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Synthesis, Characteristics, and Antimicrobial Activity of Some Complexes of Mn(II), Fe(III) Co(II), Ni(II), Cu(II), and Sb(III) Containing Bidentate Schiff Base of SMDTC[1]

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Abstract—A novel series of transition metal complexes of Mn(II), Fe(III) Co(II), Ni(II), Cu(II), and Sb(III) containing the bidentate Schiff base derived from condensation of *S*-methyldithiocarbazate and cinnamaldehyde were synthesized and characterized by IR, ^{1}H NMR, UV-Vis, and some physical measurements. IR spectral studies indicated the binding sites of the Schiff base ligand with the metal ions. Molar conductance data and magnetic susceptibility measurements indicated monomeric and neutral nature of the complexes. The complexes demonstrated moderate to strong antimicrobial activity.

Keywords: transition metal complex, SMDTC, antimicrobial activity, Schiff base

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INTRODUCTION

The classical synthesis of Schiff bases [1] is a primary amine condensation with a carbonyl compound [2] under specific conditions. Cinnamaldehyde is the main component of bark extract of cinnamon [3]. It is active against a range of forborne pathogens bacteria [4]. Nontoxic doses of cinnamaldehyde and its derivatives have been reported to potentiate the cell-inactivating effect of cis- diaminodichloroplatinum(II) in human NHIK 3025 cells culture [5]. Nowadays, the increasing microbial resistance to antibiotics in use necessitates the search for new compounds with potential effects against pathogenic bacteria. The nitro group and halogen containing Schiff bases demonstrated such activities as antimicrobial, antitumor [6] and antifungal [7].

The Schiff bases, namely dithiocarbazate NH_2NHCS_2 (DTC) substituted derivatives, have been synthesized and studied over recent decades [8–18] for the following major reasons: (1) they provide interesting series of ligands whose properties can be modified by introducing organic substituents, thereby causing a variation in the ultimate donor properties, (2) the interaction of such donors with metal ions give complexes of different structures and properties, and (3) the complexes are potentially biologically active.

Previously, we had synthesized few complexes of such type and studied their antimicrobial activity [19–22]. In this paper we present synthesis of a Schiff base formed by condensation of cinnamaldehyde with S-methyldithiocarbazate, its complexation with Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Sb(III) and antimicrobial activity of the complexes.

EXPERIMENTAL

Reagents and chemicals. All the reagents used were of analytical or chemical grade purity. Solvents were purified and dried according to the standard procedures.

Physical measurements. Melting points of all metal complexes were measured by an electro thermal melting point apparatus model no. AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present study. Infrared spectra (KBr) were recorded in a SIMADZU FTIR-8400 (Japan) spectrophotometer in the range 4000–400 cm^{-1}.

Procedure. SMDTC was prepared in accordance with the method of Akbar Ali [23].

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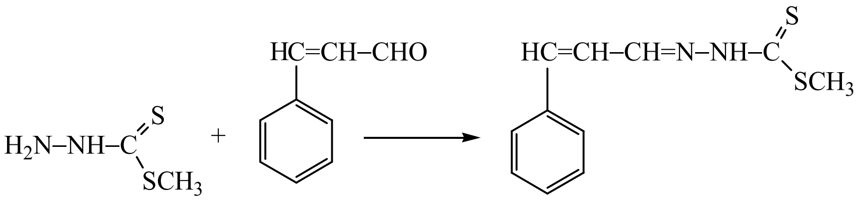
[1] The text was submitted by the authors in English.

Scheme 1.


Schiff base (NS)

Preparation of the cinnamaldehyde Schiff base of SMDTC. To the solution of SMDTC (0.122 mol) in hot absolute ethanol (35 mL) a solution of the equimolar amount of cinnamaldehyde in hot absolute ethanol (20 mL) was added and the mixture was heated for 20 min. Upon cooling down the orange precipitate was formed. It was separated and dried in vacuo over anhydrous $CaCl_2$ (Scheme 1).

