



Synthesis, Spectroscopic and Biological Characterization of the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with a New Macrocyclic Tridentate [ONO] Ligand

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Complexes of general formula $[ML_2]$ where M = manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II), L = ethyl 2-[[{(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino}-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate have been prepared. All the complexes were characterized by analytical analysis and physico-chemical methods. The ligand behaves as a tridentate chelating agent and bonded to the metal ion through azomethine nitrogen, ester carbonyl and oximino oxygen atom. Electronic spectra and magnetic susceptibility measurement reveal octahedral geometry. The complexes are found to be non-electrolytic in nature on the basis of low molar conductance. The metal complexes have been screened for their antibacterial activity.

Key Words: Characterization, Metal complexes, Schiff base.

INTRODUCTION

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff base containing nitrogen and other donors¹⁻³. Metal complexes of Schiff bases prepared from heterocyclic system constitute an interesting class of compound with diverse analytical, technological and biological application⁴⁻⁶. Among the variety of heterocyclic Schiff base ligand system those containing thiophene moiety deserve special attention because of the biosteric relationship of thiophene to benzene that has led to several studies on drug analogue in which benzene rings have been replaced by thiophene rings⁷. A literature survey indicates those tetrahydrobenzo (b) thiophene derivatives possess biological activities like antimalarial⁸, anti-inflammatory⁹, antibacterial¹⁰, anticancer¹¹, antibreast cancer¹², potent analgesic activity¹³, antiarrhythmic, serotonin antagonist and antianxiety activities of novel substituted thiophene derivatives synthesized from 2-amino-4,5,6,7-tetrahydro-N-phenylbenzo[b]thiophene-3-carboxamide have been observed¹⁴ a novel clubbed triazolyl thiophene series of Cdk5/p25 inhibitors are potentially useful for the treatment of Alzheimer's disease¹⁵, CNS depressant, skeletal muscle relaxant and anticonvulsant activities are also shown by thiophene derivatives¹⁶.

In this investigation substituted 2-amino thiophene namely ethyl 2-amino-4,5,6,7-tetrahydro benzo(b)thiophene 3-carboxylate has been condensed with (2E)-2-(hydroximino)

1-phenyl ethanone to form a potentially tridentate ligand *viz.*, ethyl 2-[[{(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino}-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate have been synthesized and characterized by their elemental analysis, UV, IR and NMR studies. This ligand was used to synthesize Mn(II), Co(II), Ni(II) Cu(II) and Zn(II) complexes. The complexes were characterized by elemental analysis, magnetic moments, molar conductance, thermal analysis along with electronic, infrared and NMR spectral analysis. The octahedral geometry around these metal ions has been proposed on the basis of magnetic and spectral studies. The antibacterial activities of metal complexes have been screened.

EXPERIMENTAL

All the chemicals used in the project work were of AR grade and were recrystallized while the solvents were purified and double distilled before use. Metal content was determined by standard methods¹⁷. Molar conductance was measured in DMF (10^{-3} M solution) on an ELICO Digital Conductivity meter Model CM-180. The IR spectra were recorded in KBr disc on a Perkin Elmer Model 1600 FTIR spectrophotometer. The electronic spectra of the complex in DMF were recorded on UV-systronic spectrophotometer. The ¹H NMR spectra were recorded in DMSO on a VXR-300S Varian Supercon NMR spectrometer using TMS as the internal reference. Magnetic susceptibility measurements were carried out by employing

the Gouy method using $\text{Hg} [\text{Co}(\text{SCN})_4]$ as a calibrant. Thermo gravimetric studies of the complex were done on Netzsch-429 Thermoanalyser recording at a rate of $10^\circ\text{C min}^{-1}$. Antibacterial activity was determined by Agar cup method. The investigated pathogenic microorganisms were *Pseudomonas aeruginosa*, *Proteus vulgaris*, *E. coli*, *Staphylococcus aureus* and *Staphylococcus aureus* strain 6538p. The metal complexes were dissolved in absolute alcohol to obtain final concentration of $0.5\text{ mg}/0.1\text{ mL}$. A loopful of the given test strain was inoculated in 10 mL of Brain Heart infusion broth and incubated at 37°C for 24 h in order to activate the bacterial strain activity. Sterile 20 mL of Luria Bertani agar was melted and cooled and 0.2 mL test strain ($0.1\text{ O.D. at }530\text{ nm}$) was seeded and poured into a 9 cm diameter aneubra Petri plate. After solidification of the medium agar cups were punched in the plate with the help of a cup borer. The cups were then filled with $50\ \mu\text{L}$ different concentration of the test sample solution. Controls were run (for each bacterial strain and solvent) where pure solvent was added into the cup. The plates were incubated at 37°C for 24 h . The inhibitory zone formed by these compounds against the particular test bacterial strain determined the antibacterial activity of the synthetic compounds (zone size measured in mm). The mean value obtained for three individual replicates was used to calculate the zone growth of inhibition of each plate.

