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Synthesis, Spectral Characterization and Bioactivity of Co(II), Mn(II), Fe(II) and Fe(III) Complexes of Bidentate N,S Schiff Base of S-Benzyl Dithiocarbazate with *p*-(Dimethylamino)benzaldehyde

NILESH V. JUNGHARE[1], SHRIKANT B. JAGTAP[2,*], RAHUL R. JADHAV[3] and JYOTI P. JADHAV[3]

[1]Department of Chemistry, Shri Yashwantrao Patil Science College, Solankur-416212, India
[2]Department of Chemistry, Annasaheb Magar Mahavidyalaya, Hadapsar, Pune-411028, India
[3]Department of Biotechnology, Shivaji University, Kolhapur-416004, India

*Corresponding author: E-mail: drshrikantjagtap@yahoo.com

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Metal complexes of $(ML_2)X_2$ type (X = H_2O) of Co(II), Mn(II), Fe(II) and Fe(III) (X is NO_3^- and H_2O) were synthesized using Schiff base, S-benzyl-β-N-(*p*-dimethylaminophenyl)methylene dithiocarbazate (HL), which was synthesized by the condensation of equimolar concentrations of *p*-(dimethylamino)benzaldehyde and S-benzyldithiocarbazate. The metal complexes and dithiocarbazate ligands were confirmed by elemental study and spectroscopic techniques such as ^{1}H and ^{13}C NMR, electronic absorption spectroscopy, molar conductance, infrared techniques. The magnetic susceptibility and UV-vis spectral data suggest that the metal complexes $(ML_2)X_2$ show octahedral geometry. The bioactivity of ligand and its metal complexes were investigated by the well diffusion method against one fungus (*Candida albicans*) and three pathogenic bacteria (*E. coli* and *B. cereus* and *S. aureus*). Bioactivity analysis revealed that the $(ML_2)X_2$ complex of Fe(II) and Fe(III) shows enhanced antibacterial activity than free ligand. Comparatively, among all metal complexes, the Fe(III) complex shows higher antibacterial activity and moderate antifungal activity.

Keywords: Schiff base, S-Benzyldithiocarbazate, Metal complexes, Antimicrobial activity, Antifungal activity.

INTRODUCTION

Nowadays, researchers are extensively attracted towards the metal complexes synthesized from S-alkyl or aryl dithiocarbazate based Schiff base with metal precursors due to their wide variety in the mode of hydrogen bonding, presence of different substituents, or availability on either side of the N_2S_2 as a chromophore group and its stereochemistry [1-3]. Further, they have also been characterized by various spectral techniques as well as biological studies. Moreover, organic dithiocarbazate ligands can be produced by the condensation of carbonyl compounds and S-aryl/alkyl dithiocarbazate with nitrogen and sulphur as a donating atom [4-11]. Sharma *et al.* [1] reported as 2,4,5-trimethoxy benzaldehyde-S-benzyldithiocarbazate as Schiff base synthesized by conden-sation between 2,4,5-trimethoxybenzaldehyde and S-benzyl-dithiocarbazone (SBDTC) and shows significant antibacterial activity with *Escherichia coli* and *Staphylococcus aureus* patho-gens. Generally, a minute change in the organic constituent of dithiocarbazate Schiff base, so which alters the properties of Schiff base while replacement of metal for complexation also changed the molecular structure of complexes. According to literature the dithiocarbazate ligands and its metal complexes were reported distinct biological activity like antibacterial [12-16], antifungal [12,14,15,17,18] and cytotoxic [5,19], trypanocidal [6], antitripansoma cruzi [9], antiamoebic [10] and analgesic and anti-inflammatory activity, respectively [20,21].

