

## Synthesis, Spectroscopic Characterization and Thermal Study of Some Transition Metal Complexes of 2-Amino-N'-[(1E,2Z)-2-(hydroxyimino)-1-phenylethylidene]-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazide

SAKINA Z. BOOTWALA

Department of Chemistry, Wilson College, Mumbai-400 007, India

Corresponding author: E-mail: szbootwala@gmail.com

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Complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with an asymmetric tridentate hydrazones derivative synthesized from 2-amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazide and (2E)-2-(hydroxyimino)-1-phenylethanone were synthesized and characterized by analytical analysis and physical-chemical methods. The IR spectral data suggested that the ligand behaves as a monobasic tridentate ligand towards the central metal ion with an ONO donor atom sequentially. From the micro analytical data, the stoichiometry of the complexes 1:1 (metal: ligand) of Cu(II) and Zn(II) complexes, where as 1:2 (metal:ligand) of Mn(II),Co(II) and Ni(II) complexes. The physico-chemical data suggested distorted square planer geometry of Cu(II) complex, tetrahedral geometry of Zn(II) complex and octahedral geometry for the Mn(II), Co(II) and Ni(II) complexes. The thermal behaviour (TGA/DTA) of the complexes were studied and kinetic parameter were determined by Coats-Redfern method.

**Key Words:** Hydrazones derivative, Asymmetrical tridentate, Transition metal complexes, Thermal analysis.

### INTRODUCTION

Hydrazones and their metal complexes have attracted considerable attention due to their application in numerous industrial and biological fields. Applications such as extraction and spectrophotometric determination of metal ions<sup>1,2</sup> and spectrophotometric determination of some species in pharmaceutical formulation<sup>3</sup> as well as in catalytic processes<sup>4,5</sup> and wastewater treatment<sup>6</sup> are reported. Especially, isonicotin-hydrazide and its N-isopropyl acylhydrazone have been used as effective drugs in curing human tuberculosis in the past few years<sup>7</sup>. Metal complexes of acylhydrazones, particularly the copper(II) complexes of 2-pyridine-carboxyaldehyde-2-pyridylhydrazone and salicylaldehyde benzoylhydrazone show antitumour activity<sup>8</sup>.

Due to the biological importance and strong ability to form stable chelates with metal ions of acylhydrazones, we synthesized a new ligand 2-amino-N'-[(1E,2Z)-2-(hydroxyimino)-1-phenylethylidene]-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazide and characterized by their elemental analysis, UV, IR and NMR studies. This ligand were used to synthesized Mn(II), Co(II), Ni(II) Cu(II) and Zn(II) complexes. The complexes were characterized by elemental analysis, magnetic moments, molar conductance and thermal analysis along with electronic, infrared, NMR and EPR spectral analysis.

### EXPERIMENTAL

All the chemical used in the project work were of AR grade and was recrystallized while the solvent were purified and double distilled before use. Metal content was determined by the standard methods<sup>9</sup>. 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 <sup>1</sup>H NMR spectra was recorded in DMSO on a VXR-300S Varian Supercon NMR Spectrometer using TMS as the internal reference. The EPR spectrum of the copper(II) complex was recorded using a Varian-112EPR spectrometer using DPPH as reference material. Magnetic susceptibility measurements were carried out by employing the Gouy method using Hg[Co(SCN)<sub>4</sub>] as a calibrant. Thermo gravimetric studies of the complex were done on Netzch-429 Thermoanalyser recording at a rate of 10 °C min<sup>-1</sup>.

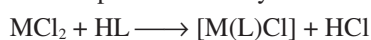
**Preparation of ligand 2-amino-N'-[(1E,2Z)-2-(hydroxyimino)-1-phenylethylidene]-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazide:** 2-Amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazide and (2Z)-2-(hydroxyimino)-1-phenyl ethanone was prepared according to

a reported method<sup>10,11</sup>, respectively. To a solution of this thiophene carbohydrazone derivatives (0.01 mol) in ethanol (20 mL) was added to a solution of (2Z)-2-(hydroxyimino)-1-phenylethanone (0.01 mol) dissolved in ethanol (20 mL) in small portion with constant stirring. The resulting solution was refluxed on a water bath for *ca.* 4 h. On cooling the solution, the hydrazone crystallized. It was then filtered, washed and sucked dry. Further purification was done by crystallization from ethanol (m.p. 114 °C).

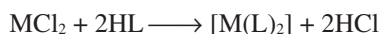
**Preparation of metal complexes:** All the transition metal complexes were prepared by the following general procedure. To a magnetically stirred and warmed ethanolic solution (20 mL) of the ligand (0.01 mol) added an ethanolic solution of the corresponding metal(II) chloride in appropriate ratios dissolved 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 *ca.* 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<sub>4</sub>O<sub>10</sub>.

