b) tautomerism. However, its IR Spectrum in KBr does not exhibit any ν(S-H) band at approximately 2700, but displays a medium intensity band at 2912cm<sup>-1</sup> attributable to the ν(N-H) of the thione form. This is strong evidence that, like other Schiff bases of S-alkyldithiocarbazates, it also remains as the thione tautomer in the solid state. But when it is dissolved in ethanol and a metal [Cu(II)], Mn(II) and Zn(II)] salt is added to the solution, it quickly converts to the thiol form with the concomitant formation of a metal (II) complex of the deprotonated thiolate form of the Schiff base.

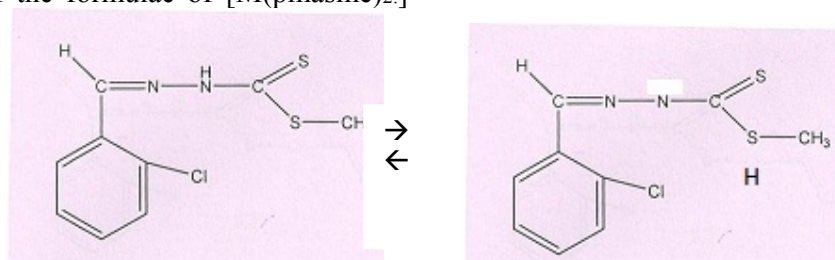


Fig.1. H2cbsme: (a) thione form and (b) thiol form.

Table 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE SCHIFF BASE AND ITS COMPLEXES.

S.No.	Compounds <sup>a</sup>	Colour	Yield (%)	M.P. (°C)	Molar Conductance <sup>b</sup>	Analytical data <sup>c</sup>		
						N	Cl	S
2a.	H2cbsme	Yellow	70	156	-----	11.10		25.28

						(11.02)		(25.20)
3a.	[Cu(2cbsme)Cl <sub>2</sub> ]	Yellow	62	146	7.1	7.3 (7.4)	28.2  (28.5)	17.1 (16.9)
3b.	[Cu(2cbsme) <sub>2</sub> ]	Brown	60	150	6.3	10.8  (10.2)	11.8  (12.9)	23.1  (23.3)
3c.	[Mn(2cbsme) <sub>2</sub> ]	Light brown	67	148	4.2	10.8  (10.2)	11.8  (12.9)	23.1  (23.3)
3d.	[Zn(2cbsme) <sub>2</sub> ]	Yellow	72.5	186	3.2	10.5  (10.1)	12.7  (12.9)	22.7  (23.2)

<sup>a</sup>H<sub>2</sub>cbsme anionic form of the Schiff base of S-methyldithiocarbamate with 2-chlorobenzaldehyde.

<sup>b</sup>Molar conductance of approximately 10<sup>-3</sup> M solutions in DMF (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>).

<sup>c</sup>Calculated values are given in parenthesis.

**Table 2**

SPECTRAL DATA OF SCHIFF BASE AND THEIR COMPLEXES.

S.No.	Compounds	IR absorption bands (cm <sup>-1</sup> )					UV-Vis  nm
		v(C=N)	v(N-H)	v(C=S)	v(C-Cl)	v(N-N)	
2a.	H <sub>2</sub> cbsme	1593	2912	1284	752	1041	251, 300
3a.	[Cu(2cbsme)Cl <sub>2</sub> ]	1601	---	---	750	1031	251, 364, 370
3b.	[Cu(2cbsme) <sub>2</sub> ]	1599	---	---	756	1030	429, 605
3c.	[Mn(2cbsme) <sub>2</sub> ]	1601			755	1032	252, 310, 398
3d.	[Zn(2cbsme) <sub>2</sub> ]	1605			755	1034	262, 342, 412

The <sup>1</sup>H NMR spectra of the Schiff bases in due to the -S-H proton, indicating that in DMSO-d<sub>6</sub> does not show any signal at 4.0 ppm DMSO, it remains in their thione form.

Thiosemicarbazones, which are closely related to H<sub>2</sub>cbsme, have been found to coordinate to metal ions in both the protonated thione form<sup>8</sup> and the deprotonated thiolate form<sup>9</sup>. There are examples of metal complexes in which both the protonated thione and the deprotonated thiolate forms of a thiosemicarbazone ligand are present in the same complex<sup>10</sup>.

However Schiff bases derived from S-alkyl esters of dithiocarbazic acid invariably deprotonate while coordinating with metal ions yielding complexes containing only the thiolate form of the ligand. So far, there has not been a single example of a metal-dithiocarbazate complex in which a thione tautomer has been found to be coordinated to a metal ion.