General method for preparation of the complexes of cinnamaldehyde Schiff base of SMDTC. 1 mmol of either hydrated salt [$Mn(NO_3)_2\cdot 6H_2O$], [$Cucl_2\cdot 6H_2O$], [$Ni(NO_3)_2\cdot 6H_2O$], [$CoCl_2\cdot 6H_2O$], [$Sb(NO_3)_3\cdot 3H_2O$], or [$Fe(NO_3)_3\cdot 9H_2O$] was dissolved in absolute ethanol (15 mL). The Schiff base (NS) (2 mmol) solution in hot absolute ethanol (50 mL) was added to a salt solution. The mixture was refluxed for 30 min and then cooled down. The precipitate was filtered off, washed with hot ethanol and dried in vacuo over anhydrous $CaCl_2$.

$$M(NO_3)_2\cdot nH_2O + NS \rightarrow [M(II)(NS)_2],$$

$$M'(NO_3)_3\cdot nH_2O + NS \rightarrow [M'(II)(NS)_2(NO_3)(H_2O)],$$

$$M''Cl_2\cdot nH_2O + NS \rightarrow [M''(II)(NS)_2(H_2O)_2],$$

where M = Mn(II), Ni(II), Cu(II); M' = Sb(III), Fe(III); M'' = Co(II), NS = Cinnamaldehyde Schiff base of SMDTC.

RESULTS AND DISCUSSION

Physical properties and molar conductance. Physical properties of the complexes are listed in Table 1. The analytical data were in good agreement with the proposed empirical formula of the complexes. The conductance values of the complexes revealed that those were non electrolytes [24].

IR spectra. IR spectra of SMDTC contained all characteristic bands that had been reported earlier [25]. IR spectra of Schiff base did not contain ν(S–H) bands (ca 2570 cm^{-1}) indicating that in the solid state it existed in the thioketo form. However, in solutions both thione and thiol tautomeric forms were possible.

According to IR spectra in alkaline media the ligand was deprotonated (loss of the proton =N$\underline{H}$) in favor of formation of the C=N bond (Fig. 1).

Based on comparison of IR spectra of free SMDTC and the corresponding complexes the former can have three modes of coordination.

Table 1. Analytical data and physical properties of the complexes

Complexes	Color	Melting point or decomposition temperature(± 5°C)	Yield, %	Molar conductance, Ω^{-1} cm^2 mol^{-1}	μ_{eff}, B.M.
SMDTC	White	81	75	9.90	–
[NS]	Orange	171	70	8.39	–
[$Mn(II)(NS)_2$]	Greenish	210	65	5.96	Dia
[$Fe(III)(NS)_2(NO_3)(H_2O)$]	Black	196	68	10.15	5.94
[$Co(II)(NS)_2(H_2O)_2$]	Reddish	223	70	3.50	3.94
[$Ni(II)(NS)_2$]	Greenish brown	261	68	6.56	Dia
[$Cu(II)(NS)_2$]	Reddish	190	58	7.83	1.86
[$Sb(III)(NS)_2(NO_3)(H_2O)$]	Cream	191	60	2.42	Dia

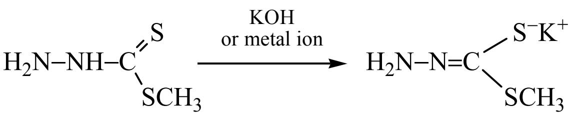


Fig. 1. Reaction of SMDTC with KOH/metal ion.

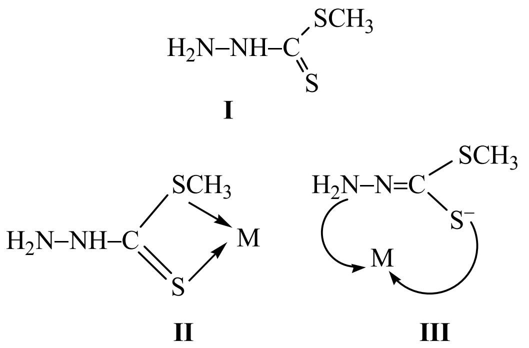


Fig. 2. Modes of coordination of SMDTC.