Further, different factors include coordination number of metals, type of chelate rings with metal, molecular packing and π-electron delocalization of Schiff base as well as lipophilicity were responsible for the biological activity of metal complexes [22,23]. Some first transition series of metal complexes with NS donor ligands of dithiocarbazates and thiosemicarbazones also being researched for therapeutic purposes [24-27]. The metal complexes with dithiocarbazate ligand were reported with simply octahedral or sometimes distorted octahedral geometry [28-31]. Latif *et al.* [32] reported the spectral characterization and biological analysis of dithiocarbazate

ligand (prepared from SBDTC and *p*-dimethylaminobenzaldehyde) and its (ML_2) metal complexes (M(II) = Zn, Cu and Ni).

In the present study, by considering the bioactivity effects of dithiocarbazate Schiff base, herein the synthesis, characterization and bioactivity studies of a bidentate nitrogen and sulfur donor ligand and its (ML_2)X_2 type metal complexes. After reviewing literatures, we come to know that, the synthesis and bioactivity studies of Cu(II), Ni(II), Zn(II) metal complexes with dithiocarbazate ligands are extensively reported while complexes of Fe(II), Mn(II), Co(II) and Fe(III) are less reported. Therefore, it is decided to study the bioactivity of dithiocarbazate ligand and its complexes of Fe(II), Mn(II), Co(II) and Fe(III).

EXPERIMENTAL

For the synthesis of dithiocarbazate ligand and complexes, the Analytical grade (A.R.) solvents and chemicals (hydrazine hydrate (80%), potassium hydroxide, *p*-(dimethylamino)-benzaldehyde, carbon disulfide, benzyl chloride and metal salts of Co(II), Mn(II), Fe(II)) were utilized, procured from Merck (India) and used as without any further purification.

The FT-IR spectra (4000-400 cm^{-1}) were acquired utilizing KBr pellets on a Shimadzu 8201 PC, FT-IR spectrophotometer. The absorption spectra (UV-Vis) were obtained using a Jasco spectrophotometer (range of 200-800 nm). The ^1H, as well as ^{13}C NMR spectra, were taken using Bruker AV III HD NMR (500 MHz) in $CDCl_3$ with TMS as internal standard at common instrumentation facility center, Savitribai Phule Pune University, Pune, India. Magnetic susceptibility balance was utilized to determine magnetic measurements of dithiocarbazate ligand and metal complexes by Gouy's Method. Further, A CHNS microanalyzer was used to record microanalyses for the elements C, H, N and S.

Synthesis of S-benzyl-β-N-(*p*-dimethylaminophenyl)-methylenedithiocarbazate (HL): The dithiocarbazate Schiff base was derived by reported method [33]. The mixture of KOH (2.8 g, 50 mmol) and 80% hydrazine hydrate (2.5 mL, 50 mmol) in 40 mL ethanol was cooled down to 5 ºC, solutions of carbon disulfide (3.8 g, 50 mmol) and *p*-chlorobenzyl chloride (6.3 g, 50 mmol) were added simultaneously with stirring and cooling in ice bath. After sufficient time, the carbonyl compound *p*-dimethylaminobenzaldehyde (7.45 g, 50 mmol) was added in 20 mL alcohol and mixed to S-benzyldithiocarbazate solution. The above solution was then heated for about 45 min before being permitted to attain room temperature. The orange-coloured precipitate was removed from the mother liquor, which was then washed with hot 95% ethanol and desiccated for a few days on anhydrous silica gel. The product appears as an orange powder. After recrystallization with absolute ethanol, the Schiff base ligand emerged as a yellow coloured product. Yield 68%, melting point 179 ºC. ^1H NMR, δ, ppm (500 MHz, $CDCl_3$): 9.93 s (1H, NH–N), 7.71 s (1H, azomethine, CH=N),7.56 d (J = 8.9 Hz, 2H, C_6H_4), 7.43 d (J = 7.3 Hz, 2H, C_6H_5), 7.33 t (J = 7.4 Hz, 2H, Ar, C_6H_5), 7.28 d (J = 7.3 Hz, 1H, Ar, C_6H_5), 6.65 d (J = 8.9 Hz, 2H, C_6H_4), 4.56 s (2H, S-CH_2), 3.02 s (6H, N-dimethyl moiety). ^{13}C NMR, δ_C, ppm: 39.42, 40.33, 42.86, 113.20, 113.28, 121.08, 128.46, 128.86, 128.92, 129.20, 129.26, 129.50, 129.76, 137.22, 147.82, 154.25, 197.45. Elemental analysis of $C_{17}H_{19}S_2N_3$ calcd. (found) %: C 62.00 (62.02); H 5.77 (5.74); S 19.44 (19.49); N 12.79 (12.75).

