ISSN : 0974 - 746X Volume 9 Issue 3

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 9(3), 2014 [078-084]

Synthesis, characterization and biological activities of Ni(II) and Cu(II) complexes of Schiff base ligand derived from p-dimethylaminocinnamaldehyde

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ABSTRACT

Some new metal (Ni(II) and Cu(II)) complexes of Schiff base derived from p-dimethylaminocinnamaldehyde and *S*-alkyl dithiocarbazate were synthesized and characterized by various physico-chemical (conductance measurements, elemental analyses, solubility, magnetic susceptibility) and spectral (infrared, nuclear magnetic resonance and ultra violet-visible spectroscopy) techniques. The newly synthesized metal complexes were evaluated for their antibacterial and antifungal activity against *Staphylococcus Aureus*, *Staphylococcus Albus*, *Escherichia Coli*, and *Aspergillus Niger*, *Alternaria Alternate* strains respectively. The metal complexes exhibited moderate to significant biological activities against the same. Based on the analytical data and spectral analysis, the structure of the complexes has also been proposed.

KEYWORDS

Schiff base;
Metal complexes;
Antibacterial activity;
Antifungal activity.

INTRODUCTION

Schiff base and their metal complexes have aroused considerable research interest for several decades[1-4]. In Schiff base, azomethine nitrogen and other donor atoms like sulfur play a vital role in coordination chemistry. Schiff bases are condensation products of primary amines and aldehydes, represent novel intermediates in organic synthesis with various applications in synthetic chemistry. These novel compouds act as valuable ligands whose biological activity has shown to be increased on complexation. Schiff bases also resemble their structural similarities with natural biological substances, which import in elucidating the mechanistic pathway of rasemination and transformation reactions in biological systems[6].

Dithiocarbazate, NH_2NHCS_2, its substituted derivatives and Schiff bases derived from them through condensation with various aldehydes and ketones show enormous biological properties[7-9]. Metal complexes of Schiff bases derived from *S*-alkyl dithiocarbazate are found to be biologically active exhibiting antibacterial[10], antifungal[11] and antitumour[12] activities. Literature survey reveals that Schiff base containing polyfunctional groups can coordinate with transition metal ions[13,14]. Several transition metal complexes are also screened for cytotoxic activity[15]. The potential biological and theurapeutic properties of these ligands and their metal complexes have been correlated with the chemical nature of the moieties attached to the C=S or C=N car-

bon atom of the ligand. Moreover, interesting biological properties are associated with thiol-thione tautomerism of ligands involved in the formation of metal complexes[16-19].

To study the effect of complexation of Schiff base of p-dimethylamino cinnamaldehyde with *S*-alkyldithiocarbazate on bioactivity, and to understand structure-bioactivity relationship, a few chelate complexes have been prepared, characterized by various physicochemical and spectral techniques for structure determination, and their antibacterial and antifungal activities have been measured against some bacteria and fungi.

EXPERIMENTAL

Materials

All the Chemicals used in this investigation were analytical reagent grade and used without further purification. Ethanol, DMSO and DMF were use as solvent.

Preparation of the ligand (Hpdacsme)

An alcoholic solution of *S*-methyldithiocarbazate (10 mmol in 20 mL of ethanol) was added to the solution of p-dimethylaminocinnamaldehyde (10 mmol in 20 mL of ethanol), with constant stirring and resultant solution mixture was refluxed on a steam bath for 2 hours. The progress of reaction was monitored on TLC. After the completion of the reaction, the content of the flask was concentrated under vacuum. The product was separated, collected by suction filtration, washed with ethanol and recrystallised in ethanol. The light yellow crystals were dried over silica gel.

Yield; 1.9 gm (68%)

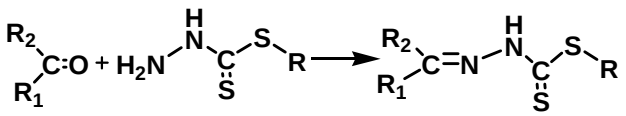
M. P.; 182°C.

Anal (%) Found: C 59.6, H 6.2, N 14.8, S 23.2 %.

Calculated for $C_{13}H_{17}N_3S_2$:C 60.0, H 6.1, N 15.1; S 23.0 %.

