Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7224-7228

Synthesis, Spectral and Biological Studies of Cu(II), Zn(II) and Cd(II) Complexes with Schiff Base Ligand

Snehika Shrivastava*, Anil Kumar, Yogesh Pandey and S.N. Dikshit†
Department of Chemistry, Bipin Bihari Postgraduate College, Jhansi-284 001, India
E-mail: snehikashrivastava@yahoo.co.in

The bidentate Schiff bases having nitrogen and sulphur donor atoms were derived from the condensation of S-methyldithiocarbazate with 4-chloroacetophenone. Reaction of Schiff base ligand with Cu(II), Zn(II) and Cd(II) salts gave solid complexes. All the complexes were characterized by a variety of physico-chemical techniques, *viz.* molar conductivity, elemental analysis, IR, ^{1}H NMR and electronic spectral studies. Schiff bases and their corresponding complexes have also been screened for their antibacterial and antifungal activities and found to be quite active in the respect.

Key Words: Schiff base, Metal complex, Biological studies.

INTRODUCTION

Transition metal complexes of Schiff bases derived from S-alkyl esters of dithiocarbazic acid have generated considerable interested because of their interesting physico-chemical properties[1-3] and potentially useful biological activities[4-6]. Considerable interest has been shown in metal complexes of thiocarbazate derivatives especially those having NNS donor sequences[7]. The Schiff base has been found to exhibit promising activity against leukemia cells. Metal complexes of sulfur nitrogen chelating agents derived from thiosemicarbazide[8,9] and S-alkyl esters of thiocarbazic acid[10] have been investigated over the past several years. It is because of their interesting potentially beneficial chemotherapeutic properties[11]. These ligands interact with metal ion to give structure of different geometry and properties and they are often biological active[12,13].

As part of our continuing study of metal complexes Schiff bases derived from S-alkyl esters of dithiocarbazic acid, we report here the preparation, spectroscopic characterization and biological activity of some mono and *bis*-chelated Cu(II), Zn(II) and Cd(II) complexes of the 4-chloroacetophenone Schiff base of S-methyldithiocarbazate.

---

†Department of Chemistry, S.M.S. Government Model Science College, Gwalior-474 001, India.

EXPERIMENTAL

All the chemicals were analytical reagent grade and used without any further purification. Melting points were determined in open capillaries and are uncorrected. The IR spectra of ligand and its complexes 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-Avance 400 spectrophotometer using TMS as an internal standard. Elemental analysis (N and S) 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 in 10^{-3} M solution of the complexes in DMF solvent at 298 K using Decibel DB1011. Purity of the compounds was checked on TLC using silica gel-G.

Preparation of the ligand (Hpcasme): To a solution of S-methyldithiocarbazate (0.1 mol) in absolute ethanol (40 mL) was added to an equimolar solution of 4-chloro acetophenone in 50 mL of the same solvent. The solution was heated on a steam bath for 2 h and then cooled to room temperature. Precipitated Schiff base were filtered off, washed with ethanol and recrystallized with ethanol in light yellow crystals and dried over silica gel. Yield: 1.9 g (73 %); m.p. 165 °C; Anal (%) Found: N, 10.3; S, 24.2 %; Calc. for $C_{11}H_{14}N_2S_2Cl$: N, 10.8; S, 24.8 %.

Preparation of the complexes: The Schiff base (0.002 mol) and metal salt (0.001 mol) ($CuCl_2.2H_2O$, $Zn(CH_3COO)_2.2H_2O$ and $Cd(CH_3COO)_2.2H_2O$) was dissolved in ethanol (30 mL). After refluxing for 2-5 h, the mixture was cooled in an ice bath to 0 °C and the product were filtered off, washed with ethanol and dried in dessicator over silica gel. The coloured solid are obtained and are mostly soluble in common organic solvents, DMSO and DMF. The spectral and analytical data are shown in Tables 1 and 2.

TABLE-1
ANALYTICAL, ^1H NMR SPECTRAL DATA AND OTHER PHYSICAL PROPERTIES OF THE COMPLEXES

*Ligand/ complexes	Colour	Elemental analysis (%): Found (Calcd.)		Molar cond.** (ohm^{-1} cm^2 mol^{-1})	**Chemical shifts		
		N	S		δ-NH	δ-SCH_3	Ar-H
Hpcasme	Yellow	10.3 (10.8)	24.2 (24.8)	–	10.2 br w	2.8	7.1-7.5
[Cu(pcasme)Cl_2]	Brown	6.8 (7.1)	16.9 (16.4)	21	–	2.6	7.2-7.5
[Zn$(pcasme)_2$]	Cream	10.2 (9.6)	22.4 (22.1)	23	–	2.4	7.2-7.4
[Cd$(pcasme)_2$]	Cream	19.8 (20.4)	8.5 (8.9)	37	–	2.9	6.8-7.3

*Hpcasme anionic form of the Schiff base of S-methyldithiocarbazate with 4-chloro acetophenone; *δ (ppm) relative to TMS.