Synthesis of $M(L_2)X_2$ complexes: For synthesis of metal complexes (**2-5**) dithiocarbazate ligand refluxed with hydrated metal(II) salt solutions (Co, Mn, Fe) in ethanol. In absolute ethanol, a solution Schiff base, HL (0.329 g, 1 mmol) was refluxed for about 40 min with an adequate quantity of metal(II) salt hydrate solution under stirring. A hot ethanoic solution Schiff base ligand, HL (0.329 g, 1 mmol) and an appropriate amount of metal salt hydrate solution 0.5 mmol ($CoCl_2 \cdot 6H_2O$, 0.119 g), [$Mn(CH_3COO)_2 \cdot 4H_2O$, 0.123 g], [$Fe(SO_4) \cdot 7H_2O$, 0.139 g], [$Fe(NO_3)_2 \cdot 9H_2O$, 0.202 g] in absolute ethanol was refluxed for about 40 min under stirring. The precipitate was removed from the mother liquor and washed in ethanol before being dried on anhydrous silica gel.

[$Co(L)_2(H_2O)_2$]: Yield 64%, colour faint black, m.p.: 202 ºC. Elemental analysis of $C_{34}H_{40}N_6S_4O_2Co$, calcd. (found)%: C, 54.30 (54.30); H, 5.32 (5.33); N, 11.18 (11.19); S, 17.04 (17.05). ^1H NMR, (500 MHz, $CDCl_3$): δ 8.36 (s, 2H, azomethine, CH=N), 7.92-6.95 [(m, 14H), C_6H_4 (4H) and C_6H_5 (10H) Ar-protons], 6.68-6.45 (m, 4H C_6H_4, Ar-protons), 4.57 (s, J = 16.9, 12.9 Hz, 4H, S-CH_2), 3.07-2.96 (s, 12H, N-$(CH_3)_2$).

[$Mn(L)_2(H_2O)_2$]: Yield 68%, bluish black, m.p.: 215 ºC. Elemental analysis of $C_{34}H_{40}N_6S_4O_2Mn$ calcd. (found) %: C, 54.61 (54.62); H, 5.35 (5.37); N, 11.63 (11.62); S, 17.13 (17.12). ^1H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 2H, CH=N), 7.80-6.93 [(m, 14H) C_6H_4 (4H) and C_6H_5 (10H) Ar-protons], 6.67-6.44 (m, 4H, C_6H_4, Ar-protons), 4.56 (s, J = 16.9, 12.9 Hz, 4H, S-CH_2), 3.07-2.94 (s, 12H, N-$(CH_3)_2$).

[$Fe(L)_2(H_2O)_2$]: Yield 66%, bluish brown, m.p.: 223 ºC. Elemental analysis of $C_{34}H_{40}N_6S_4O_2Fe$ calcd. (found) %: C, 54.54 (54.55); H, 5.34 (5.35); N, 11.22 (11.20); S, 17.11 (17.09).

[$Fe(L)_2(NO_3)(H_2O)$]: Yield 66%, greenish brown, m.p.: 218 ºC. Elemental analysis of $C_{34}H_{38}N_7S_4O_4Fe$ calcd. (found) %: C, 51.51 (51.48); H, 4.79 (4.78); N, 12.37 (12.40); S, 16.16 (16.17).