Synthesis of the Complexes [M(pdacsme)$_2$] (M=Cu, Ni)

The alcoholic solution of Schiff base (2 mmol in 15 mL of ethanol) was added slowly to $Cu(CH_3COO)_2$ solution (1 mmol in 15 mL of ethanol) with constant stirring. After refluxing for 3 h, the resulting solution was cooled in an ice bath and the product was filtered, washed with ethanol and dried in desiccator over silica gel. The colored solid obtained was soluble in organic solvents like DMSO and DMF.



Where, R= CH_3, R_1= $C_{11}H_{12}N$ and R_2=H.

Similar experimentation was carried out for synthesis of Ni(II) complex. Alcoholic solution of Schiff base (2 mmol in 15 mL of ethanol) was added slowly to $Ni(CH_3COO)_2$ solution (1 mmol in 15 mL of ethanol), the resulting solution mixture was refluxed for 3 h, cooled in ice bath, filtered, washed with ethanol and dried over silica gel. The product was soluble in DMSO and DMF.

$$M(CH_3COO)_2 + 2L \xrightarrow[\text{heat and reflux}]{\text{Ethanol}} [M(L)_2]$$

(M = Ni and Cu) (L = Hpdacsme)

Synthesis of the complexes [Cu(pdacsme)Cl$_2$]

The Schiff base solution (1 mmol in 15 mL of ethanol) was added slowly to metal salt solution (1 mmol of $CuCl_2$ in 15 mL of ethanol). After refluxing for 4 h, the mixture was cooled in an ice bath and the product was filtered off, washed with ethanol and dried in desiccator over silica gel. The resulting colored solid product was solubile in organic solvents, like DMSO and DMF.

$$CuCl_2 + L \xrightarrow{\text{Ethanol/ }\Delta} [Cu(L)Cl_2]$$

(L = Hpdacsme)

The spectra and analytical data of the ligand and complexes are shown in TABLE 1, 2 and 3.

Analysis and instrumentation

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 4000-400cm^{-1} region. Electronic absorption spectra were obtained on a Schimadzu UV 2400 PC Series, using dimethylsulphoxide solution in the 200-800 nm region. The ^{1}H-NMR spectral analysis were performed on a Bruker Avance 400 MHz spectrophotometer using deuterated solvents and TMS as an standard. Room temperature magnetic susceptibility was carried out on a Faraday type balance (Cahn-elec-

tronic balance 75570) using catena-tetrathiocyanatocobalt(II) mercury(II), $[CoHg(SCN)_4]$ as standard. Experimental magnetic susceptibility (χ_M) was corrected for diamagnetism using the procedure of Figgis and Lewis[20] Elemental analyses (C, H, 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 298K using Decibel DB1011 at room temperature. Purity of the compounds was ascertained by TLC using silica gel-G.

Biology

All newly synthesized complexes were biologically evaluated for their invitro antibacterial and antifungal activities against *S. Aureus*, *S. Albus*, *E. Coli*, and *A. Niger*, *A. Alternate* strains respectively. The invitro screening in present investigation were performed by Disk diffusion method[21]. Disks measuring 5.60 mm in radial diameter were punched from Whatmann no.1 filter paper.

Disks were dispensed to each screw-caped glass aliquot and sterilized by application of dry heat at 135 °C for a period of 45 minutes. The testing were carried out in DMSO at a concentration of 30µg/mL for antibacterial screening. Disks were placed in nutrient agar medium seeded with fresh bacterial culture separately. The incubation was carried out at 37 °C for 24 hours. Ofloxacin was used as the standard drug. The results are summarized in TABLE4.

The testing for antifungal screening was carried out at 50µg/mL. Disks were placed in Mueller-Hinton agar media seeded with fresh fungal culture separately. The incubation was carried out at 37 °C for 48 hours. Amphotericin B disks were used as a standard. The results are summarized in TABLE5.

RESULTS AND DISCUSSION

All the metal complexes were colored and stable in air. The elemental analyses results and physical properties of the ligand and its metal complexes are listed in TABLE1. The Schiff base Hpdcasme (Schiff base p-dimethylaminocinnamaldehyde with *S*-methyldithocarbazate) reacts readily with nickel(II) and copper(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 $[Cu(pdacsme)Cl_2]$ were obtained, whereas in the presence of a weakly coordination ion such as acetate ion, bis-ligand complexes of formula, $[M(pdacsme)_2]$ resulted. The molar conductance of the complexes in DMF, indicate that they are essentially non-electrolyte in this solvent[22]. The non-electrolytic nature of the complexes indicates that the ligand is coordinated as a uninegatively charged anion.

