



Co(II), Ni(II), Cu(II) and Zn(II) complexes with chelating thiosemicarbazone ligand incorporating benzo[b]-thiophene and thiosemicarbazide moieties: Spectroscopic, electrochemical behavior, biological and thermal decomposition studies

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Abstract

A novel thiosemicarbazone ligands 2-hydroxybenzaldehyde-4-(3-chlorobenzothiophene-carbonyl)-3-thiosemicarbazone (SL1) /thiophen-2-aldehyde-4-(3-chlorobenzothiophenecarbonyl)-3-thiosemicarbazone(SL2) obtained by the condensation of 3-chlorobenzo[b]-thiophene-2-carbonylchloride with thiophene-2-ylmethylenethiosemicarbazide/2-hydroxyphenylmethylenethiosemicarbazide and its newly synthesized Co(II), Ni(II), Cu(II) and Zn(II) complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements thermal analysis and various spectral studies like UV-Visible, FT-IR, ¹H NMR, ¹³C NMR, mass and EPR. The ligands behaved as tetra dentate donor and forms the complexes of type [ML(Cl)₂]. The molar conductance data reveal that the chelates were non-electrolytes. From the Ultraviolet/Visible spectra and magnetic moment data, the complexes were found to have octahedral geometrical structure. *In vivo* evaluation of the antimicrobial activities of the metal complexes and the ligands, complexes showed greater activity against some micro-organisms when compared to the parent compounds. The redox behavior of complexes was investigated by cyclic voltammetry.

Keywords: thiosemicarbazone, electrochemical studies, metal complexes, antimicrobial activity

1. Introduction

The ligands containing N and S donor atoms possess a number of biological activities such as antimicrobial, antifungal, antiviral, anticonvulsant, anti-inflammatory, anti malarial etc. They are also used as powerful pesticides and insecticides apart from other biological applications ^[1]. These properties are enhanced when ligands form complexes with metals. The presence of donor atoms like N and S etc., play an important role in the formation of a stable chelate ring and this situation facilitates the complexation process ^[2]. Thiosemicarbazone are of current interest with respect to their biological activity and chemotherapeutic properties ^[3]. In addition, these compounds have many applications especially as reagents for the microanalytical determination as well as their ability to form chelated complexes with transition metal ions ^[4-7]. Thiosemicarbazones and their metal complexes have been extensively studied during recent years mainly due to their various biological activities ^[8,9]. They usually act as chelating ligands especially with transition metal ions, joint through the sulfur and azomethine nitrogen atoms ^[10].

The present paper described the synthesis and characterization of 2-hydroxybenzaldehyde-4-(3-chlorobenzothiophene-carbonyl)-3-thiosemicarbazone(SL1)/ thiophen-2-aldehyde-4-(3-chlorobenzothiophene-carbonyl)-3-thiosemicarbazone(SL2) ligands and their new complexes with Co(II), Ni(II), Cu(II) and Zn(II).

2. Experimental

2.1. Material and Measurements

All the chemicals and solvents from Sigma Aldrich/ Merck were of AR grade and used as received. Melting point of all

synthesized compounds was determined in open glass capillaries and was uncorrected. Purity of the compounds was checked by TLC and the spots were observed in iodine vapor. The elemental analysis was done on a Perkin-Elmer Analyzer 2440. Molar conductance was measured on the ELICO (CM-185) conductivity bridge using 10⁻³ M solution of dry DMF by dip-type conductivity cell fitted with a platinum electrode. Electronic spectra of the Co(II), Ni(II), Cu(II) and Zn(II) complexes were recorded at 25°C on a Systronic double beam spectrometer in quartz cells in the range 200 – 800 nm (ca.10⁻³ M in DMF). Magnetic susceptibility of complexes was measured by Gouy's method using copper sulphate as calibrant. IR spectra were recorded on Jasco Fourier transform IR spectrophotometer (4000 to 250 cm⁻¹, KBr pellets). ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz spectrometer in *d*₆-DMSO as solvent. The mass spectral analysis was carried out using JEOL D-300 (EI) mass spectrometer. EPR measurement of the copper complexes was recorded at liquid nitrogen temperature using a JEOL Model JES FA200 instrument. The thermal analysis (DTA and TGA) were carried out on a Shimadzu DT-30 and TG-50 thermal analyzers in the range 27- 900°C at the heating rate of 10°Cmin⁻¹ in nitrogen atmosphere. All the synthesized compounds were screened for their pharmacological activity using disc diffusion method and the bacterial strains were obtained from National Chemical Laboratory, Pune.

2.2. Synthesis of ligand

2.2.1. Synthesis of 3-chlorobenzo[b]thiophene-2-carbonylchloride (CBT)

Cinnamic acid (0.01mol) in 1 ml pyridine and 40 ml thionyl

chloride was heated at 95-98°C for 21 hours. Excess thionyl chloride was removed by distillation and pale yellow residue was taken up in hot hexane (500ml) and decanted. On cooling

yellow solid was obtained. It was dried in a vacuum desiccator over anhydrous calcium chloride at room temperature. (Fig 1)