Antimicrobial activity: Antimicrobial activity of dithiocarbazate ligand and (ML_2)X_2 type complexes were carried out at the Department of Biotechnology, Shivaji University, Kolhapur, India. A biological experiment was also performed against one fungus, *Candida albicans* and three pathogens, involving two Gram-positive. Dimethyl sulfoxide (DMSO) solvent was used to dissolve test compounds, sterilized by process of filtration using a sintered glass filter and stockpiled at 4 ºC. The bioactivity of the synthesized compounds was verified using the well-diffusion method on nutrient agar medium. Microorganisms were overnight grown at 37 ºC on nutrient agar plates and 100 µL of microbial suspension was spread on the nutrient agar surface in plates using sterile glass spreader. Wells with diameters of 6 mm were prepared and filled with 50 µL of each compound (1 mg mL^{-1}). The reference compound were used such as kanamycin (Sigma-Aldrich, Germany) (1.0 mg mL^{-1}), nystatin (Sigma-Aldrich, Germany) (1.0 mg mL^{-1}) and DMSO. Fungal strains were grown on potato dextrose agar plates (PDA; Himedia) at 30 ºC for 5 days. The plates were incubated for 2 days for bacterial strains (37 ºC)

and 4 days for fungal strains (30 ºC). The valuation of antimicrobial response was based on the size of inhibition zones in mm on the agar surface around the well [two Gram-positive (*B. cereus* and *S. aureus*) and one Gram-negative (*E. coli*)]. The zones of inhibition (mm) produced by dithiocarbazate ligands and metal complexes (Co^{2+}, Mn^{2+}, Fe^{2+}/Fe^{3+}) were compared to conventional antibiotics (kanamycin 30 µg/disc and amoxycillin).

RESULTS AND DISCUSSION

S-Benzyl-β-N-(4-dimethylaminophenyl)methylenedithiocarbazate dithiocarbazate ligand (HL) was synthesized by 1:1 condensation of S-benzyldithiocarbazate and *p*-(dimethylamino)benzaldehyde in absolute ethanol under reflux conditions (**Scheme-I**).

The reaction of Schiff base with metal salts (iron, cobalt and manganese salts) in 2:1 ratio respectively yielded metal complex.

$$MX_2{\cdot}nH_2O + HL \longrightarrow [M(II)(L)_2(H_2O)_2]$$

where $X_2 = (Cl)_2$ or $(CH_3COO)_2$ or SO_4 and M = Co(II), Mn(II), Fe(II).

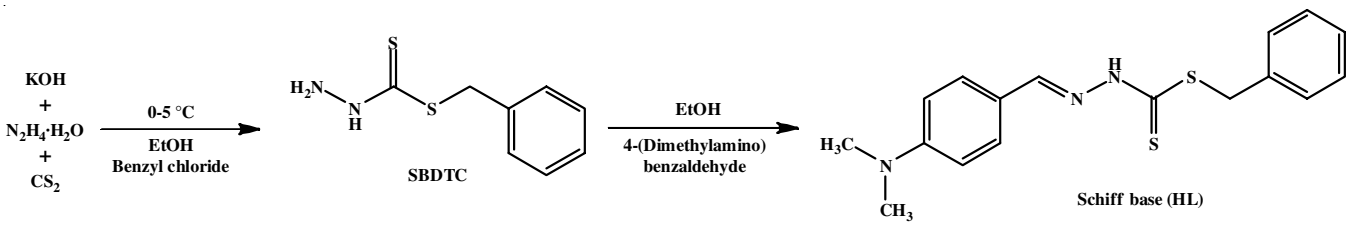
$$Fe(NO_3)_3{\cdot}nH_2O + HL \longrightarrow [Fe(III)(L)_2(NO_3)(H_2O)]$$

Synthesized dithiocarbazate ligand and their metal(II)/(III) complexes $(ML_2)X_2$ are air-stable and non-hygroscopic. The dithiocarbazate ligand was soluble in almost all the common organic solvents *e.g.* chloroform, dichloromethane, DMF, DMSO and other organic solvents.