The p-dimethylaminocinnamaldehyde Schiff base of S-methyl dithiocarbazate has the –N(H)C(S) (thioamide) functional group and therefore, it can exhibit thione (Figure1a) and thiol (Figure 1b) tautomerism. However, its IR Spectrum in KBr does not exhibit any ν(S-H) band at approximately 2700 cm^{-1}, but displays a medium intensity band at 2859 cm^{-1} attributable

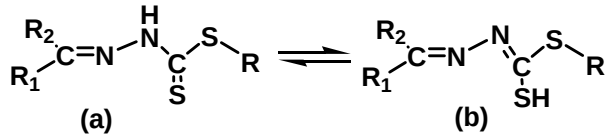
TABLE 1 : Analytical data and other physical properties of the ligand and metal complexes

Entry	Ligand/ Complexes	Color	m.p. (°C)	Elemental analysis found (calculated)			
				C	H	N	S
1.	Hpdacsme	Red	143	57.7 (57.8)	5.84 (5.6)	14.4 (14.1)	22.0 (22.1)
2.	$[Cu(pdacsme)Cl_2]$	Green	198	39.5 (39.8)	4.0 (4.1)	9.8 (10.1)	15.0 (15.5)
3.	$[Ni(pdacsme)_2]$	Brown	195	52.6 (52.1)	5.01 (5.2)	13.15 (13.7)	20.04 (20.0)
4.	$[Cu(pdacsme)_2]$	Brown	205	52.25 (52.3)	4.97 (5.0)	13.06 (13.5)	19.90 (20.1)

TABLE 2 : Infra red (cm^{-1}), molar conductivity and magnetic moments of ligand and metal complexes

Entry	Ligand/ complexes	ν(C=N) (cm^{-1})	ν(N-N) (cm^{-1})	ν(N-H) (cm^{-1})	ν(C=S) (cm^{-1})	ν(C-S) (cm^{-1})	Molar Conductance ($ohm^{-1}cm^2mol^{-1}$)	Effective magnetic moment (BM)
1.	Hpdacsme	1604 (m)	1022 (m)	2859 (w)	1226 (m)	677 (m)	-----	-----
2.	$[Cu(pdacsme)Cl_2]$	1572 (m)	1066 (m)	2810 (w)	1195 (m)	672 (m)	9.1	1.81
3.	$[Ni(pdacsme)_2]$	1589 (s)	1065 (s)	-----	-----	676 (m)	7.2	Zero
4.	$[Cu(pdacsme)_2]$	1570 (m)	1068 (m)	-----	-----	675 (m)	5.9	1.79

Where w= weak, m= medium, s=strong; Hpdacsme anionic form of the Schiff base of *S*-methyldithiocarbazate with p-dimethylaminocinnamaldehyde, Molar conductance of 10^{-3} M solutions in DMF (ohm^{-1} cm^2 mol^{-1})



Where, R= CH_3, R_1= $C_{11}H_{12}N$ and R_2=H

Figure 1 : Tautomeric forms: (a) thione form and (b) thiol form of Schiff base ligand

to the ν(N-H) of the thione form. This observation strongly support the existence and prominence of thione tautomer in polar protic solvent (ethanol). But when it is dissolved in ethanol and added to alcoholic solutions of metal acetates ($Ni(CH_3COO)_2$ and $Cu(CH_3COO)_2$), it quickly converts to the thiol form with the concomitant formation of a $[ML_2]$ complexes ($[Ni(pdacsme)_2]$ and $[Cu(pdacsme)_2]$) of the deprotonated thiol form of the Schiff base.

The coordination sites of the ligand have been determined by a careful comparison of the IR pectra of the $[ML_2]$ complexes with that of the parent ligand. A broad and weak band observed in IR spectra of ligand at 2859 cm^{-1}, attributable to ν(N-H), was disappeared in the spectra of the complexes, indicating the ligand is coordinated in its deprotonated form. Literature survey reveals the 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 higher to lower wave numbers in the spectra of metal[23]. However, shifting of this band to both lower[23,24] and higher[24,25] wave numbers have been reported[26]. Since the ν(C=N) band is expected to couple with other bands, the shifting of this band is dependent on the extent of combination with other bands. In the IR spectra of the present complexes, the ν(C=N) band at 1604 cm^{-1} in the free ligand shifts to negative frequency on complexation suggesting coordination via the azomethine group[27]. Also the sharp.C=S) band at 1226 cm^{-1} of the ligand was not observed in the metal complexes, suggesting coordination through the thiol sulfur with metal ions. In case of $[CuLCl_2]$ complex, a sharp band at 1195 cm^{-1} due to ν(C=S) and a broad weak band at 2810 cm^{-1} due to ν(N-H) have been appeared, indicating coordination of Cu(II) with thione sulfur.