In neutral media condensation of SMDTC with cinnamaldehyde gave the isomeric Schiff base (NS) in high yield. The Schiff base existed in tautomeric forms through the loss of thiol protons (Fig. 3). IR spectrum of the Schiff base contained the strong band at 3113 cm^{-1} which was attributed to the secondary amine of free ligands. The thione group is relatively unstable in the monomeric form and tends to turn to the more stable thiol form by enethiolization in a solution. The absence of S–H bands at ca 2570 cm^{-1} indicated that in the solid state the base existed primarily in the thione form. Disappearance of N–H bands in the spectra of metal complexes indicated deprotonation and consequent coordination with the thiolate anions. The Schiff base spectra contained strong bands at ca 1579 cm^{-1} assigned to the C=N bond of the free ligand. In the metal complexes the band was shifted towards lower frequencies due to the lower C=N bond order and formation of the metal–nitrogen bond. The C=S band (1037 cm^{-1}) observed in spectra of the free ligand was not registered in the spectra of complexes, thus supporting the thiolate bonding with metal ions.

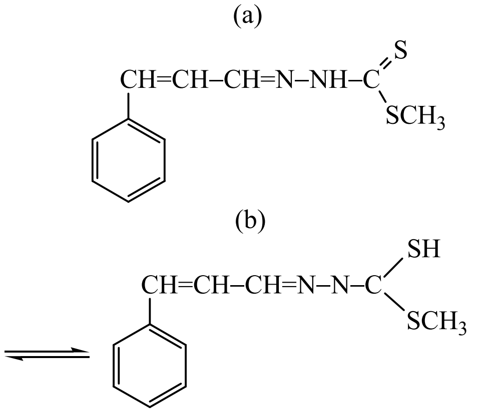


Fig. 3. Tautomeric forms of Schiff base (a) thione form and (b) thiol form.

In neutral media condensation of SMDTC with cinnamaldehyde gave the isomeric Schiff base (NS) in high yield. The Schiff base existst in tautomeric forms (Fig. 3) and acted as anionic bidentate ligand that coordinated by the thiol sulfur and the azomethine nitrogen.

The C=N bond stretching vibration in the free NS Schiff base was registered at 1579 cm^{-1}, which upon complexation, shifted towards lower frequency region (ca 1478 cm^{-1}) supporting coordination with the nitrogen atom. The free Schiff base band (1037 cm^{-1}) was not registered in the spectra of metal complexes indicating coordination with the thiolate anion.

In IR spectra of the complex $[Co(NS)_2(H_2O)_2]$ the band at 3250–3300 cm^{-1} indicated the presence of the coordinated water. The ionized NO_3 group of complexes $[Sb(NS)_2(NO_3)(H_2O)]$ and $[Fe(III)(NS)_2(NO_3)(H_2O)]$ was registered at 1458 and 1296 cm^{-1}.

Magnetic moment and electronic spectra. The magnetic susceptibility measurements (Table 1) the paramagnetic character of the complex $[Cu(II)(NS)_2]$. The greenish brown paramagnetic copper complex had the magnetic moment 1.86 B.M. (one unpaired electron). UV-Vis spectrum of the complex contained d-d bands at 640 and 420 nm ($^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions respectively), characteristic for a square planar stereostructure. The intensive band at 310 nm was attributed to the charge transfer.

The magnetic susceptibility measurements (Table 1) indicated that the complexes $[Ni(II)(NS)_2]$ and $[Mn(II)(NS)_2]$ were diamagnetic. The diamagnetic nature of complex indicated a singlet ground state characteristic for square planar Ni(II) and Mn(II).