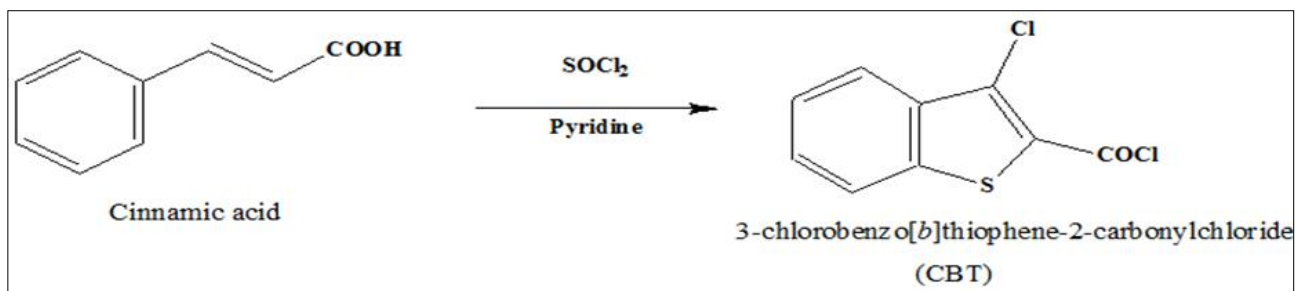


Fig 1: Synthesis of CBT

2.2.2. Synthesis of 2-hydroxyphenylmethylenethiosemicarbazide (SHC)/ Thiophen-2-ylmethylenethio-semicarbazide (THC)
2-hydroxybenzaldehyde/ 2-thiophene carboxaldehyde (0.01mol) in 10 ml ethanol with thiosemicarbazide (0.01mol). Then the mixture was refluxed for 7 hours in presence of 2-5

drops conc. HCl, after completion of the reaction (monitored by TLC) the pale yellow/ light brown precipitate of SHC/ THC was obtained then the mixture cooled and filtered off, washed with cold ethanol and dried in vacuum and recrystallised using methanol. (Fig 2/ Fig 3)

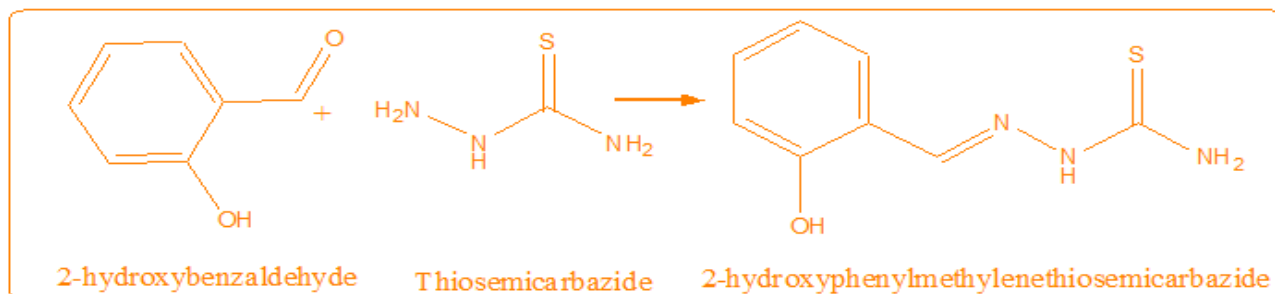


Fig 2: Synthesis of SHC

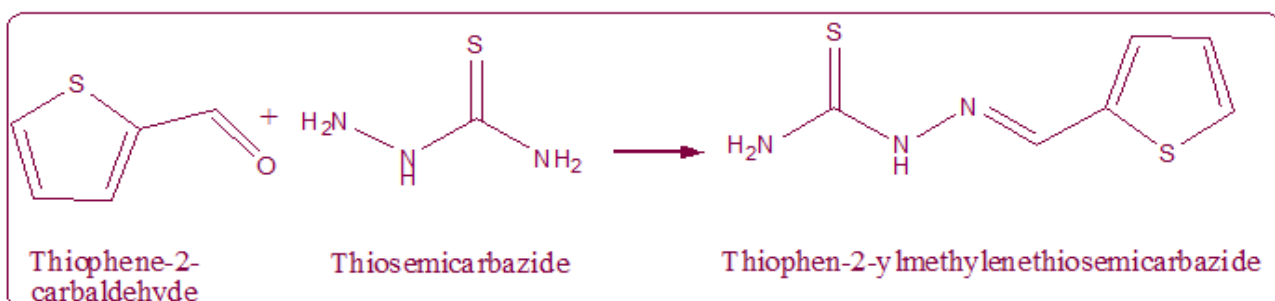


Fig 3: Synthesis of THC

2.2.3. Synthesis of the ligands 2-hydroxybenzaldehyde-4-(3-chlorobenzothiothiophene-carbonyl)-3-thiosemicarbazone(SL1) / thiophen-2-aldehyde-4-(3-chlorobenzothiothiophene-carbonyl)-3-thiosemicarbazone(SL2)

An ethanolic solution of SHC/THC (1 mmol, 25 mL) was added to an ethanolic solution of CBT (1 mmol, 25 mL) and refluxed for 4 hours in a water bath. After concentration of the solution, the precipitate was separated, filtered, washed with ethanol, and dried over anhydrous calcium chloride under

vacuum.

2.2.4. Synthesis of the complexes

A hot ethanolic solution of the ligand SL1/SL2 (0.01 mol) and the corresponding hydrated metal (II) chlorides (Co, Ni, Cu and Zn) (0.01 mol) in 1:1 ratio were mixed together with constant stirring for 4 hours. Then the mixture was refluxed for 6 hours. On cooling, a colored precipitates formed which was filtered off, washed with cold ethanol and dried under vacuum.