IR spectra: Some selected FT-IR absorption frequency peaks of the dithiocarbazate ligand and their $(ML_2)X_2$ complexes are reported in Table-1. The ligand belongs to the dithiocarbazates category exhibited thiol to thione tautomerism was reported by Yazdanbankhsh *et al*. [34]. Further such ligand complexed with metal ions either through thione form or thiol from or in some cases shows coordination of metal ions with thione and thiol form as evident from literature review of previous work [32]. The FT-IR spectrum of dithiocarbazate ligand displayed a strong peak at 3105 cm^{-1} allocated to N-H moiety and another UV-vis absorption peak at 1078 cm^{-1} predicted for C=S moiety. Further, FT-IR bands at 3105 and 1078 cm^{-1} become vanished in metal(II/III) complexes spectra. The absence of absorption band of C=S and -NH stretching peak in the IR spectrum of $(ML_2)X_2$ type complexes indicated the complexation of dithiocarbazates Schiff base ligand through deprotonated sulfur anion of thiolate form to the metal ion. However, the Schiff base does not show an absorption band near to 2570 cm^{-1} corresponds to the C=S stretching band that indicates that the dithiocarbazate ligand primarily occurs in thione form of tautomers solid-state. Due to metal-nitrogen bond formation in metal complexes, the stretching frequency of C=N bond in free ligands assigned at 1594 cm^{-1} lifted to a lower stretching frequency (1582-1563 cm^{-1}) supports the azomethine nitrogen (C=N) atom undergoes complexation to the central metal ($M^{2+/3+}$) ion in the complexes.

Again, the stretching frequency of C-S bond in free ligand appeared at 808 cm^{-1} shifted to lower stretching frequency (805-775 cm^{-1}) indicated complexation of a sulfur atom to central metal ion supporting metal-sulphur bond formation. In metal complexes, FT-IR absorption peak at 578-512 cm^{-1} predicted for metal-nitrogen bond and absorption peak at 478-446 cm^{-1} allotted for metal-sulphur bond indicates that coordination of dithiocarbazate ligand by azomethine nitrogen (C=N) moiety and thiolate sulfur anion moiety to the central metal ion.

^{1}H & ^{13}C NMR spectra: In ^{1}H NMR spectrum of dithiocarbazate ligand (HL) in $CDCl_3$ displays a sharp singlet peak at δ 9.93 ppm for the (N-H) proton that was vanished in its metal complexes. It suggested that Schiff base existing in solution in the thione tautomeric form. Schiff base undergoes deprotonation of the thiol form and then complexed with the central metal ions to produce metal complexes [26,33-35]. In the case of the free ligand, four aromatic ring protons of *p*-dimethylaminobenzaldehyde were assigned as a doublet at δ 7.56 ppm for 2 protons and doublet δ 6.65 ppm for another two protons. The five aromatic ring protons of SBDTC were assigned at δ 7.28 ppm as a doublet for one proton, δ 7.33 ppm (triplet) for two protons and δ 7.43 ppm (doublet) for two protons. Further, a singlet at δ 7.71 ppm in a spectrum of dithiocarbazate ligand was predicted for azomethine (CH=N) proton. The (CH=N) proton of metal complexes spectra was



Scheme-I

TABLE-1
KEY IR BANDS (cm^{-1}) OF LIGAND AND $(ML_2)X_2$ COMPLEXES

Compounds	ν(N-H)	ν(C=S)	ν(C=N)	ν(C-S)	ν(M-S)	ν(M-N)	ν(M-OH_2)
HL	3105	1078	1594	808	–	–	–
$Co(L)_2(H_2O)_2$	–	–	1567	794	478	516	3434
$Mn(L)_2(H_2O)_2$	–	–	1563	775	446	512	3435
$Fe(L)_2(H_2O)_2$	–	–	1572	804	460	503	3434
$Fe(L)_2(NO_3)(H_2O)$	–	–	1582	805	446	578	3436

deshielded (above δ 8.00 ppm) suggested complexation to the metal ion by the nitrogen atom of (C=N) moiety [26,33-35]. In Schiff base, S-CH_2 protons exhibited a singlet peak at δ 4.56 ppm while in the complexes same protons shown singlet at near same δ 4.56 ppm for S-benzyl moiety so showed no notable change in its complexes. In Schiff base, N-CH_3 protons of *p*-dimethylaminobenzaldehyde exhibited a singlet peak at δ 3.02 ppm. In the metal complexes, N-CH_3 protons showed singlet at near same δ 3.07-2.96 ppm for N-dimethyl moiety, so showed no notable change in its complexes.