The IR bands of Schiff base and its complexes are summarized in Table 2. A comparison of the IR spectrum of the ligand with those of its complexes shows that the broad and weak band at 2912cm<sup>-1</sup> attributable to  $\nu(\text{N-H})$ , is not present in the spectra of the complexes indicating that the ligand is coordinated in its deprotonated form. In the past, evidence of coordination of thiosemicarbazone and dithiocarbazate ligands to metal ions via the azomethine nitrogen atom was based on shifting of the azomethine C=N band of the free ligand from lower to higher wave numbers in the spectra of metal complexes<sup>11</sup>. However, shifting of this band to both higher<sup>12</sup> and lower<sup>13</sup> wave numbers have been reported. Since the  $\nu(\text{C=N})$  band is expected to couple with other bands, the shifting of this band will be dependent on how much it is in combination with other bands. In the IR spectra of the present complexes, the

$\nu(\text{C=N})$  band is not shifted but the  $\nu(\text{N-N})$  band of the free ligand shifts considerably to lower wave numbers supporting coordination via the azomethine nitrogen atom<sup>14</sup>.

The sharp  $\nu(\text{C=S})$  bands at 1284 cm<sup>-1</sup> for ligands were also not observed in the metal complexes, thus supporting the suggestion of coordination through the thione sulphur and from the IR studies a band  $\nu(\text{C-Cl})$  at 752 cm<sup>-1</sup> due to chloride group remains unchanged in all the complexes, suggesting non participation of chloride group in coordination with central metal ion.

Electronic spectral data are given in Table 2. The Schiff base spectral data exhibit a band in the 300 nm range, due to the  $\pi-\pi$  transition within the azomethine group, affected by the intramolecular charge transfer within the ligand molecule. The electronic spectra of the Schiff base complexes under investigation do not resemble the free Schiff base, which is the supporting evidences for complex formation.

The electronic spectrum of the Mn(II) complex exhibited absorption band at 398 nm which are assigned to  ${}^4\text{T}_{1g} \leftarrow {}^6\text{A}_{1g}$  transition, a square planar geometry has been suggested<sup>15-17</sup>.

The Cu(II) complex displays two bands at 429, 605 nm attributed to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ , and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$  transitions (d-d), suggesting square planner geometry .

From the forgoing observations, the suggested chemical structures for the prepared Schiff base complexes under investigation are as follows:

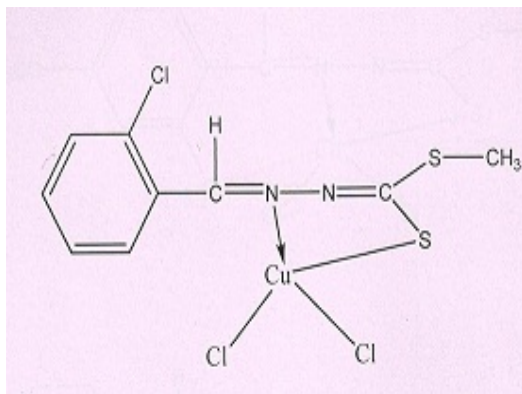
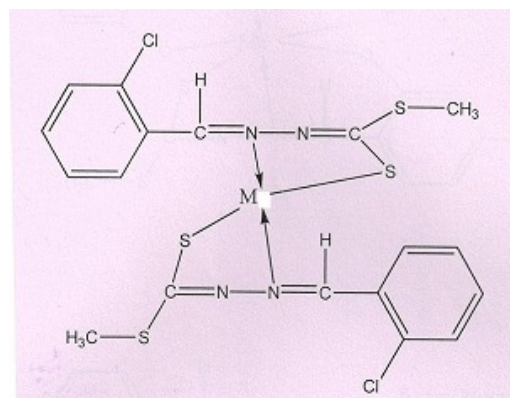


Fig 2. Proposed structure of the monochelated complexes,



M= Cu(II), Mn(II) and Zn(II)

Fig.3. Proposed structure of the bischelated complex.

**Anti-microbial activity**

The anti-bacterial activities were tested by disc diffusion method at 30µg/ml concentration and Ampicillin and tetracycline was used as a reference compound. *E. coli*, *S. aureus*, *pseudomonas* species and *S. albus* used as the bacterial test organisms. All the new complexes were also screened for anti-fungal activity against *Aspergillus niger*, *alternaria alternata* and *Candida* species at concentration of 50µg/ml using subroad and dextrose agar media, Amphotericin B disc were used as the standard drugs. 3b have shown moderate activity against bacteria and also shown significant activity against *Aspergillus niger* and *Candida* species. Compound 3c exhibit very little activity against these organisms.

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