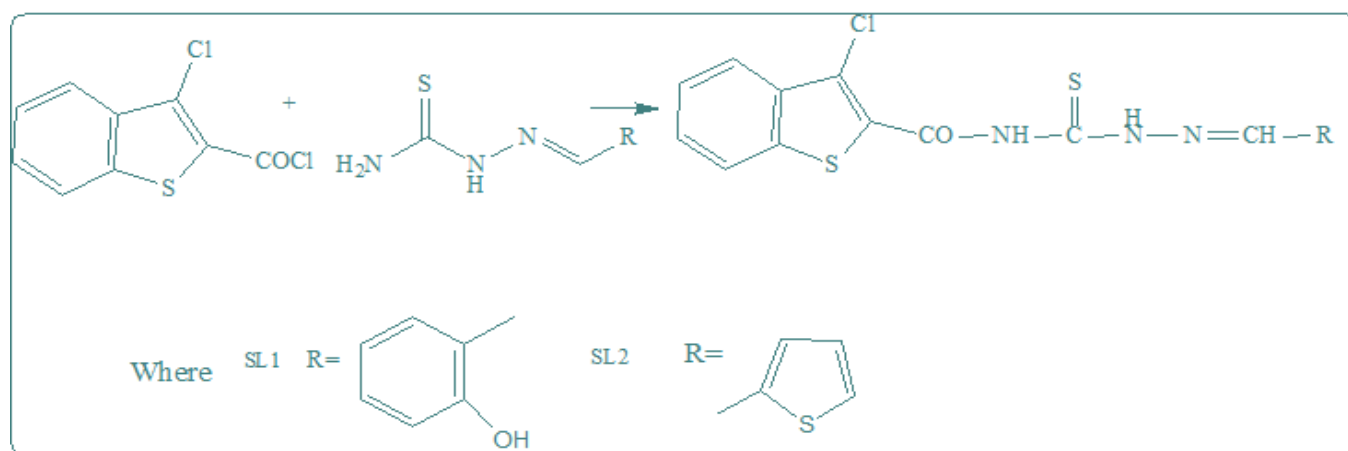


Fig 4: Synthesis of ligands (SL1, SL2)

3. Results and Discussion

The complexes were found to be stable in air and non-hygroscopic. The complexes were insoluble in water, ethanol and diethyl ether but are completely soluble in DMF and DMSO. The physical properties and analytical data of the complexes are given in Table 1. Elemental analysis suggests that the complexes have 1:1 (metal-ligand) molar ratio.

3.1. Molar conductance data

The molar conductance of the solid complexes (λ_m , $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) was calculated. The DMF solubility of the above complexes made calculations of the molar conductivity (λ_m) of $10^{-3} \text{ mol dm}^{-3}$ solution at 25°C possible. The data in Table 1 showed that the molar conductance values of the Co(II), Ni(II), Cu(II) and Zn(II) complexes were relatively low, indicating the non-electrolytic nature of these complexes^[11].

Table 1: Physical properties and analytical data of the ligands and its complexes

Mol. Formula	Mol. Weight	% Yield	Mp $^\circ\text{C}$	Color	Calculated(Found) %				MolCond. ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
					C	N	S	Metal	
SL1 $\text{C}_{17}\text{H}_{12} \text{N}_3\text{O}_2\text{S}_2\text{Cl}$	389.87	76%	160	Brown	52.37 (50.32)	10.78 (10.83)	16.45 (20.24)	-	-
[Co(SL1)Cl ₂] $\text{CoC}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2\text{Cl}_3$	518.71	73.4%	222	Light Green	39.36 (37.55)	8.1 (7.23)	12.36 (11.56)	11.36 (12.36)	11.0
[Ni(SL1)Cl ₂] $\text{NiC}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2\text{Cl}_3$	518.48	72.5%	226	Pale Yellow	39.38 (37.88)	8.1 (9.22)	12.37 (13.56)	11.37 (11.02)	8.0
[Cu(SL1)Cl ₂] $\text{CuC}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2\text{Cl}_3$	523.32	80.1%	195	Brown	39.02 (35.20)	8.03 (8.45)	12.25 (10.78)	12.14 (11.77)	5.06
[Zn(SL1)Cl ₂] $\text{ZnC}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2\text{Cl}_3$	525.15	76.2%	208	White	38.88 (36.50)	8.0 (8.12)	12.21 (15.42)	12.45 (11.13)	9.4
SL2 $\text{C}_{15}\text{H}_{10} \text{N}_3\text{OS}_3\text{Cl}$	379.97	73%	188	Pale Yellow	47.42 (46.30)	11.06 (10.83)	25.32 (24.24)	-	-
[Co(SL2)Cl ₂] $\text{CoC}_{15}\text{H}_{10} \text{N}_3\text{OS}_3\text{Cl}_3$	509.74	75.7%	216	Green	35.34 (34.15)	8.24 (8.95)	18.87 (19.24)	11.56 (12.27)	13.0
[Ni(SL2)Cl ₂] $\text{NiC}_{15}\text{H}_{10} \text{N}_3\text{OS}_3\text{Cl}_3$	509.51	72.6%	218	Yellow	35.36 (36.51)	8.25 (9.11)	18.88 (17.97)	11.52 (10.85)	10.0
[Cu(SL2)Cl ₂] $\text{CuC}_{15}\text{H}_{10} \text{N}_3\text{OS}_3\text{Cl}_3$	514.35	81.5%	204	Light Brown	35.03 (34.23)	8.17 (8.65)	18.70 (17.68)	12.35 (11.67)	8.5
[Zn(SL2)Cl ₂] $\text{ZnC}_{15}\text{H}_{10} \text{N}_3\text{OS}_3\text{Cl}_3$	516.18	74.4%	208	Dirty white	35.90 (33.45)	8.14 (8.45)	18.63 (19.42)	12.67 (11.43)	9.2

3.2. Electronic spectral studies

The study of the electronic spectra in the ultraviolet and visible (UV-Vis) ranges for the ligand and metal complexes were carried out in DMF. Solid-state electronic spectra of all thiosemicarbazone, exhibited two bands (430, 435 nm and 250, 252 nm). An intense band at $\sim 433 \text{ nm}$ is attributed to the $n-\pi^*$ transitions of C=S group, C=N group^[12] and thiophene ring, which are overlapped. The $\pi-\pi^*$ transitions of the thiophene ring and thiosemicarbazone imine function are rather weak, and observed at 250-252 nm.