The ^{13}C NMR spectrum of dithiocarbazate ligand shown signals at δ 196.71 and 144.11 ppm, which are predicted due to the thione (C=S) and azomethine (C=N) fragments, respectively. The ^{13}C peaks due to methylene group (S-CH_2), methyl of (N-CH_3)$_2$ moiety appear at δ 42.32 and 41.91 ppm, respectively while other peaks due to aromatic carbon.

Magnetic moments, molar conductance and UV-visible spectra: The molar conductance measurements of ligand and $(ML_2)X_2$ metal complexes suggested the non-electrolyte behaviour [36,37]. While magnetic susceptibility data (Table-2) presented that metal complexes $(ML_2)X_2$ have an octahedral configuration.

TABLE-2
MAGNETIC MOMENTS AND MOLAR CONDUCTANCE OF LIGAND AND ITS $(ML_2)X_2$ COMPLEXES

Compounds	Molar conductance (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (B.M)
HL	2.22	–
$Co(L)_2(H_2O)_2$	2.37	4.67
$Mn(L)_2(H_2O)_2$	2.54	5.86
$Fe(L)_2(H_2O)_2$	2.65	5.61
$Fe(L)_2(NO_3)(H_2O)$	2.30	5.82

The electronic spectrum of ligand solution (HL) exhibited average to sharp intensity bands at 281.5 and 329 nm predicted tentatively for (π→π*, azomethine group, CH=N), (n→π*, azomethine group, CH=N), respectively and another two bands at 391 nm and a weak band at 461 nm were allotted cautiously for (π→π*, dithiocarbazate constituent) or (n→π*, dithiocarbazate constituent), respectively [14,38-40]. The UV-vis absorption band at 329 of n→π* transition assigned for CH=N chromophore in the free dithiocarbazate ligand that was missing in its metal complexes spectra (**2-5**) indicates its coordination through the nitrogen of the azomethine moiety to the central metal atom with the successive blue shift, (π→π*, CH=N, azomethine) [14,38-40]. In metal complexes spectra, the UV-Vis absorption band of π→π* and n→π* transitions of dithiocarbazate constituent of ligand were combined to a single broadband (range 374-405 nm), suggesting its complexation of ligand *via* the thiolate sulfur atom to central metal ion as mentioned previously [14,40]. Furthermore, while S→M charge transfer shifts were familiar in dithiocarbazate based transition metal complexes most of the time, this band of transition was not visible in the current spectra due to the smoothness of the UV-Vis band in free ligand within the area of 374-405 nm that prolonged up to the visible region in metal complex spectra (*ca.* 510 nm) (Table-3). Based on the above studies, the proposed structure of the synthesized metal(II/III) complexes are shown in Fig. 1.

TABLE-3
ELECTRONIC ABSORPTION (UV-Vis) MEASUREMENTS OF LIGAND AND $(ML_2)X_2$ COMPLEXES

Compounds	Wavelength (nm)			
	Band-I	Band-II	Band-III	Band-I
HL	281.5	329	391	461
$Co(L)_2(H_2O)_2$	260	300	380	–
$Mn(L)_2(H_2O)_2$	251	312	386	–
$Fe(L)_2(H_2O)_2$	–	–	379	–
$Fe(L)_2(NO_3)(H_2O)$	255	317	389	–