TABLE-2
INFRA RED (CM^{-1}) AND ELECTRONIC ABSORPTION
SPECTRA OF LIGAND AND COMPLEXES

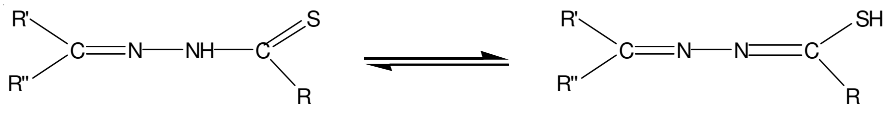
*Ligand/ complexes	ν(C=N)	ν(N-N)	ν(N-H)	ν(C=S)	ν(C-Cl)	UV-vis (nm)
Hpcasme	1602	1055	2910	1282	780	356, 386
$[Cu(pcasme)_2Cl_2]$	1565	1079	–	–	771	356, 378, 439, 610
$[Zn(pcasme)_2]$	1576	1093	–	–	778	356, 375, 450
$[Cd(pcasme)_2]$	1580	1101	–	–	775	357, 379, 440

*Hpcasme anionic form of the Schiff base of S-methyldithiocarbazate with 4-chloro acetophenone.

RESULTS AND DISCUSSION

The reaction of 4-chlroacetophenone and S-methyldithiocarbazate in ethanol yields the Schiff base (Fig. 1a), the formulation of which is supported by analytical and spectral data.

Its ^1H NMR spectrum in DMSO-d_6 shows signals at 2.4-2.9, 10.8 and 6.8-7.5 corresponding to the $-SCH_3$, -NH and phenyl proton, respectively[14]. The IR spectrum of the Schiff base displays the ν(C=N) and ν(N-N) bands at 1602 and 1055 cm^{-1}, respectively. The IR spectrum display the ν(N-H) at 2910 cm^{-1} suggesting that in the solid state, the Schiff base remains in the thioketo form (Fig. 1a), but in presence of metal salt it converts into thiol form (Fig. 1b).



(a) (b)

(R, R' = CH_3 and R'' = C_6H_4Cl)

Fig. 1. (a) thione and (b) thiol forms of the ligand

Reaction of the Schiff base with metal salts yielded crystalline complexes which were found to be quite stable in the atmosphere. The complexes which were isolated in the present study are listed in Table-1 along with some of their physical properties.

The ν(C=N) band of the free ligand were shifted to lower (20-40 cm^{-1}) frequencies in the complexes, suggesting coordination via the azomethine nitrogen atom. The occurrence of the N-N band at higher frequency in the IR spectra of the complexes compared to that in the ligand, suggests a reduction of the repulsion between the lone pairs of electrons on the nitrogen atoms[15] due to coordination by the azomethine nitrogen.

The ^1H NMR spectra in DMSO-d_6 of ligands do not show any resonance at *ca.* 4.0 ppm attributable to the S-H proton resonance, but they do show a broad peak at *ca.* 10.2 ppm due to the -NH proton (Table-1), indicating that even in a polar solvent such as DMSO, they remain in the thione form. However, as soon as metal salts are added to the solution of the ligand, it quickly converts into the thiolato form. This behaviour is common to all Schiff base ligands derived from S-alkyldithiocarbazates[16].

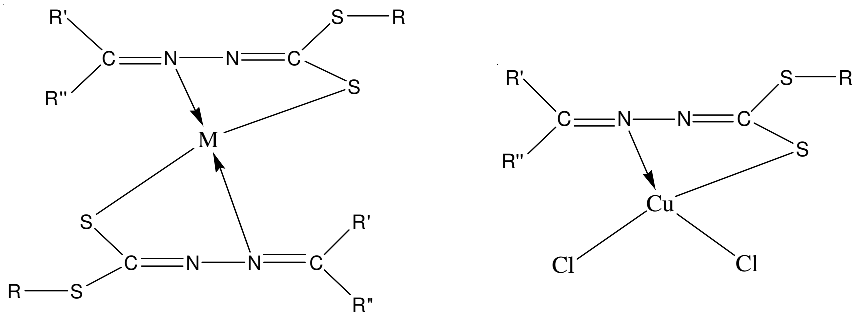
The very negligible shifts of the -SCH_3 proton resonance in the ^1H NMR spectra of the complexes relative to those of the free ligand (Table-1), indicate that the thioether sulfur atoms do not participate in coordination with the metal ions[17]. The chloride ion being present in the para position has no effect on the basicity of -N as it is at the farthest position.

The Schiff base Hpcasme (Schiff base 4-chloroacetophenone with S-methyldithocarbazate) reacts readily with zinc(II) and cadmium(II) salts in ethanol producing stable compounds, the composition of which depend on the nature of the anion present in the reaction mixture. Thus, with a coordinating anion such as chloride ion, mono-ligand complex of empirical formula [Cu(pcasme)Cl_2] were obtained, whereas in the presence of a weakly coordination ion such as acetate ion, *bis*-ligand complexes of formula, [M(pcasme)$_2$] resulted. The molar conductance 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.