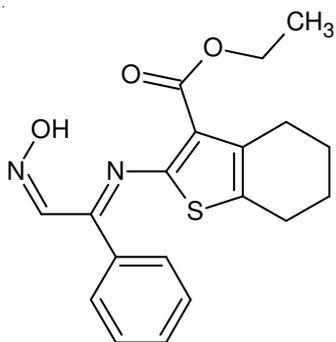
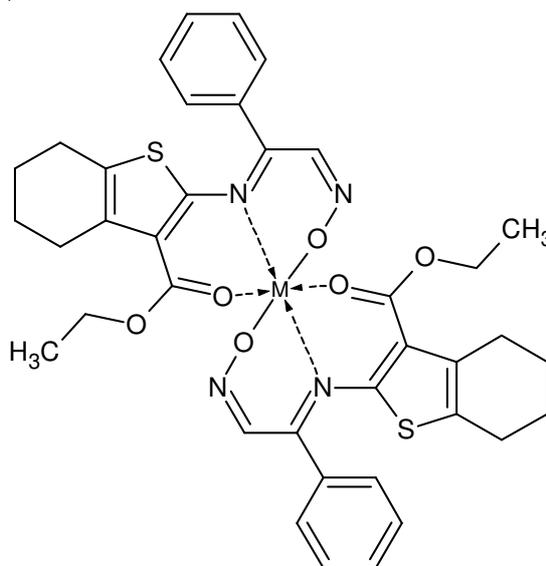


Fig. 1. Structure of ethyl 2-[[[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino]-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate

Preparation of ligand ethyl 2-[[[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino]-4,5,6,7 tetrahydro-1-benzothiophene-3-carboxylate: Ethyl 2-amino-4,5,6,7-tetrahydro benzo(b)thiophene 3-carboxylate and (2E)-2-

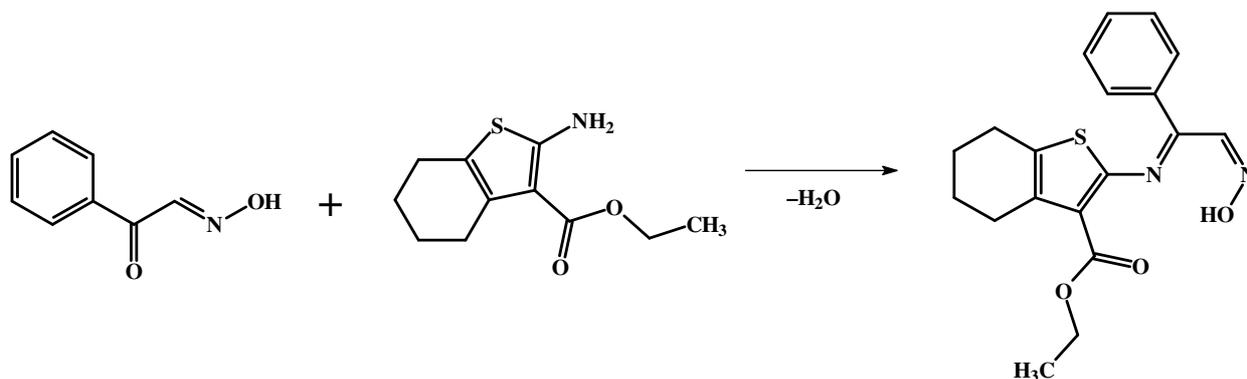
(hydroximino)-1-phenyl ethanone was prepared according to a reported method^{18,19}. To a solution of this thiophene derivatives (0.01 mol) in ethanol (20 mL) was added to a solution of (2E)-2-(hydroximino)1-phenyl ethanone (0.01 mol) dissolved in ethanol (20 mL) in small portion with constant stirring. The resulting solution was refluxed on a water bath for about 4 h . On cooling the solution, the Schiff base crystallized. It was then filtered, washed and sucked dry. Further purification was done by crystallization from ethanol (m.p. 130°C).