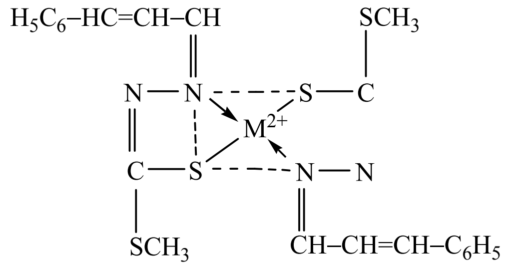


Fig. 4. Square planar structure of the complex. M^{2+} = Mn(II), Ni(II), and Cu(II)

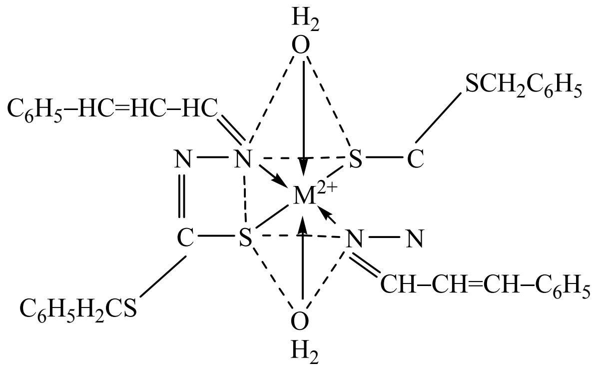


Fig. 5. Octahedral structure of M(II) complex. M^{2+} = Co(II).

Three bands of the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ (314 and 340 nm), $^1A_{1g} \rightarrow {}^1B_{1g}$ (358 and 420 nm) and $^1A_{1g} \rightarrow {}^1E_g$ (416 and 530 nm) were observed in the spectra of a square-planar Ni(II) complex.

The complex $[Co(II)(NS)_2(H_2O)_2]$ had magnetic moment about 3.94 B.M. (Table 1) that indicated its octahedral structure. The electronic spectra of the complex contained three bands at 380, 420 and 550 nm assigned to the transitions $^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$, $^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$, $^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_3)$. UV-Vis spectrum of the complex $[Sb(III)(NS)_2(NO_3)(H_2O)]$ exhibited the band at 320 nm assigned to the charge transfer transition. The complex was diamagnetic and had octahedral structure.

The magnetic moment of Fe(III) (5.96 B.M.) indicated that the complex $[Fe(III)(NS)_2(NO_3)(H_2O)]$ was paramagnetic with five unpaired electrons and hence, had octahedral structure with sp^3d^2 hybridization. The electronic spectra of the complex contained four bands at 536, 480, 410, and 390 nm assigned to the transitions $[^6A_{1g} \rightarrow {}^4T_{1g}(G); {}^6A_{1g} \rightarrow {}^4T_{2g}(G); {}^6A_{1g} \rightarrow {}^4E_g(G); {}^6A_{1g} \rightarrow {}^4A_{1g}(G)]$, respectively.

The above observations indicated that the complexes $[Cu(II)(NS)_2]$, $[Ni(II)(NS)_2]$, and $[Mn(II)(NS)_2]$ had square planar structure with two ligands. The complexes $[Co(II)(NS)_2(H_2O)_2]$, $Sb(II)(NS)_2(NO_3)(H_2O)]$, and $[Fe(III)(NS)_2(NO_3)(H_2O)]$ had octahedral structure.

^1H NMR spectra. **Complex $[Cu(II)(NS)_2]$.** 7.67–7.64 d.d (J = 8.2 Hz, 4H, Ar-H), 7.20–7.06 m (6H, Ar-H), 5.13 d (J = 12 Hz, 2H, –CH), 4.93 d (J = 8 Hz, 2H, –CH), 4.48 d.d (J = 12, 8 Hz, 2H, –CH), 2.65 s (6H, SCH_3).

Complex $[Co(II)(NS)_2(H_2O)_2]$. 7.99–7.61 d.d (J = 8.2 Hz, 4H, Ar-H), 7.59–7.43 m (6H, Ar-H), 7.27 s (4H, H_2O), 5.15 d (J = 12 Hz, 2H, –CH), 5.05 d (J = 8 Hz, 2H, –CH), 4.10 d.d (J = 12 Hz, 8 Hz, 2H, –CH), 2.76 s (6H, SCH_3).

The –OH signals were registered at low field probably due to formation of the intramolecular hydrogen bond.