The electronic spectra of Co(II) complex of SL1 exhibit three d-d absorption bands in the region 435, 631, 736 cm^{-1} which can be assigned to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ respectively which are characteristic of octahedral geometry. This geometry was further supported by its magnetic susceptibility value (4.42 BM)^[13]. The Ni(II) complexes shown three bands around 420, 630 and 760 cm^{-1} which are assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ transition respectively, indicating octahedral geometry. The magnetic

moment is 2.90 B.M^[14]. These findings are in favor of an octahedral geometry for the Ni(II) complex. The electronic spectra of Co(II) complex of SL1 shows three d-d absorption bands in the region 434, 638, 724 cm^{-1} which can be assigned to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ respectively which are characteristic of octahedral geometry. This geometry was further supported by its magnetic susceptibility value (4.35 BM). The Ni(II) complexes shown three bands around 425, 630 and 766 cm^{-1} which are assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ transition respectively, indicating octahedral geometry. The magnetic moment is 2.85 B.M. These findings are in favor of an octahedral geometry for the Ni(II) complex. The Cu(II) complexes of ligands (SL1, SL2) exhibited a high intensity band at $\sim 745 \text{ cm}^{-1}$ which are assigned to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$. Its magnetic moment is 1.94 B.M. These values were characteristic of octahedral geometry. The diamagnetic Zn(II) (d^{10}) complexes do not exhibit any characteristic d-d transitions and its geometry was most probably octahedral

similar to the Co(II), Ni(II) and Cu(II) complexes of the ligands SL1 and SL2. The parameters were listed in Table 2.

Table 2: Electronic spectral data of ligands and their complexes

Mol. Formula	Abs. in nm	Transitions	Geometry	Mol. Formula	Abs. in nm	Transitions	Geometry
SL1	430 250	n- π^* π - π^*	-	SL2	435 252	n- π^* π - π^*	-
Co(SL1)Cl ₂	435 631 736	⁴ T _{1g} (F) → ⁴ T _{1g} (F) ⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{2g} (P)	Oh.	Co(SL2)Cl ₂	434 638 724	⁴ T _{1g} (F) → ⁴ T _{1g} (F) ⁴ T _{1g} (F) → ⁴ A _{2g} (F) ⁴ T _{1g} (F) → ⁴ T _{2g} (P)	Oh.
Ni(SL1)Cl ₂	420 630 760	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F) ³ A _{2g} (F) → ³ T _{2g} (F)	Oh.	Ni(SL2)Cl ₂	425 630 766	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F) ³ A _{2g} (F) → ³ T _{2g} (F)	Oh.
Cu(SL1)Cl ₂	745	² E _g → ² T _{2g}	Oh	Cu(SL2)Cl ₂	742	² E _g → ² T _{2g}	Oh.
Zn(SL1)Cl ₂	395 336	n → π^* π → π^*	Oh	Zn(SL2)Cl ₂	390 325	n → π^* π → π^*	Oh.

3.3. IR spectral studies

The most important infrared spectra of the ligand and their complexes are listed in Table 3. The IR spectra of the ligands showed band at 1624-1640 cm⁻¹ in the ligand spectrum assigned to (C=N), this band has been shifted to lower frequency indicating the participation of azomethine nitrogen in coordination [15]. The spectrum of the ligand showed (N-N) at (1072-1010) cm⁻¹. The spectra of the ligand showed band at the region 810 cm⁻¹ in ligand SL1, 815 cm⁻¹ in ligand SL2 due to (C=S), in the spectra of the complexes this band appeared at the range (802-758) cm⁻¹ showing that the coordination occurs through the sulfur of C=S bond with the metal ion [16]. The IR spectrum of ligand SL1 displays a broadband in the region of

3396 cm⁻¹ due to (-OH) in ligand (SL1). In metal complexes formation, the disappearance of one (-OH) groups indicates the involvement of phenolic oxygen bonding with metal ion via deprotonation. Further, the ligand SL2 revealed a sharp band at 860 at cm⁻¹ due to ν (C-S) (thiophene cyclic) which undergo downward shift by 20-40 cm⁻¹ in the complexes suggesting the participation of the sulphur of this entity in bonding with the metals [17]. The other new bands in the range (518-560) cm⁻¹ in the spectra of the complexes were assigned to (M-N). The bands occurring at (450-505) cm⁻¹ and (410-450) cm⁻¹ have been assigned to the (M-S) and (M-Cl) modes, respectively [18].