Preparation of metal complexes: To a magnetically stirred and warmed ethanolic solution (20 mL) of the ligand (0.01 mol) added an ethanolic solution of metal(II) chloride (0.005 mol) dissolved in ethanol (10 mL) in small parts. After complete additions of the metal salt solution, the pH was adjusted to 7.5 by adding ethanolic ammonia. It was then refluxed for about 6 h in a water bath and the resulting solution was reduced to half the initial volume and allow to stand overnight. The complex formed was filtered, washed successively with aqueous ethanol and ether. Finally the complex was dried in vacuum over P_4O_{10} .



where $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II)

Fig. 2. Metal complexes of ethyl 2-[[[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino]-4,5,6,7 tetrahydro-1-benzothiophene-3-carboxylate



Scheme-I

RESULTS AND DISCUSSION

Analytical data gave clear evidence that condensation of the ethyl 2-amino-4,5,6,7-tetrahydrobenzo(b)thiophene 3-carboxylate and (2E)-2-(hydroximino)-1-phenyl ethanone occurred in 1:1 molar ratio and the structure of the novel Schiff base formed has been elucidated on the basis of UV-visible, infrared and proton NMR spectral studies. The UV spectrum of the present ligand in ethanol exhibit at 235 and 310 nm characteristic of hydroxyimine form, these band can be assignable to π - π^* and n - π^* transition, respectively of the azomethine group. Infrared spectrum of the ligand exhibit a broad band spreading well over the region 3300-3000 cm^{-1} and centered at 3200 cm^{-1} , which can be attributed to hydrogen bonded hydroxyimino $\nu(\text{NOH})$. A strong band appearing at 1710 cm^{-1} , medium intensity band appearing at 1630 and 1596 cm^{-1} could be assignable to ester carbonyl group, azomethine $\nu(\text{C}=\text{N})$ and oximino $\nu(\text{C}=\text{NOH})$ vibration. Characteristic bands due to phenyl ring system in the ligand are found in the region 1500-1440 cm^{-1} , the $\nu(\text{N}-\text{O})$ stretching vibration are observed in the form of medium intensity band at 987 cm^{-1} . The strong band at 2930 cm^{-1} is assign to $\nu(\text{C}-\text{H})$ of cyclohexane where as medium intensity band at 608 cm^{-1} is of $\nu(\text{C}-\text{S})$ mode of thiophene moiety. Proton NMR spectral data of the ligand supported the conclusion drawn on the basis of UV and IR spectral data the absence of NH_2 proton signal in the NMR spectrum of ligand in $\text{DMSO}-d_6$ indicates successful Schiff base formation by replacement of the $\text{C}=\text{O}$ group of (2E)-2-(hydroximino)-1-phenyl ethanone. A signal at 12.4 δ reveals the oximino proton since it is expected to be rather acidic and therefore the weakest shielded proton in the molecule. The signals appearing at 1.50 δ (d) and 4.30 δ (m) can be attributed to methyl and methylene proton, respectively of the ester group. The aromatic proton have been observed in the range 6.18-7.53 δ . A multiplet at 1.7 δ is due to four hydrogen of tetrahydrobenzothiophene.

Elemental analysis data of the complexes of ethyl 2-[[{(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino}-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate (L) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) can be represented by the general formula ML_2 (Table-1). All the complex are insoluble in water, while partly soluble in methanol, ethanol and chloroform and highly soluble in DMF and DMSO. The

complexes are all stable up to 200 °C indicating high thermal stability and hence strong metal to ligand bond. The results of the electrical conductance measurements of the soluble complex in DMF show that they are non-electrolyte in nature (Table-1).