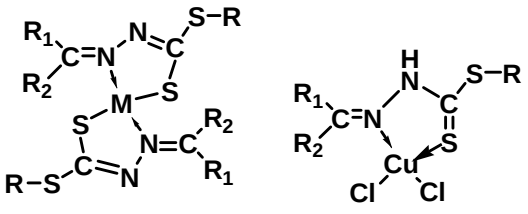
The proton NMR of ligand and its metal complexes were recorded using DMSO-d_6 solvent and TMS as an internal standard. The assignment of protons is summarized in TABLE-3. Spectrum of Schiff bases does not show any signal at 4.0 ppm due to the –SH proton, indicating that in DMSO-d_6, the Schiff bases exists in thione form. Thiosemicarbazones, which are closely related to Hpdacsme, have been found to coordinate to metal ions in both the protonated thione form[28] and the deprotonated thiolate form[29]. There are several examples of metal complexes in which both the protonated thione and the deprotonated thiol forms of a thiosemicarbazone ligand are present in the same complex[30,31]. However Schiff bases derived from *S*-alkyl esters of dithiocarbazic acid invariably deprotonated while coordinating with metal ions yielding complexes containing only the thiol form of the ligand.

Electronic spectral data of the ligand and complexes are given in TABLE 3. The spectral data of Schiff base exhibit a band in the 382-391 nm range, due to the π-π* transition within the azomethine group, affected by the intramolecular charge transfer within the ligand molecule. The electronic spectra of Ni(II) complex show two bands at 449 and 515 corresponding to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions, characteristics of square planar Ni(II) configuration [32]. The electronic spectra of $[Cu(pdacsme)_2]$ and $[Cu(pdacsbz)Cl_2]$ show intense bands at 427 and 429 nm respectively corresponding

TABLE 3 : NMR and UV-Vis spectral data of the ligand and metal complexes

Entry	Ligand/ Complexes	Chemical shifts			UV-vis (nm)
		δ –NH	δ- SCH_3	Ar-H	
1.	Hpdacsme	s,12.01	s, 2.56	m, 6.7-7.3	382-391
2.	$[Cu(pdacsme)Cl_2]$	s,12.02	s, 2.58	m, 6.6-7.0	429
3.	$[Ni(pdacsme)_2]$	-----	s, 2.61	m, 6.9-7.2	449, 515
4.	$[Cu(pdacsme)_2]$	-----	2.61 s	6.7-7.2 m	427

Hpdacsme anionic form of the schiff base of S-methyldithiocarbazate with p-dimethylaminocinnamaldehyde



M= Cu, Ni

(a) (b)

Where, R= CH_3, R_1= $C_{11}H_{12}N$ and R_2=H

Figure 2 : Proposed structures of the metal complexes

to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, suggesting square planar geometry of Cu(II) complexes[32]. The observed magnetic moment of [Ni(pdacsme)$_2$] complex indicates it is diamagnetic in nature, which is in consistence with its square planar geometry found in electronic spectra of the complex. In case of [Cu(pdacsme)$_2$] and [Cu(pdacsbz)Cl$_2$] complexes, the χ_{eff} have been found to be 1.79 and 1.81 BM respectively, suggesting square planar geometry around Cu(II) ions(TABLE 2)[33].

From the present observations, the proposed chemical structures for the prepared Schiff base complexes under investigation are shown in Figure 2a and 2b.

ANTIMICROBIAL SCREENING

In order to study the effect of metal chelates on microorganism like fungi, bacteria, virus etc, it is obligatory to understand the cellular structure, cellular composition, and cellular mechanism of a cell. A living cell is a biounit which is self-contained, self-perpetuating, self-assembling and self-adjusting isothermal system of organic molecules which regulates energy dynamics inside the cell[34]. Cell wall of microorganism exhibits porosities through which hydrated metal ions are unable to pass through due to inheritant lipophobocity. However, due to chelate formation, lipophilicity increases markedly and rendering the easy passage of chelates through cell walls, due to matching structural attachment with the cell[8,35].