The electronic spectra of the Schiff base and its zinc(II) and cadmium(II) complexes are compiled in Table-2. The spectra of the ligand in solution, exhibit bands at *ca.* 386 and 356 nm attributable to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. In the complexes, these bands do not shift significantly but a new band at *ca.* 450 nm, probably a charge transfer band, is observed. Such bands are common in the electronic spectra of metal-thiosemicarbazone and metal-dithiocarbazate complexes[18]. Zinc(II) and cadmium(II) complexes were suggested to be four coordinated having tetrahedral geometry based on analytical, spectral and conductance studies.

For the Cu(II) complex two band is observed at 439, 610 nm, this band is specific to the Cu(II) ion in square planer geometry and corresponds[19] to the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$.

On the basis of analytical and spectral data, a possible structure for complexes are presented in Fig. 2.



R, R' = CH_3, R''= C_6H_4Cl, M = Zn or Cd

Fig. 2. Tentative structures of the metal complexes

Biological activity: All the compounds were screened *in vitro* for their antimicrobial activity against bacteria and fungi. The antibacterial activities were tested by disc diffusion method[20] at 30 μg/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 antifungal activity against *Aspergillus niger, Alternaria alternata* and *Candida* species at concentration of 50 μg/mL using subroad and dextrose agar media, ampho-*tericin B disc were used as the standard drugs. Cu(II) and Zn(II) complexes have shown moderate activity against *E. coli, S. aureus* and *Candida albicans*.

ACKNOWLEDGEMENTS

The authors are thankful to Principal Bipin Bihari P.G. Science College, Jhansi for providing laboratory facilities. We are also greatful to Director C.D.R.I. Lucknow for elemental analysis D.R.D.E. Gwalior for spectral studies and Birla Institute of Medical and Research, Gwalior for Biological activities.

REFERENCES

1. A. Abu-Raqabah, G. Davies, M.A. El-Sayad, A. El-Toukhy, S.N. Shaikh and J. Zubeita, *Inorg. Chim. Acta*, **193**, 43 (1992).
2. S. Al-Shehri, G. Davies, M.A. El-Sayad and A. El-Toukhy, *Inorg. Chem.*, **29**, 1198 (1990).
3. M.T.H. Tarafder, N. Saravanan, K.A. Crouse and A.M. Ali, *Transition Met. Chem.*, **26**, 613 (2001).
4. Y.-P. Tian, D. Chung-Ying, X.-X. You, T.C.W. Mak, L. Quing and Z. Jian-Ying, *Transition Met. Chem.*, **23**, 17 (1998).
5. M.T.H. Tarafder, Teng-Jin Khoo, K.A. Crouse, A.M. Ali B.M. Yamin and H.-K. Fun, *Polyhedron*, **21**, 2691 (2002).
6. M.T.H. Tarafder, M.A. Ali, D.J. Wee, K. Azahari, S. Silong and K.A. Crouse, *Transition Met. Chem.*, **25**, 456 (2000).
7. M.T.H. Tarafder, A. Kasbollah, K.A. Crouse, A.M. Ali, B.M. Yamin and H.-K. Fun, *Polyhedron*, **20**, 2363 (2001).
8. D.X. West and N.C. Lewis, *Transition Met. Chem.*, **13**, 277 (1988).
9. M.A. Ali and S.E. Livingstone, *Coord. Chem. Rev.*, **13**, 101 (1974).
10. M.T.H. Tarafder, M.A. Ali, D.J. Wee, K. Azahari, S. Silong and K.A. Crouse, *Transition Met. Chem.*, **25**, 456 (2000).
11. M.T.H. Tarafder, A. Asmadi, S.M.S. Talib, A.M. Ali and K.A. Crouse, *Transition Met. Chem.*, **26**, 170 (2001).
12. M.A. Ali and S.E. Livingstone, *Coord. Chem. Rev.*, **13**, 101 (1974).
13. C.Y. Duan, Y.P. Tian, X.Z. You and T.C.M. Mak, *Polyhedron*, **16**, 4097 (1997).
14. M.A. Ali and A.H. Mirza, *Transition Met. Chem.*, **25**, 430 (2000).
15. A. Monaci and F. Trali, *J. Chem. Soc. Dalton Trans.*, 417 (1977).
16. M.A. Ali and A.H. Mirza, *Transition Met. Chem.*, **25**, 430 (2000).
17. R. Singh, S.P. Mittal, S. Malik and R.V. Singh, *Indian J. Chem.*, **46A**, 1406 (2007).
18. M.A. Ali, S.M.G. Hossain, S.M.M.H. Majumder, M. Nazimuddin and M.T.H. Tarafder, *Polyhedron*, **6**, 1653 (1987).
19. M.A. Ali and M.T.H. Tarafder, *J. Inorg. Nucl. Chem.*, **39**, 1785 (1977).
20. C.H. Collins, P.M. Lyne and J.M. Grange, Microbiological Methods, London, UK, Butterworths, edn. 6 (1989).

(*Received*: 30 January 2009; *Accepted*: 19 August 2009) AJC-7755