The UV spectral bands characteristic of the ligand is only marginally red shifted in the spectra of the metal complexes indicating that no structural alteration of the ligand occurs on coordination with the metal ions. The disappearance of the entire IR band due to intramolecular hydrogen bonding in the spectra of all the complexes indicates deprotonation of oximino oxygen on complex formation. In the metal complexes, the $\nu(\text{C}=\text{N})$ is displaced to lower wave number by about 20-25 cm^{-1} on bond stabilization of the azomethine moiety upon coordination. The bond corresponding to the ester $\nu(\text{C}=\text{O})$ has been shifted to lower frequency by about 30-35 cm^{-1} in the metal complexes indicating coordination by ester function²⁰. A medium to strong intensity band observed in the range of 1012-997 cm^{-1} in all the complexes, which is assigned of oxygen-bonded $\nu(\text{N}-\text{O})$ of coordinated deprotonated oxime group, which lead to a six-membered ring structure around metal ions^{21,22}. A strong band around 2930 cm^{-1} due to $\nu(\text{C}-\text{H})$ of cyclohexane did not show any appreciable change in metal complexes. Infra spectra of the complexes also showed non-ligand band in the region 430-419 and 520-510 cm^{-1} , which could be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ modes, respectively²³. Absence of $\nu(\text{M}-\text{S})$ band in the far infrared spectra of the metal complexes gives direct evidence to non-involvement of ring sulphur in bond formation (Table-2).

The ^1H NMR spectrum of the ligand and complexes are recorded in $\text{DMSO}-d_6$. Comparison of the ^1H NMR spectra of the ligand and it complexes reveal that the ligand behaves as a tridentate mononegative ONO donor. The disappearance of the signal at 12.4 δ was ascribed to the fact that the ligand underwent deprotonation of the oximino group during complexation. Signals due to the other proton were found in the expected region and shifted by about 0.20-0.50 δ in the spectra of the metal complexes.

The electronic spectra of Mn(II) complex shows absorption band at 17850, 24246 and 27985 cm^{-1} assigned to the transition $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{G})$, $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}(\text{G})$ and $^6\text{A}_{1g} \rightarrow ^4\text{E}_g(\text{G})$, respectively indicating octahedral geometry, which is supported by magnetic

TABLE -1
PHYSICO-CHEMICAL CHARACTERISTIC OF SCHIFF BASE LIGAND AND ITS METAL COMPLEXES

Compound	Colour	f.w.	Elemental analysis (%) found (calcd.) (%)				Molar cond. ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
			C	N	S	M	
L	Yellow	356.44	63.2 (64.02)	6.93 (7.86)	8.5 (9.0)	—	—
MnL ₂	Light brown	765.79	60.25 (59.60)	7.95 (7.32)	8.24 (8.37)	6.95 (7.17)	10.53
CoL ₂	Red	769.79	61.05 (59.29)	7.12 (7.28)	7.95 (8.33)	6.89 (7.66)	9.68
NiL ₂	Dark brown	769.55	58.82 (59.31)	6.92 (7.28)	8.95 (8.33)	8.2 (8.21)	11.62
CuL ₂	Black	774.41	57.85 (58.94)	8.02 (7.23)	7.82 (8.28)	8.23 (8.21)	7.82
ZnL ₂	Yellow	776.27	59.23 (58.79)	7.10 (7.22)	7.67 (8.26)	8.82 (6.43)	12.56

TABLE-2
IMPORTANT IR SPECTRAL BANDS OF SCHIFF BASE AND ITS METAL COMPLEXES

L	MnL ₂	CoL ₂	NiL ₂	CuL ₂	ZnL ₂	Tentative assignment
3200 br	–	–	–	–	–	v(O-H)
2930 m	2939 m	2935 w	2936 m	2938 m	2930 w	v(C-H)
1710 s	1672 s	1664 s	1679 s	1665 s	1670 s	v(C=O)
1630 s	1600 s	1608 s	1610 s	1607 s	1606 s	v(C=N) azomethine
1595m	1575 m	1580 m	1565 m	1582 m	1578 m	v(C=N) oximino
987 m	1000 m	1009 m	1012 m	997 m	1010 m	v(N-O)
608 s	608 m	609 s	608 s	609 m	608 s	v(C=S)
–	510 m	515 m	518 m	520 m	513 m	v(M-N)
–	420 m	435 m	425 m	432 m	430 m	v(M-O)

