

Synthesis and Characterization of Some Metal Complexes of Cu(II), Ni(II), Zn(II), Cd(II), Sn(II), Co(II), Sb(III) AND Fe(III) Containing Bidentate Schiff Base of Smdtc

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Abstract: A series of transition metal complexes of Cu(II), Ni(III) Zn(II), Cd(II), Co(II), Sb(III) and Fe(III)Containing Bidentate Schiff base, [*N*'-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester] derived from the condensation of S-methylthiocarbamate and P-chlorobenzaldehyde were synthesized and characterized by IR, UV- Vis., and some physical measurements. IR spectral studies show the binding sites of the Schiff base ligand with the metal ion. Molar conductance data and magnetic susceptibility measurements give evidence for monomeric and neutral nature of the complexes.

Keywords: Transition Metal Complex, SMDTC, P-chlorobenzaldehyde, Schiff Base

1. Introduction

The Chemistry of Schiff-base complexes has attracted a great deal of attention ever since Pfeiffer carried out his pioneering research in the 1930's. The Schiff-base ligands are derived by the condensation of a primary amine and an active carbonyl group, and contain the azomethine group ($-\text{CH}=\text{N}-$ or $>\text{C}=\text{N}-$). These bases can be effective chelating agents in either the carbonyl compound as the amine or both contain potentially coordinating functional groups near the site of condensation. Schiff-bases may act as mono-, di-, tri-, or tetradentate ligands depending on the number of coordinating atoms present in the molecule and can form generally five or six membered chelate rings upon reaction with a metal ion. Among many schiff-bases the dithiocarbamate (NH_2NHCS_2) and its substituted derivatives have been investigated as ligand for a long time too [1-5]. These compounds have received much attention for further studies because i) they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic substituents, thereby causing a variation of ultimate donor properties (ii) the interaction of these donor to metal ions gives complexes of different geometries and properties and (iii) these complexes are potentially biologically active [6-9].

Recently, we studied few mixed ligand complexes containing heterocyclic amine as secondary ligands and few Schiff base containing complexes [10-19]. In this paper, we describe synthesis of a Schiff base [*N*'-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester], formed by condensing cinnamaldehyde with S-methylthiocarbamate and its complexation with Mn(II), Fe(III) Co(II), Ni(II), Cu(II) and Sb(III).

2. Experimental

2.1. Reagents and Chemicals

All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to standard procedures.

2.2. Physical Measurements

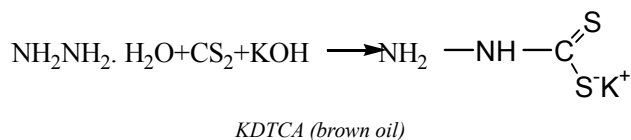
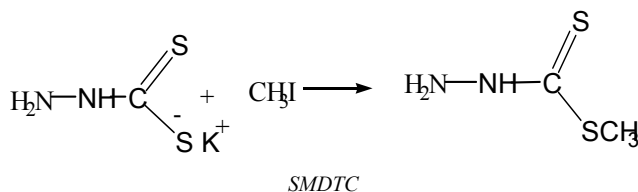
The melting or decomposition temperatures of all the prepared metal complexes were observed in an electro thermal melting point apparatus model No.AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared spectra as KBr disc were recorded in a SIMADZU FTIR-8400 (Japan)

infrared spectrophotometer, from 4000-400 cm^{-1} . The absorbances of the complexes were recorded on SHIMADZU Spectrophotometer.

3. Preparation

3.1. Preparation of the Ligand *S*-Methyldithiocarbazate (SMDTC): Reaction

Procedure: SMDTC was prepared by the method of Akbar Ali [3].



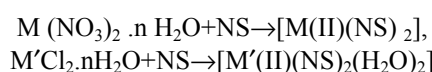
3.2. Preparation of the *P*-chlorobenzaldehyde Schiff base of SMDTC, [N^I-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester] (NS)

SMDTC (1.22 g, 10 mmol) was dissolved in hot absolute ethanol (30-40 ml). To this solution the equimolar amount of *P*-chlorobenzaldehyde in hot absolute ethanol (20 ml) was added and the mixture was heated for 20 min and then cooled. The White precipitate, which has formed was separated and

dried in *vacuo* over anhydrous CaCl_2 . (m.p. 152°C).