Antibacterial activity: Dithiocarbazate ligand (HL) and their $(ML_2)X_2$ metal complexes were examined against three pathogens, which were Gram-negative (*E. coli*) and two Gram-positive (*B. cereus* and *S. aureus*). Well diffusion method was employed to investigate the bioactivity of test compounds. A clear zone of inhibition around the well was observed for ligands and metal complexes for all bacterial strains with all test compounds. In comparison to standard antibacterial kanamycin drug, metal complexes $Fe(L)_2(H_2O)_2$ and $Fe(L)_2(NO_3)$-(H_2O) type revealed moderate bioactivity against *E. coli* (Table-4). The Fe(III)/Fe(II) complexes displayed moderate to strong activity (18-20 mm, inhibition zone) against *B. cereus* and *S. aureus* pathogens as compared to other metal complexes. While other complexes $Co(L)_2(H_2O)_2$ and $Mn(L)_2(H_2O)_2$ showed the least antibacterial activity (8 to 9 mm, inhibition zone) against *S. aureus* and *E. coli* pathogens while exhibited potential activity against *B. cereus* (17 to 18 mm, inhibition zone, respectively). Overall data suggest that due to incorporation of metal with ligands in metal complexes exhibits higher antibacterial activity than dithiocarbazate ligand. The activity produced by metal complexes and dithiocarbazate ligand were compared with standard antibiotic kanamycin drug.

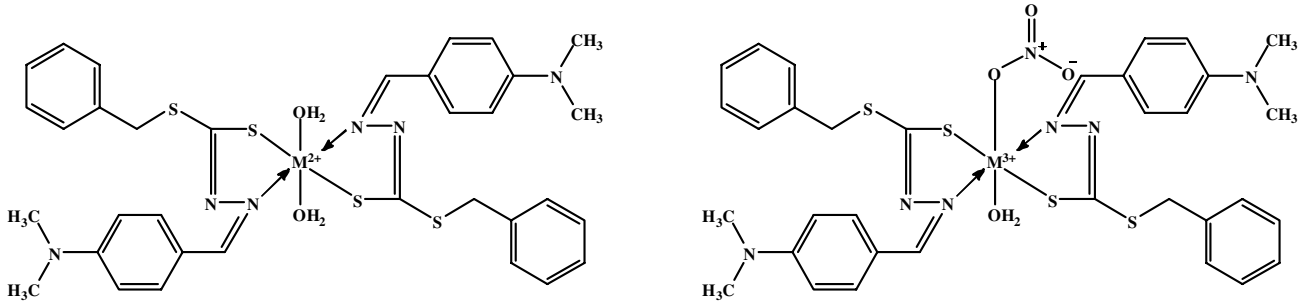


Fig. 1. Proposed structure of metal (M^{2+} and M^{3+}) complexes

TABLE-4
BIOACTIVITY DATA OF LIGAND AND ITS METAL COMPLEXES

Compounds	Zone of inhibition (mm)			
	Gram-negative	Gram-positive		Fungi
	E. coli	*S. aureus*	*B. cereus*	*C. albicans*
HL	5	6	12	-
$Co(L)_2(H_2O)_2$	8	8	18	-
$Mn(L)_2(H_2O)_2$	8	9	17	4
$Fe(L)_2(H_2O)_2$	14	18	19	5
$Fe(L)_2(NO_3)(H_2O)$	15	19	20	9
Reference	20	22	22	21

Antifungal activity: The metal complexes and ligand were analyzed for antifungal studies against *Candida albicans*. The Fe(III) complexes showed higher antifungal activity (9 mm, zone of inhibition) against *Candida albicans* as compared to other complexes. While, other metal complexes and ligand had the least antifungal activity (about 4-5 mm, zone of inhibition). The action of the dithiocarbazate ligand and $(ML_2)X_2$ metal complexes were compared to that of the conventional antibiotic amoxicillin (Table-4).

Conclusion

The dithiocarbazate ligand performances as a bidentate mono negative ligand with NS donor atoms in their structure. Both in the solid and solution state, the ligand (HL) was mainly in the thione tautomeric form while in presence of metal center (Co^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+}), thiol form of it undergoes subsequent deprotonation and forms metal complexes. All dithiocarbazate ligand and its metal complexes exhibited prominent antimicrobial action, whereas the metal complexes of Fe(III) exhibited significantly potential antibacterial activity against some selected bacterial strains.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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