Structure of the complexes. On the basis of experimental and literature data the following structures of the complexes are considered (Figs. 4–6).

Antibacterial activity of the metal complexes. Complexes of Zn(II) and Cd(II) with tridentate ONS donor Schiff base ligands were synthesized and biological activity was studied by Gunthkal et al. [26]. Wang et al. [27] have synthesized and studied the biological activity of Cu(II), Co(II), and Ni(II) complexes with thiosemicarbazones. Complexes of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with 3-aminophenol-*N*-benzylidine Schiff base ligand were synthesized and their antibacterial activity was studied

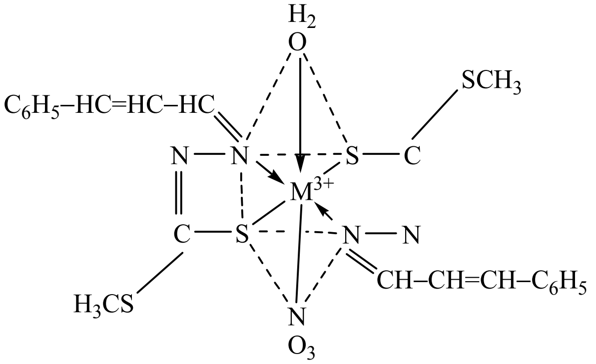


Fig. 6. Octahedral structure of the complex. M^{3+} = Fe(III) and Sb(III).

Table 2. *In vitro* antibacterial activities of the complexes and Kanamycine (K-30)

Bacteria	Gram staining	Diameter of zone inhibition, mm[a]				
		$[Mn(II)(NS)_2]$ × 100 mg/disc	$[Fe(III)(NS)_2(NO_3)(H_2O)]$ × 100 mg/disc	$[Co(II)(NS)_2(H_2O_2]$ × 100 mg/disc	$[Ni(II)(NS)_2]$ × 100 mg/disc	K-30, mg/disc
Bacillus subtilis	Positive	4	7	12	4	25
Staphlococcus aureus	Positive	7	8	6	12	24
Bacillus megatherium	Positive	6	9	5	9	26
Streptococcus-β-haemolyticus	Positive	19	10	11	9	25
Escherichia coli	Negative	15	2	12	7	20
Shigella dysenteriae	Negative	15	14	15	14	21
Shigella sonnei	Negative	4	3	16	17	22
Shigella shiga	Negative	5	16	17	13	24

[a] (SMDTC) = *S*-methyldithiocarbazate, (NS) = Cinnamaldehyde Schiff base of SMDTC.

Table 3. Antifungal activities of the complexes and standard Fluconazole

Fungal Status	Diameter of zone of inhibition, mm[a]				
	$[Mn(II)(NS)_2]$ × 100 mg/disc	$[Fe(III)(NS)_2(NO_3)(H_2O)]$ × 100 mg/disc	$[Co(II)(NS)_2(H_2O_2]$ × 100 mg/disc	$[Ni(II)(NS)_2]$ × 100 mg/disc	Fluconazole F-50, mg/disc
Aspergillus Candidus	17	7	17	10	20
Penicillium Marneffei	11	15	9	13	18
Candida Albicans	14	16	9	11	17
Aspergilius niger	14	4	11	6	17

[a] (SMDTC) = *S*-methyldithiocarbazate, (NS) = Cinnamaldehyde Schiff base of SMDTC.

by Patil and co-workers [28]. The susceptibility of microorganism to antimicrobial agents can be determined *in vitro* by a number of methods. The disc diffusion technique is widely acceptable for preliminary investigations of compounds.

The accumulated data revealed that the complexes were of higher microbial toxicity than free metal ions or ligands. The Co(II), Ni(II), Mn(II), and Fe(III) metal Schiff bases complexes (Table 2) demonstrated moderate to strong activity against both Gram positive and Gram negative bacteria compared to standard Kanamycine.

Antifungal activity of the metal complexes. The zone of inhibition indicated that all complexes of Co(II), Ni(II), Mn(II), and Fe(III) (Table 3) demonstrated significant activity towards all the fungi tested.

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