3.3. General Method for the Preparation of the Complexes with [N^I-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester] (NS)

Metal salt with hydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}]$ (0.241 g, 1 mmol); $[\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}]$ (0.290 g, 1 mmol); $[\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}]$ (0.297 g, 1 mmol); $[\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}]$ (0.238 g 1 mmol) was dissolved in absolute ethanol (15 ml). The Schiff base, [N^I-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester] (0.24477 g, 1 mmol) in hot absolute ethanol (50 ml) was added to the metal solution. The mixture was then refluxed for 30 mins and then cooled. The precipitate was filtered off and washed with hot ethanol and dried in *vacuo* over anhydrous CaCl_2 .



Where, M = Cu(II), Ni(II) and Zn(II); M' = Co(II), NS' = *P*-Chlorobenzaldehyde Schiff base of SMDTC.

4. Results and Discussion

4.1. Physical Properties and Molar Conductance

Physical properties of the complexes were given in Table 1. The analytical data were in good agreement with the proposed empirical formula of the present complexes. The conductance values of the complexes reveal that these were non electrolyte in nature [3].

Table 1. Analytical data and physical properties of the complexes.

Complexes	Colour	Melting point or decomposition temperature ($\pm 5^\circ\text{C}$)	Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (B.M)
SMDTC	White	81	2.45	-
[NS]	White	152	2.25	-
$[\text{Cu}(\text{II})(\text{NS})_2]$	Greenish brown	188	3.28	1.98
$[\text{Ni}(\text{II})(\text{NS})_2]$	Golden brown	240	5.19	Dia
$[\text{Zn}(\text{II})(\text{NS})_2]$	Light yellow	218	3.58	Dia
$[\text{Co}(\text{II})(\text{NS})_2(\text{H}_2\text{O})_2]$	Reddish black	220	2.50	3.94

Where, NS = [N^I-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester]

4.2. IR Studies

SMDTC showed all the characteristic bands as reported in the literature [3, 19]. The IR spectrum of SMDTC (Table 2) showed strong intensity bands at 3415 cm^{-1} and 3262 cm^{-1} which were assigned to the asymmetric $\nu(\text{N-H})$ and symmetric $\nu(\text{N-H})$ modes of the NH_2 group, respectively. The $\nu(\text{C=S})$ band for SMDTC appeared at 1006 cm^{-1} . SMDTC had a proton adjacent to the thione group. The thione group was relatively unstable in the monomeric form and tends to turn to the more stable C-S bond by enethiolisation if there was at least one proton adjacent to the thione group. The IR spectrum of Schiff bases did not display $\nu(\text{S-H})$ bands at around 2570 cm^{-1} indicating that in the solid state it remained

in the thioketo forms. However, in solution, both the thion and thiole tautomeric forms are possible. In alkaline medium, the ligand deprotonates by the loss of the proton from the sec. NH group appearance of $\nu(\text{C=N})$ and disappearance of $\nu(\text{N-H})$ will indicate deprotonation. This will be further evident from the absence of $\nu(\text{C=S})$ in the complexes. The Schiff-base exist in tautomeric forms through the loss of thio protons. Schiff base behaved as uninegatively charged bidentate ligands by co-ordinating through the thiole sulfur and the azomethine nitrogen.