Table 3: Infrared spectral data of ligands and their complexes

Mol. Formula	ν max (cm ⁻¹)							
	N-H	C=S	OH	N-N	C=N	M-N	M-S	M-Cl
SL1	3310, 3124	810	3396	1072	1624	-	-	-
Co(SL1)Cl ₂	3311	758	-	1020	1604	554	472	440
Ni(SL1)Cl ₂	3120	760	-	1010	1610	550	450	420
Cu(SL1)Cl ₂	3120	800	-	1024	1612	552	460	410
Zn(SL1)Cl ₂	3125	770	-	1044	1602	559	470	430
SL2	3320, 2996	815	-	1070	1640	-	-	-
Co(SL2)Cl ₂	3300, 3176	802	-	1036	1625	550	455	425
Ni(SL2)Cl ₂	3304	774	-	1055	1620	518	450	430
Cu(SL2)Cl ₂	3315	776	-	1020	1618	540	505	450
Zn(SL2)Cl ₂	3325	804	-	1038	1610	560	455	420

3.4. NMR spectral analysis

¹H NMR spectra of ligands and their metal complexes recorded in DMSO-d₆ exhibited a sharp singlet peak at δ 11.42 ppm due to the -CONH proton and at δ 11.60 ppm due to the -N-NH proton. A singlet peak at δ 7.60 ppm due to the -HC=N group [19]. The signals of the HC=N protons shift to downfield in all complexes. This information indicates the coordination of the metal center to the azomethine nitrogen, thioamide sulfur and the thiophene sulfur group were coordinated to the metal ion. All aromatic protons were observed at the expected region (δ 7.17-7.98 ppm) in the NMR spectrum of the ligands, these signals do not afford relevant changes in the chemical shifts for the metal complexes.

¹³C NMR spectra of the ligands were recorded in DMSO-d₆ and gave the spectral signals in good agreement with the probable chemical structure. Ligands exhibited two important signals at δ 185.0 and δ 145.7 ppm assigned to the thioamide (C=S) and imine (C=N) carbon atoms, respectively. The signals at δ 123.60-156.22 ppm were observed in the spectra due to the aromatic carbons. For complexes, the δ (C=N) shifted upfield by about 1 ppm as compared to the free ligand. The upfield shift was attributed to the lowering of the δ (C=N) bond strength producing a partial double bond character in the C-N bond. The shift difference of the C=S resonance associated to the strength of the metal-sulfur bond. A small deshielding effect is observed for the other carbon atoms, due to an increase in the π -character of the C-N bond [20].

3.5. Mass spectral analysis

The formation of ligands (SL1, SL2) and its complexes was further confirmed by their mass spectral study. All the spectra exhibit parent peaks due to molecular ions (M⁺) and the isotopic peak owing to the chlorine substitution. The molecular formula of each compound was confirmed by its molecular formula weight with *m/z* values. The mass spectra of ligand SL1 showed the formation of a molecular ion peak at *m/z* 389.87[M]⁺, whereas Co(II), Ni(II), Cu(II) and Zn(II) complexes show the formation of molecular ion peaks along with isotopic peaks at *m/z* 519.51 [M]⁺, 520.1 [M]⁺, 524.5 [M]⁺ and 528.8 [M+2]⁺ respectively corresponding to their molecular formula [21]. The mass spectra of ligand SL2 showed the formation of a molecular ion peak at *m/z* 379.87[M]⁺, whereas Co(II), Ni(II), Cu(II) and Zn(II) complexes show the formation of molecular ion peaks along with isotopic peaks at *m/z* 509.74 [M]⁺, 514.35 [M]⁺, 509.51 [M]⁺ and 516.5 [M+2]⁺, respectively, corresponding to their molecular formula.

3.6. EPR spectra

EPR spectrum of Cu(II) complexes were recorded at room temperature as samples and in DMSO solution, on the X-band at 9.1 GHz under the magnetic field strength 3400 G. The

analysis of spectra give $g_{\parallel} = 2.19$ and $g_{\perp} = 2.11$. The trend $g_{\parallel} > g_{\perp} > 2.0023$, observed for the complex, under study, indicates that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral features are characteristic for axial symmetry. Octahedral elongated geometry is thus confirmed for the aforesaid complex [22].

3.7. Thermal decomposition studies

The simultaneous TGA/DTA analysis of the Co(II), Ni(II), Cu(II) and Zn(II) metal complexes were studied from ambient temperature to 800°C under nitrogen atmosphere using α -Al₂O₃ as the reference. The data from thermo gravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. The loss of chloride ions occurs in the first step at 80-100°C. The successive decomposition occurs within a temperature range of 350-390 °C and equals the loss of the organic moiety (C₈H₄S), the next stage was the loss of the remaining organic moiety, between 500-650 °C with mass losses of (obs. = 39.22%, calc. = 41.22 %). Finally, the mass decomposes gradually with the formation of metal oxide above 650°C [23]. The nature of proposed chemical change with the temperature range and the percentage of metal oxide obtained are given in Table 4.