L = Ethyl 2-[[[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino]-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate.

moments value of 4.92 BM. The electronic spectrum of Co(II) show absorption band at 9826, 16852 and 23574 cm⁻¹ attributed to the transition ⁴T_{1g}(F) → ⁴T_{2g}(F)(v₁), ⁴T_{1g}(F) → ⁴A_{2g}(F)(v₂) and ⁴T_{1g}(F) → ⁴T_{1g}(P)(v₃), respectively. This confirms octahedral geometry for the Co(II) complex. The magnetic moment value of 4.52 BM is found to be well within the range as expected for octahedral Co(II) complexes. Ni(II) complex exhibit three absorption band 11363, 16357 and 27685 cm⁻¹, which may be assigned to the ³A_{2g}(F) → ³T_{2g}(F)(v₁), ³A_{2g}(F) → ³T_{1g}(F)(v₂) and ³A_{2g}(F) → ³T_{1g}(P)(v₃) transition, respectively indicating octahedral geometry²⁴. The magnetic moment value of 3.18 BM supports octahedral geometry. The structure is further confirmed by ratio v₂/v₁ = 1.44 which is being less than 2 as required for octahedral complex. The electronic spectrum of Cu(II) complex show a band at 16543 cm⁻¹ assignable to ²E_g → ²T_{2g} characteristic of octahedral geometry and a band at 26852 cm⁻¹ may be assigned due to charge transfer. The magnetic moment of 1.67 BM supporting the octahedral structure (Table-3). The Zn(II) complex is diamagnetic and there is no *d-d* transition. The elemental analyses are in good agreement with the proposed formula suggesting octahedral structure.

TABLE-3
ELECTRONIC SPECTRAL DATA AND MAGNETIC VALUES OF THE METAL COMPLEXES

Complex	Absorption band (cm ⁻¹)	Tentative assignment	Magnetic moment (BM)
MnL ₂	17850	⁶ A _{1g} → ⁴ T _{1g} (G),	4.92
	24246	⁶ A _{1g} → ⁴ T _{2g} (G)	
	27985	⁶ A _{1g} → ⁴ E _g (G)	
CoL ₂	9826,	⁴ T _{1g} (F) → ⁴ T _{2g} (F) (v ₁)	4.52
	16852	⁴ T _{1g} (F) → ⁴ A _{2g} (F)(v ₂)	
	23574	⁴ T _{1g} (F) → ⁴ T _{1g} (P)(v ₃)	
NiL ₂	11363	³ A _{2g} (F) → ³ T _{2g} (F) (v ₁)	3.18
	16357	³ A _{2g} (F) → ³ T _{1g} (F) (v ₂)	
	27685	³ A _{2g} (F) → ³ T _{1g} (P)(v ₃)	
CuL ₂	16543 26852	² E _g → ² T _{2g} charge transfer	1.67

Thermal decomposition of the complexes was studied by TG technique in nitrogen atmosphere. There is no weight loss up to 230 °C and this ruled out the presence of any water molecule in the complexes (Fig. 3).

The thermogram of Mn(II) complex indicated that it was stable upto 220 °C thermal decomposition took place in the temperature range of 230-500 °C. First TG loss was observed

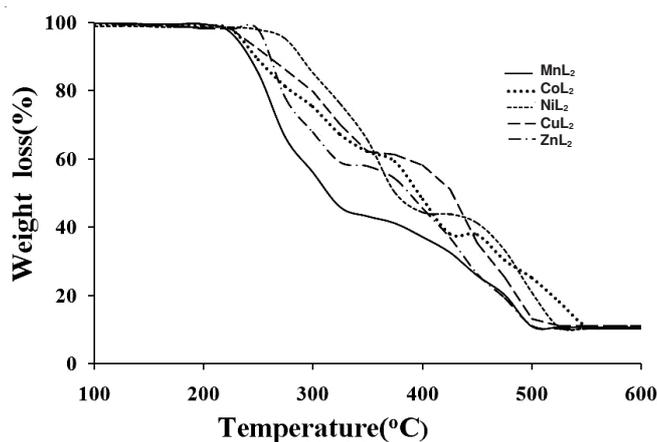


Fig. 3. TGA pattern of metal complexes of ethyl 2-[[[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino]-4,5,6,7 tetrahydro-1-benzothiophene-3-carboxylate