The IR spectrum (Table 2) of the Schiff base showed strong bands at 3106 cm^{-1} . This was attributed to the secondary amine $\nu(\text{N-H})$ mode of the free ligands. The thione groups are

relatively unstable in the monomeric form and tend to turn to the more stable thiol form by enethiolization in solution. The absence of $\nu(\text{S-H})$ absorbance at approximately 2570 cm^{-1} indicates that in the solid state, the bases exist primarily in the thione form. The disappearance of $\nu(\text{N-H})$ bands in the spectra of the metal complexes suggests deprotonation and consequent co-ordination through the thiolate anions. The Schiff base also showed strong bands at 1596 cm^{-1} . These are assigned to the $\nu(\text{C=N})$ modes for the free ligand. In the metal complexes, this stretching band shifted to lower frequencies, due to the lowering of the C=N bond order as a result of the metal-nitrogen bond formation. The Schiff base also showed $\nu(\text{C=S})$ modes at 1038 cm^{-1} . The $\nu(\text{C=S})$ mode observed in the free ligand disappeared in the complexes, thus supporting the above contention of thiolate bonding with metal ions. Consequently the $\nu(\text{C-S})$ mode was observed in the spectra of the complexes supporting thiolate bindings.

Table 2. Selected infrared spectral bands of the ligands and metal complexes.

Complexes	$\nu(\text{NH}_2)$ cm^{-1}	$\nu(\text{N-H})$ cm^{-1}	$\nu(\text{C=S})$ cm^{-1}	$\nu(\text{C=N})$ cm^{-1}	$\nu(\text{C-S})$ cm^{-1}	$\nu(\text{M-S})$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}	$\nu(\text{OH})$ cm^{-1}
SMDTC	3415 3262	3154	1006	-	-	-	-	-
[NS]	-	3106	1038	1596	-	-	-	-
[Cu(II)(NS) ₂]	-	-	-	1584	603	360	405	-
[Ni(II)(NS) ₂]	-	-	-	1478	612	401	484	-
[Zn(II)(NS) ₂]	-	-	-	1519	617	395	455	-
[Co(II)(NS) ₂ (H ₂ O) ₂]	-	-	-	1581	604	414	492	3414

Where, NS = [*N'*-(4-chloro-benzylidene)-hydrazecarbo-dithioic acid methyl ester]

4.3. Magnetic Moment and Electronic Spectra

The magnetic susceptibility measurement (Table 1) showed that the complex [Cu(II)(NS)₂] was paramagnetic. The greenish brown paramagnetic copper complex gave a magnetic moment of 1.98 B.M corresponding to one unpaired electron. The UV-vis spectrum, of the complex showed d-d-bands at 420 nm and 325 nm, arising from the $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ and $^2\text{B}_{1g} \rightarrow ^2\text{E}_{1g}$ transitions, respectively, characteristic of a square planer stereochemistry. The intense band at 220 nm was presumably caused by charge transfer.

The magnetic susceptibility measurement (Table 1) showed that the complex [Ni(II)(NS)₂] was diamagnetic. For the electronic spectra, the diamagnetic nature of complex indicated a singlet ground state characteristic of square planer Ni(II). Three bands corresponding to the transitions $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ (300 nm), $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ (350 nm) and $^1\text{A}_{1g} \rightarrow ^1\text{E}_g$ (400 nm) were observed in the electronic spectra of a square-planer nickel(II) complex as expected.

Table 3. Selected electronic spectral data of the complexes.

Complexes	Band I	Band II	Band III
[Cu(II)(NS) ₂]	220	325	420
[Ni(II)(NS) ₂]	300	350	400
[Zn(II)(NS) ₂]	320	-	-
[Co(II)(NS) ₂ (H ₂ O) ₂]	390	430	560

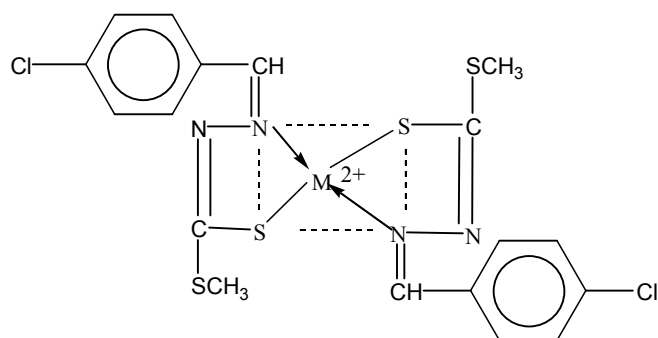
Where, NS = [*N'*-(4-chloro-benzylidene)-hydrazecarbo-dithioic acid methyl ester]