Table 4: Thermal analysis results of metal complexes

Complexes	Peak Temp.	Mass Loss %		Assignment
		Found	Calculated	
SL1	95	8.9	9.1	loss of two chloride ions
	360	30.55	33.85	decomposition of chlorobenzo[b]-thiophene ring
	505	60.35	57.11	decomposition of organic content
Co(SL1)Cl ₂	98	19.33	20.53	loss of two chloride ions
	374	26.01	25.45	decomposition of chlorobenzo[b]-thiophene ring
	512	38.14	39.56	decomposition of organic content
	~700	16.52	14.46	further decomposition and formation of CoO as final product
Ni(SL1)Cl ₂	98	19.41	20.44	loss of chloride ion
	370	24.59	25.45	decomposition of chlorobenzo[b]-thiophene ring
	515	23.56	39.82	decomposition of organic content
	~700	32.44	14.27	Complete decomposition of material and formation of NiO.
Cu(SL1)Cl ₂	90	19.56	20.35	loss of chloride ion
	370	24.05	25.22	decomposition of chlorobenzo[b]-thiophene ring
	510	23.34	39.32	Elimination of organic content
	~700	33.03	15.20	Complete decomposition of material and formation of CuO.
Zn(SL1)Cl ₂	96	21.55	20.28	loss of chloride ion
	378	24.87	25.14	decomposition of chlorobenzo[b]-thiophene ring
	514	23.22	39.08	Elimination of organic content
	~700	30.36	15.50	Complete decomposition of material and formation of ZnO.
SL1	90	9.41	9.3	Loss of chloride ions.
	360	34.59	34.74	Elimination of organic content
	525	56.00	55.9	
Co(SL1)Cl ₂	100	20.61	20.89	Loss of two chloride ions.
	370	24.44	25.89	decomposition of chlorobenzo[b]-thiophene ring
	560	23.00	38.59	Elimination of organic content
	~700	31.95	14.71	Complete decomposition and formation of CoO
Ni(SL1)Cl ₂	95	21.35	20.70	Loss of two chloride ions.
	390	24.60	25.66	decomposition of chlorobenzo[b]-thiophene ring
	625	23.55	39.11	Elimination of organic content
	~700	30.5	14.52	Complete decomposition and formation of NiO
Cu(SL1)Cl ₂	98	20.41	20.90	Loss of two chloride ions.
	370	24.57	25.91	decomposition of chlorobenzo[b]-thiophene ring
	640	23.79	37.57	Elimination of organic content

	~700	31.23	15.61	Complete decomposition and formation of CuO
Zn(SL1)Cl ₂	100	18.41	20.63	Loss of two chloride ions.
	350	26.39	25.57	decomposition of chlorobenzo[b]-thiophene ring
	605	22.66	38.12	Elimination of organic content
	~700	15.68	15.77	Complete decomposition and formation of ZnO

3.8. Electrochemical studies-cyclic voltammetry

The electrochemical behavior of ligands and its metal complexes were examined by employing glassy carbon as working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMF and tetra n-butylammonium hexafluorophosphate (n-Bu₄NClO₄) as supporting electrolyte. The cyclic voltammogram of all compounds in 10⁻³ M solution was recorded at room temperature in the potential range -3.0 V to +2.4V with a scan rate 50 mV s⁻¹, their electrochemical data were summarized in Table.5. The complex shows a redox process corresponding to the Cu(II)/Cu(I) couple at E_{pa} = +1.24 V and associated cathodic peak at E_{pc} = +0.72 V. This couple was found to be quasi-reversible as the peak separation between the anodic and cathodic potential was very high. But the ratio between the anodic and cathodic currents suggests that the process was simple one-electron transfer, quasi-reversible process [24]. On comparing the cyclic voltammograms we observed that the variation in oxidation and reduction potential may be due to distortion in the geometry of the complex which arises due to different anions coordinated to the metal ion. The cyclic voltammogram of [Co(SL1)Cl₂] shows a well defined redox couple with reduction peak potential, (E_{pc}) at -0.25V and 0.55V, the corresponding oxidation peak potential (E_{pa}) at -0.475V and 0.25V. The peak separation of the redox couple was 0.225V and 0.3V. The ratio of the cathodic peak current, I_{pc} and anodic peak current, I_{pa} was found to be less than one which indicates that the electron transfer was quasireversible nature of the CoII/CoI redox couple. A cyclic voltammogram of Ni(II) complex [Ni(SL1)Cl₂] were displays a reduction peak at E_{pc} = -0.375V with an associated oxidation peak at E_{pa} = -0.575V at a scan rate of 50mV/s. The peak separation of this couple (ΔE_p) was 0.2V. The electrochemical behavior of [Cu(SL1)Cl₂] was displays two waves at E_{pc} values -0.35 V and 0.6 V. When the potential scan in the positive direction was reversed at -0.55 V and 0.4 V. ΔE_p value was (E_{pc} - E_{pa}) = 0.2V V, the ratio *ip,c* / *ip,a* > 1 exhibited two quasi-reversible peaks. The Zn(II) complex exhibited two quasi-reversible peaks. A cyclic voltammogram of Zn(II) displays two reduction peaks at E_{pc} = -0.45 V and 0.65V with an associated oxidation peaks at E_{pa} = 0.65 V and 0.575V corresponding to the Zn(II)/Zn(I) at a scan rate of 50mV/s, it was evidence for quasi-reversible nature associated with one electron reduction.

The Co(II) complex [Co(SL2)Cl₂] exhibits two electron quasi reversible transfer process with a reduction peak at E_{pc} = -0.4V and 0.575V with a corresponding oxidation peak at E_{pa} = -0.6V and 0.35 at a scan rate of 50mV/s. The peak separation (ΔE_p) of this couple was 0.2V and 0.22V. The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility. The ratio of cathodic to anodic peak height was less than one. A cyclic

voltammogram of Ni(II) complex [Ni (SL2)Cl₂] were displays a reduction peak at E_{pc} = -0.45V and 0.675 with an associated oxidation peak at E_{pa} = -0.55V and 0.2 V. The peak separation of this couple (ΔE_p) was 0.1V and 0.475. This ΔE_p value, evidence for the quasi-reversible Ni(II)/Ni(I) couple. The first reduction wave of the copper complexes [Cu (SL2)Cl₂] was safely assigned to the irreversible couple Cu(II)/Cu(I) with E_{pc} = -0.65 and 0.75 E_{pa} = -0.75V and 0.675V, ΔE_p (E_{pc} - E_{pa}) = 0.125V and 0.150V. The ratio *ip,c* / *ip,a* > 1 confirms the irreversible nature of the electrode couple [25]. The Zn(II) complex exhibited one quasi-reversible peak. A cyclic voltammogram of Zn(II) displays one reduction peak at E_{pc} = -0.16 V with an associated oxidation peak at E_{pa} = 0.36 V corresponding to the Zn(II)/Zn(I), it was evidence for quasi-reversible nature associated with one electron reduction.