in 230-310 °C with the loss of substituted thiophene moiety 2C₁₁H₁₃O₂S (theo.54.66 %.exp., 53.82 %) followed by an exotherm at 254 °C second TG loss was in the temperature range of 390-500 °C with a loss of remaining ligand fragments 2C₈H₆N₂+O) (theo.36.08 %. exp., 35.46 %) followed by an exotherm at 475 °C the residue left was of weight correspond to MnO (theo. 9.27 %. exp., 10.72 %). The thermogram of Co(II) complex indicated that it was stable upto 225 °C thermal decomposition took place in the temperature range of 225-550 °C. First TG loss was observed in 225-375 °C with the loss of 2C₅H₉S and 2C₂H₅O (theo. 41.11 %. exp., 40.62 %) followed by an exotherm at 290 °C. Second TG loss was in the temperature range of 400-430 °C with a loss of phenyl moiety 2C₆H₅ (theo. 20.29 %. exp., 21.46 %) followed by an exotherm at 415 °C. Third TG loss for Co(II) complex occurred in the temperature range of 470-550 °C with a loss of remaining ligand moiety 2C₅N₂+O) followed by an exotherm at 514 °C the residue left was of weight correspond to CoO (theo. 9.73 %. exp, 10.74 %). The thermogram of Ni(II) complex indicated that it was stable upto 270 °C thermal decomposition took place in the temperature range of 275-520 °C. First TG loss was observed in 250-350 °C with the loss of substituted thiophene moiety 2C₁₁H₁₃O₂S (theo. 39.83 %. exp., 38.20 %) followed by an exotherm at 285 °C. Second TG loss was in the temperature range of 450-520 °C with a loss of remaining ligand fragments 2C₈H₆N₂+O) (theo.36.17 %. exp., 34.06 %) followed by an exotherm at 484 °C. The residue left was of weight correspond to NiO (theo. 9.70 %.exp., 10.32 %). The

thermogram of Cu(II) complex indicated that it was stable upto 250 °C. Thermal decomposition took place in the temperature range of 250-510 °C. First TG loss was observed in 250-350 °C with the loss of 2C₅H₉S and 2C₂H₅O (theo. 39.83 % exp., 38.20 %) followed by an exotherm at 285 °C. Second TG loss was in the temperature range of 410-510 °C with a loss of remaining ligand fragments 2C₁₁H₅N₂+(O) (theo. 49.90 % exp. 50.70 %) followed by an exotherm at 444 °C. The residue left was of weight correspond to CuO. (theo. 10.27 % exp., 11.10 %). The thermogram of Zn(II) complex indicated that it was stable upto 260 °C. Thermal decomposition took place in the temperature range of 265-510 °C. First TG loss was observed in 265-325 °C with the loss of 2C₅H₉S and 2C₂H₅O (theo. 39.74 % exp., 40.82 %) followed by an exotherm at 278 °C. Second TG loss was in the temperature range of 380-500 °C with a loss of remaining ligand fragments 2C₁₁H₅N₂+(O) (theo. 49.78 % exp., 48.95 %) followed by an exotherm at 429 °C. The residue left was of weight correspond to ZnO (theo. 10.48 % exp., 10.23 %). The TGA pattern for the complexes are shown in Fig. 3 and TGA/DTA data of complexes are given in Table-4.

The kinetic parameters such as activation energies (E*), enthalpy (ΔH*), entropy (ΔS*) and free energy change of decomposition (ΔG*) were evaluated graphically by employing the Coats-Redfern relation²⁵:

$$\log \left[\frac{\log \left\{ \frac{W_f}{(W_f - W)} \right\}}{T^2} \right] = \log \frac{AR}{\theta E^*} \left[\frac{(1-2RT)}{E^*} \right] - \frac{E^*}{2.303RT} \quad (1)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to the temperature T, R is the gas constant, E* is the activation energy in kJ mol⁻¹, θ is the heating rate and (1-(2RT/E*)) ≈ 1. A plot of the left-hand side of eqn. 1 against 1/T gives a slope from which E* was calculated and A (Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS*), enthalpy of activation (ΔH*) and the free energy of activation (ΔG*) were calculated using the following equation:

$$\Delta S^* = 2.303R \log \left(\frac{Ah}{kT} \right) \quad (2)$$

$$\Delta H^* = E^* - RT \quad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$

where k and h are the Boltzmann and Plank constants, respectively. The calculated values E*, A, ΔS*, ΔH* and ΔG* for the decomposition steps are given in Table-5. The correlation coefficient of the Arrhenius plots of the thermal decomposition