The C=N stretching vibration in the free NS Schiff base appeared at 1586 cm^{-1} , which upon complexation, shifted towards lower frequency regions, at 1584 cm^{-1} (Table 2). This lowering of C=N stretching mode on complexation supported coordination through nitrogen atom. The mode of the free Schiff base appeared at 1038 cm^{-1} . This band also disappeared in the IR spectra of the metal complexes giving evidence of coordination-through the thiolate anion. The Schiff base coordinated to the metal through the thiolate sulphur and the p-nitrogen as evident from the IR spectrum showing bands at 360 cm^{-1} and 405 cm^{-1} , corresponding to $\nu(\text{M-S})$ and $\nu(\text{M-N})$ stretching modes, respectively. In case of complexes [Ni(II)(NS)₂] and [Zn(NS)₂], the IR band at 1573 and 1583 cm^{-1} was indicated of the presence of coordinated C=N bond. The bond stretching vibration 3414 cm^{-1} for Co(II) complex was indicated the presence of coordinated water molecule.

The cobalt complex [Co(II)(NS)₂(H₂O)₂] showed magnetic moments at 3.94 B.M (Table 1) indicative of octahedral geometry. The electronic spectra of these complexes showed three bands 390, 430 and 560 nm (Table: 4.3). This bands were assigned to the transition, $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ (ν_1), $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$ (ν_2), $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ (F) (ν_3), of octahedral Co(II). The complex [Zn(II)(NS)₂] showed absorption bands at 320 nm arising from charge transfer transitions. The magnetic susceptibility measurement showed that the complex was diamagnetic in nature. The complex was found to be distorted tetrahedral in geometry. All the above observations indicated that the complexes [Cu(II)(NS)₂] and [Ni(II)(NS)₂] had square planar structure with two ligands satisfying the four stereochemical sites, where the complexes [Zn(II)(NS)₂] was distorted tetrahedral.

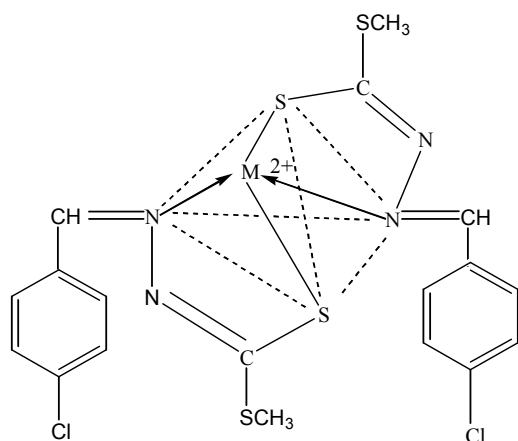
5. Structure of the Complexes

On the basis of the elemental analysis, conductivity measurements, magnetic moment data, spectroscopic studies and literature review the possible structure of the complexes.



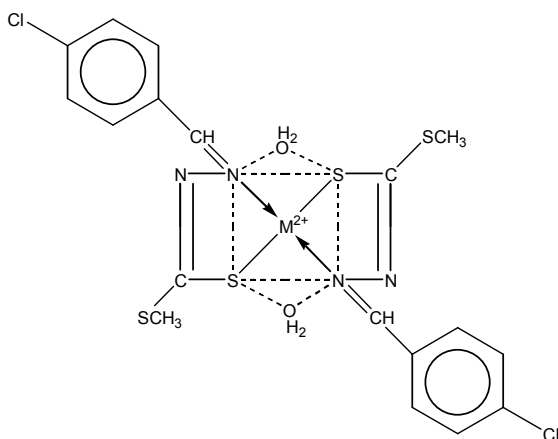
Where, $M^{2+} = \text{Cu(II)}$ and Ni(II)

Fig. 1. Proposed square planar structure of the complex.



Where, $M^{2+} = \text{Zn(II)}$ and Cd(II)

Fig. 2. Proposed tetrahedral structure of the complex.



Where, $M^{2+} = \text{Co(II)}$

Fig. 3. Proposed octahedral structure.

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