Table 5: Cyclicvoltammetry values of compounds

Compound	E _{pc1}	E _{pc2}	E _{pa1}	E _{pa2}	Δ E _{p1}	Δ E _{p2}
Co(SL1)Cl ₂	-0.25	0.55	-0.475	0.25	0.225	0.3
Ni(SL1)Cl ₂	-0.375	-	-0.575	-	0.2	-
Cu(SL1)Cl ₂	-0.35	0.6	-0.55	0.4	0.20	0.2
Zn(SL1)Cl ₂	-0.45	0.65	-0.6	0.575	0.15	0.0075
Co(SL2)Cl ₂	-0.4	0.575	-0.6	0.35	0.2	0.22
Ni(SL2)Cl ₂	-0.45	0.675	0.55	0.2	0.1	0.475
Cu(SL2)Cl ₂	-0.65	-0.75	-0.775	0.675	0.125	0.150
Zn(SL2)Cl ₂	-0.16	-	0.36	-	0.2	-

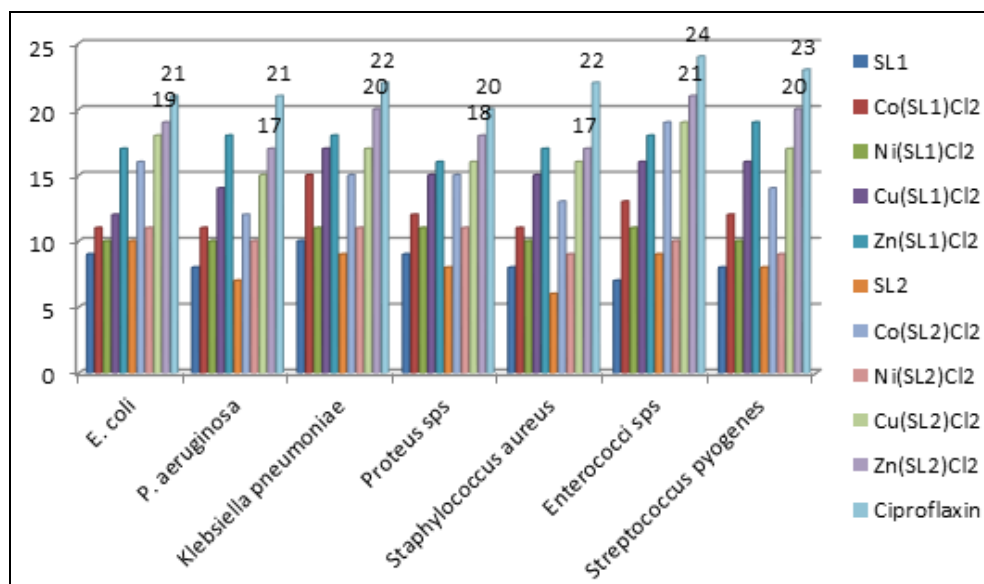
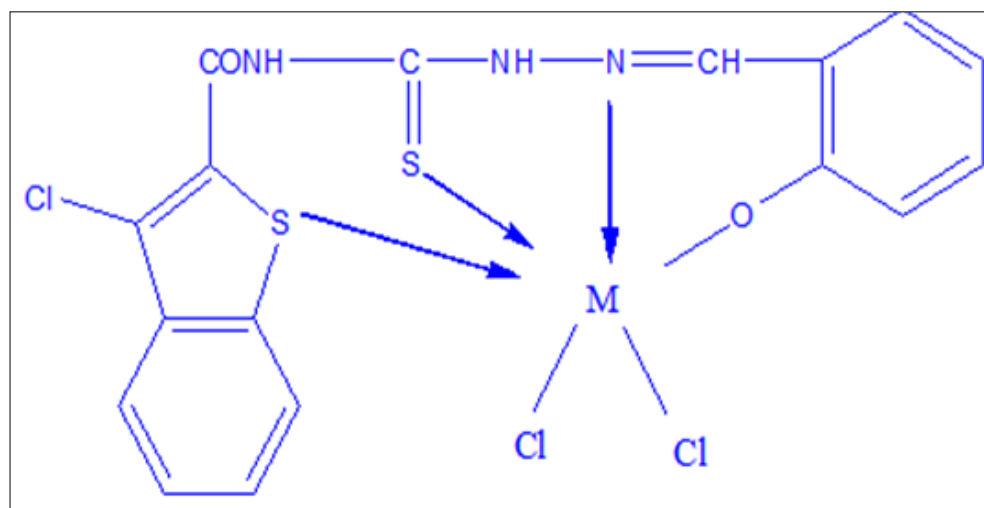
3.8. Antimicrobial Studies

The antimicrobial activity of ligand and its metal complexes were done by disc diffusion method. The tested *in-vitro* against *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, *Proteus sps*, *Staphylococcus aureus*, *Enterococci sps*, *Streptococcus pneumoniae* bacteria were tested at concentration 100 µg mm/ml in DMSO and compared with known antibiotics viz *Ciproflaxin*. For fungal activity, compounds were screened *in vitro* against *Aspergillus niger*, *Candida albicans* with Nutrient Agar medium. From the data, it is clear that the inhibition by Zinc complex was higher than that of the ligand. In the case of antimicrobial studies it was observed that, the ligand was moderately active towards *S.aureus* and less active towards *E.coli*. The activity of these complexes follow the order Zn>Cu>Co>Ni. This high antibacterial activity of ligand and its metal complexes can be attributed on the basis of Overtone's concepts and Tweedy's concepts [26]. According to these concepts, chelation reduces considerably the polarity of the metal ion mainly because of partial sharing of its positive charge with donor groups and possible π- electron delocalization of electron over chelate ring. In the case of antifungal activity, Zn(II) and Cu(II) complexes are more fungi toxic than the free ligand. Based on the above results it is come to know that the Zn(II) complex shows good antibacterial and antifungal activity.