TABLE-4
THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA) OF COMPLEXES

Complexes	Temperature Range (°C)	Weight loss (%) exp. (theo)	Decomposition product	DTA peak (°C)
MnL ₂	230-310	53.82(54.66)	2C ₁₁ H ₁₃ O S	274(exo)
	390-500	35.46(36.08)	2C ₅ H ₉ N ₂ +(O)	425(exo)
	>500 (Residue)	10.72(9.26)	MnO	
CoL ₂	225-375	40.62(41.11)	2C ₆ H ₉ S, 2C ₂ H ₅ O	290(exo)
	400-430	21.46(20.29)	2C ₅ H ₉	415(exo)
	470-550	26.98(28.87)	2C ₅ N ₂ +(O)	514(exo)
	>550(Residue)	10.94(9.73)	CoO	
NiL ₂	275-390	55.62(54.13)	2C ₁₁ H ₁₃ O S	335(exo)
	450-520	34.06(36.17)	2C ₅ H ₉ N ₂ +(O)	484(exo)
	>520(Residue)	10.32(9.70)	NiO	
CuL ₂	250-350	38.20(39.83)	2C ₆ H ₉ S, 2C ₂ H ₅ O	285(exo)
	410-510	50.70(49.90)	2C ₁₁ H ₅ N ₂ +(O)	444(exo)
	>510(Residue)	11.10(10.27)	CuO	
ZnL ₂	265-325	40.82(39.74)	2C ₆ H ₉ S, 2C ₂ H ₅ O	278(exo)
	380-500	48.95(49.78)	2C ₁₁ H ₅ N ₂ +(O)	429(exo)
	>500(Residue)	10.23(10.48)	ZnO	

TABLE -5
KINETIC DATA ON COMPLEXES

Complexes	Temp. range (K)	E* (kJ mol ⁻¹)	A (s ⁻¹)	ΔS* (JK ⁻¹ mol ⁻¹)	ΔH* (kJ mol ⁻¹)	ΔG* (kJ mol ⁻¹)	r
MnL ₂	503-583	99.87	5.82 × 10 ⁸	-82.18	95.32	140.28	0.972
	663-773	124.72	6.21 × 10 ⁷	-102.81	118.92	190.68	0.978
CoL ₂	498-648	65.90	7.93 × 10 ⁴	-156.44	61.22	149.29	0.925
	673-703	463.17	6.85 × 10 ³⁴	415.22	457.45	171.77	0.989
NiL ₂	743-823	131.39	3.69 × 10 ⁸	-89.0	456.63	526.67	0.998
	548-663	95.56	1.34 × 10 ⁷	-114.42	90.51	160.08	0.952
CuL ₂	723-793	263.67	1.83 × 10 ¹⁷	96.95	257.38	183.39	0.977
	523-623	95.28	3.96 × 10 ⁷	-104.69	90.64	149.05	0.981
ZnL ₂	683-783	161.45	3.45 × 10 ¹⁰	-50.49	155.49	191.69	0.975
	538-598	131.42	3.52 × 10 ¹¹	-28.97	126.84	142.81	0.984
	653-773	117.35	3.01 × 10 ⁷	-108.88	111.52	187.95	0.989

steps were found to lie in the range 0.92-0.99, showing a good fit with the linear function. In the present studies, the numerical values of activation energy, frequency factor and entropy of activation indicates about smoothness of the feasibility and reaction rate of the initial reactants and intermolecular stage compounds. The negative values for entropy of activated complexes (except second decomposition step of CoL_2 and NiL_2 complexes) have more ordered or more rigid structure than the reactants or intermediate and the reaction are slower than normal²⁶. These values are comparable with other observation^{27,28}. The order of stability of complexes on the basis of activation energy is $\text{ZnL}_2 > \text{MnL}_2 > \text{NiL}_2 > \text{CuL}_2 > \text{CoL}_2$ (on the basis of first decomposition stage) and $\text{CoL}_2 > \text{NiL}_2 > \text{CuL}_2 > \text{MnL}_2 > \text{ZnL}_2$ (on the basis of second decomposition stage).