Invitro antibacterial screening

Antibacterial activity of the synthesized compounds were screened against bacteria's samples *S. Aureus, S. Albus* and *E. Coli* using agar plate disc diffusion technique. The testing was carried out in dimethylsulphoxide solution at a concentration of 30µg/mL. Ofloxacin was used as the standard drug. Results are incorporated in TABLE 4.

It has been observed that the [Ni(pdacsme)$_2$] chelate complex exhibit higher zone on inhibition (10-12 mm) than the title ligand against the *S. Aureus* and *E. Coli*. The inhibitory effect of [Cu(pdacsme)$_2$] is comparable to standard drug Ofloxacin. In general the [ML$_2$] chelate complexes are more active than [MLCl$_2$] complex under identical conditions. The antibacterial activity can be ordered as [CuLCl$_2$] < [NiL$_2$] < [CuL$_2$].

TABLE 4 : Antibacterial activity of the ligand and metal complexes

Entry	Ligand/ Complexes	Zone of Inhibition (mm)		
		S. Aureus	*S. Albus*	*E.Coli*
1.	Hpdacsme	++	+	++
2.	[Cu(pdacsme)Cl$_2$]	—	+	—
3.	[Ni(pdacsme)$_2$]	+++	—	+++
4.	[Cu(pdacsme)$_2$]	++++	—	++++
5.	Ofloxacin (std.)	++++	++++	++++

Diameter of zone of inhibition; (+) 6-8 mm; (++) 8-10 mm; (+++) 10-12 mm; (++++) 12-14 mm; (—) no activity

Although several factors govern the toxicity of bacteria and fungi, chelation is known to be an important factor for microbial toxicity[36]. Amongst the compounds under study, [Cu(pdacsme)$_2$] and [Ni(pdacsme)$_2$] exhibit greater antibacterial than [Cu(pdacsbz)Cl$_2$] probably due to higher order of chelation.

Metal complexes of large organic molecules like one under study here, surrounded by *S*-alkyldithiocarbazte, are acceptable to cell wall possibly due to lipophilicity to the cell wall, thus the metal ions inter inside the cell and releases metal ions and therefore cause resulting toxic effect. Structure of metal complex is equally important if it gives matching cone and socket or key-lock type structural attachment with the cell structure. The compounds under investigation possibly have the suitable structural arrangements which are adopted/accepted by host cells and therefore migrate inside the cell, causing net toxic effect.

Invitro antifungal activities

The new products were screened for antifungal activity against *Aspergillus Niger* and *Alternaria Aalternata* using Mueller-Hinton agar media. The testing were carried out in dimethylsulphoxide solution at a concentration of 50µg/mL. Amphotericin B disks were used as the standard drugs. Schiff base, [Cu(pdacsme)Cl$_2$] and [Cu(pdacsme)$_2$] have also shown significant activity against Aspergillus niger species. Results are incorporated in TABLE5.

As the data indicate, the Cu(II) complexes show better fungicidal activity against *A. Niger* than the corresponding Ni(II) complex. Fungitoxicity of Cu(II) complexes are comparable to that of standard drug Amphotericin-B against *A. Niger*. Ni(II) chelate complex show better antifungal activity than Cu(II) complexes

TABLE 5 : Anti-fungal activity of the ligand and metal complexes

Entry	Ligand/ Complexes	Zone of inhibition (mm)	
		A. Niger	*A. Alternate*
1.	Hpdacsme	++	—
2.	[Cu(pdacsme)Cl_2	++	—
3.	[Ni(pdacsme)$_2$]	+	+
4.	[Cu(pdacsme)$_2$]	++	—
5.	Amphotericin-B (std.)	++	++

Diameter of zone of inhibition; (+) 8-12 mm; (++) 12-16 mm; (—) No inhibition

against *A. Alternate*, however the activity is lesser than the standard drug.

ACKNOWLEDGEMENTS

The authors are thankful to RSIC Department IITB, Mumbai and DRDE, Gwalior for providing spectral facilities. We are also grateful to Director CDRI, Lucknow for elemental analyses and Cancer Hospital and Research Institute, Gwalior for biological activities.

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