Table 6: Antimicrobial activity of ligands and its complexes

Mol. Formula	Zone of inhibition (mm)								
	Gram-Negative				Gram-Positive			Antifungal	
	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>Klebsiella pneumoniae</i>	<i>Proteus sps</i>	<i>Staphylococcus aureus</i>	<i>Enterococci sps</i>	<i>Streptococcus pyogenes</i>	<i>Aspergillus niger</i>	<i>Candida albicans</i>
SL1	9.0	8.0	10.0	9.0	8.0	7.0	8.0	+	+
Co(SL1)Cl ₂	11.0	11.0	15.0	12.0	11.0	13.0	12.0	+	++
Ni(SL1)Cl ₂	10.0	10.0	11.0	11.0	10.0	11.0	10.0	++	++
Cu(SL1)Cl ₂	12.0	14.0	17.0	15.0	15.0	16.0	16.0	+++	+++
Zn(SL1)Cl ₂	17.0	18.0	18.0	16.0	17.0	18.0	19.0	+++	+++
SL2	10.0	7.0	9.0	8.0	6.0	9.0	8.0	+	+
Co(SL2)Cl ₂	16.0	12.0	15.0	15.0	13.0	19.0	14.0	++	++
Ni(SL2)Cl ₂	11.0	10.0	11.0	11.0	9.0	10.0	9.0	++	++
Cu(SL2)Cl ₂	18.0	15.0	17.0	16.0	16.0	19.0	17.0	+++	+++
Zn(SL2)Cl ₂	19.0	17.0	20.0	18.0	17.0	21.0	20.0	+++	+++
Ciproflaxin	21.0	21.0	22.0	20.0	22.0	24.0	23.0	-	-
Nystatin	-	-	-	-	-	-	-	+++	+++

Standard Nystatin. Highly active = +++ (inhibition zone > 15mm); Moderately active = ++ (inhibition zone > 10mm) Slightly active = + (inhibition zone > 5mm);

**Fig 5:** The variation of antimicrobial activity of ligands (SB1, SB2) and its complexes**Fig 6:** Proposed structure of metal complexes of ligand SL1

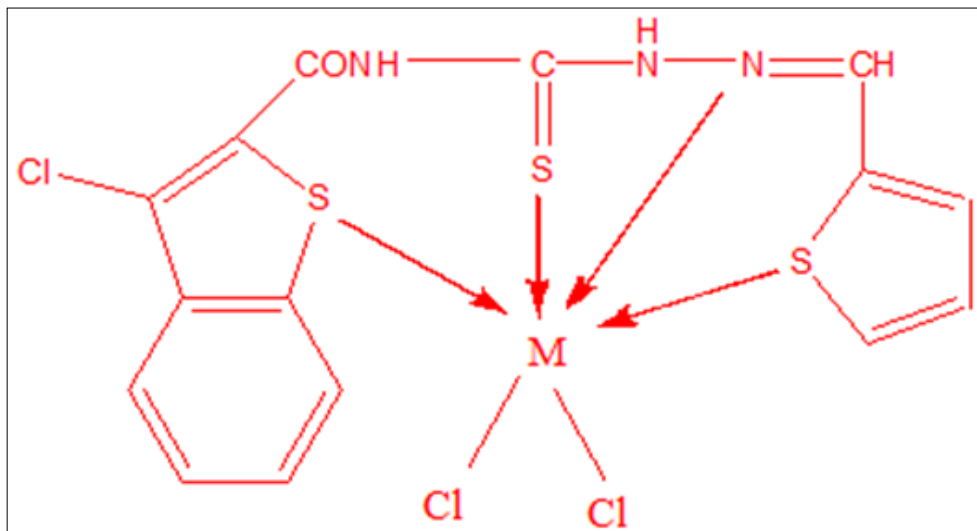


Fig 7: Proposed structure of metal complexes of ligand SL2

4. Conclusion

In this paper the synthesis of the thiosemicarbazone ligands 2-hydroxybenzaldehyde-4-(3-chlorobenzothiophene-carbonyl)-3-thiosemicarbazone(SL1)/thiophen-2-aldehyde-4-(3-chlorobenzothiophenecarbonyl)-3-thiosemicarbazone(SL2) derived by the condensation of 3-chlorobenzothiofene-2-carbonylchloride with thiophene-2-ylmethylenethiosemicarbazide / 2-hydroxyphenylmethylenethiosemicarbazide and its newly synthesized Co(II), Ni(II), Cu(II) and Zn(II) complexes have been described. The ligand coordinates with metal ions through its N and S indicating the bidentate nature of the ligand. This was supported by IR data. On the basis of ESR, electronic and magnetic data, octahedral geometry was assigned to all the complexes. All these observations put together lead us to propose the structure shown below (Fig.6, Fig.7) in which the complex has the stoichiometry of the type $[MLX_2]$. The ligands and its metal complexes show significant antimicrobial activities. Metal complexes were found to be more active against selected bacteria and fungi than the free ligand which is in accordance with the fact that the chelating of metal to ligand increases the microbial activity of the molecule. The results show that Zn(II) and Cu(II) complexes possess more antibacterial activity.

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