Evaluation of antibacterial activity was done by agar cup method. The results of antibacterial activity indicate that all the test compounds exhibited moderate activity against the tested bacteria except Ni(II) complex (Fig. 4). Cu(II) complex showed good activity against *Pseudomonas aeruginosa*, *S. aureus*, *S. aureus* 6538p strains and moderate activity against *E. coli* and minimum against *P. vulgaris*. Co(II) complex exhibited good activity against *E. coli*, moderate against *P. aeruginosa* and *P. vulgaris*, minimum activity against *S. aureus* and *S. aureus* 6538p strains. Mn(II) complex exhibited good antibacterial activity against *S. aureus* and *S. aureus* 6538p and *P. aeruginosa*, where as Zn(II) complex showed moderate activity against all five microorganisms used in this study while Ni(II) complexes did not show antibacterial activity against any of the pathogens used in this study.

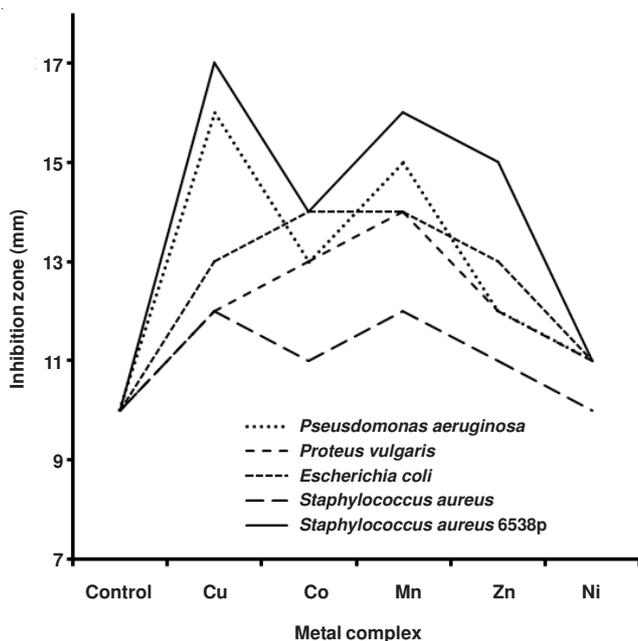


Fig. 4. Antibacterial activity of metal complexes of ethyl 2-[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate

Heavy metals can damage the cell membranes, alter enzymes specificity, disrupt cellular functions and damage the structure of the DNA. Toxicity of these heavy metals occurs through the displacement of essential metals from their native

binding sites or through ligand interactions²⁹. Also, toxicity can occur as a result of alterations in the conformational structure of the nucleic acids and proteins and interference with oxidative phosphorylation and osmotic balance^{29,30}. It is observed that metal chelates have higher antibacterial activity; this is because of an increase in cell permeability. The lipid membrane which surrounds the cell favours the passage of only lipid soluble materials and it is known that liposolubility is an important factor controlling antimicrobial activity. In the present study low activity of the some metal complexes may be because of which penetration of the complex through lipid membrane was decreased and hence could neither block nor inhibit the growth of the microorganisms. This is confirming the antibacterial activity is dependent on the molecular structure of the complex³¹. Copper(II) complex is effective against methicillin-resistant *Staphylococcus aureus*³², *Escherichia coli*³³ and other pathogens like *Enterobacter aerogenes*, *Escherichia coli* O157: H7 and *Pseudomonas aeruginosa*.

Conclusion

From the present investigation it has been observed that a new ligand ethyl 2-[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidene]amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxylate form a complex with metal ions like Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in 2:1 ratio. The data explain its octahedral geometry of the complexes. The results of antibacterial activity indicate that all the complexes exhibited moderate activity against the tested bacteria except Ni(II) complex.

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