## RESULTS AND DISCUSSION

Analytical data indicated that (2Z)-2-(hydroxylimino)-1-phenyl ethanone condensed with 2-amino-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazone in 1:1 molar ratio and the product formed well defined complexes with the metal salts. Formation of the complexes can be symbolized as follows:



M = Cu(II), Zn(II)



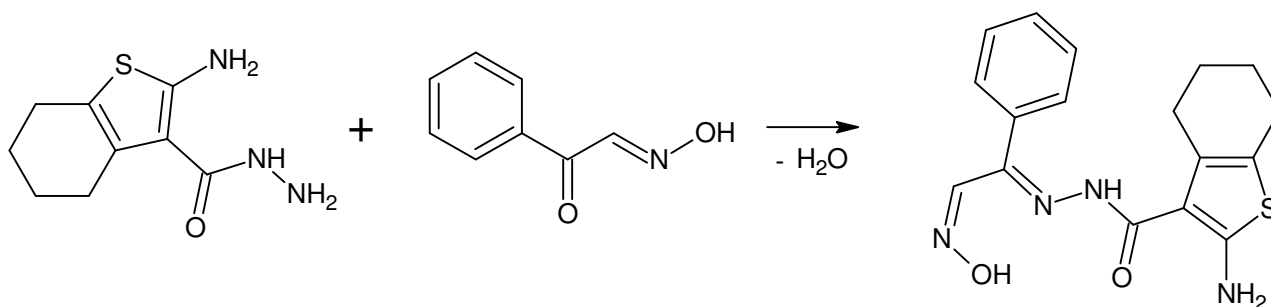
M = Mn(II), Co(II) and Ni(II), HL = 2-amino-N'-[(1E,2Z)-2-(hydroxyimino)-1-phenylethylidene]-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazone.

Formulation of the complexes has been based on their elemental analytical data, molar conductance values and magnetic susceptibility data. The stoichiometry of the complexes 1:1 (metal:ligand) of Cu(II) and Zn(II) complexes, where as 1:2 (metal:ligand) of Mn(II), Co(II) and Ni(II) complexes. All complexes are brightly coloured, non hygroscopic and decomposed above 180 °C the molar conductance values support the non-electrolyte nature of the metal complexes<sup>12</sup> (Table-1).

The spectral data of the compounds and their tentative assignments are shown in Table-2. It can be seen that the characteristic absorption peak present in IR spectra of all complexes are similar which indicate that the complexes have similar

arrangement of ligand atom around metal ions. The bonding of the ligand to the metal ions is investigated by comparing the IR spectra of the free ligand with its metal complexes. In the region 3400-3200 cm<sup>-1</sup> the infrared spectra of ligand and complex exhibit two sharp and intense band at 3275 and 3169 cm<sup>-1</sup> these two band assigned to the primary amine  $\nu(NH_2)$  of substituted thiophene which indicates non-involvement of NH<sub>2</sub> group in metal-ligand bonding. An intense broad band at 3300 cm<sup>-1</sup> tentatively assigned to the  $\nu(NOH)$  vibration which is absent in the spectrum of complexes indicates that oximino OH group takes part in the coordination to metal ions through deprotonation. A sharp band of medium intensity around 3421 cm<sup>-1</sup> is due to  $\nu(NH)$  is shifted to lower frequency by 11-28 cm<sup>-1</sup> in the complexes. The IR spectra of the complex show that the  $\nu(C=O)$  band at 1709 cm<sup>-1</sup> in the spectra of the ligand made a distinct shift towards lower frequency by 50-60 cm<sup>-1</sup>. This suggests that the bonding of the ligand through the carbonyl oxygen in the keto form hydrazones group<sup>13</sup>. The IR spectra of all complexes indicates that  $\nu(C=N)$  band at 1658 cm<sup>-1</sup> in the spectra of the ligand, due to the azomethine linkage were shifted towards lower frequency by 50-60 cm<sup>-1</sup> indicating that the ligand coordination to the metal ions have azomethine nitrogen<sup>14</sup> on the other hand, the characteristic  $\nu(N-N)$  band was found to be shifted from 946 cm<sup>-1</sup> in the spectrum of ligand to 980-976 cm<sup>-1</sup> in the spectra of all complexes confirming that the azomethine nitrogen atom participated in coordination with the metal ions<sup>15</sup>. A medium to strong intensity band observed in the range of 1027-1000 cm<sup>-1</sup> in all the complexes, which is assigned of oxygen-bonded  $\nu(N-O)$  of coordinated deprotonated oxime group, which lead to a six-membered ring structure around metal ions<sup>16</sup>. The appearance of new bands in the 610-550 cm<sup>-1</sup> range for all the complexes was taken as an indication of the presence of covalent metal oxygen bond. On the other hand, the bands present in the 520-510 and 460-430 cm<sup>-1</sup> range may be taken as an indication to the coordination between the metal ions with oxygen and nitrogen atoms, respectively<sup>17-19</sup>. The band at 395 and 385 cm<sup>-1</sup> can be assigned to the presence of  $\nu(M-Cl)$  in copper and zinc complexes<sup>20</sup>, respectively, which was recorded on Plytec 30 spectrometer using CsI disc Table-2, Fig. 1.

The <sup>1</sup>H NMR spectrum of the ligand with its complexes recorded in DMSO-*d*<sub>6</sub> solution with TMS as a standard. A following structural inference has been taken by comparison of the <sup>1</sup>H NMR spectrum of the ligand with their metal complexes. The signal at 8.4 ppm observed in the spectrum of has been assigned to the azomethine (CH=N) proton group. This signal appears downfield in the complexes, indicating the



Scheme-I

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	Cl	M	
L	Yellow	342.41	58.23 (59.63)	16.93 (16.36)	9.85 (9.36)	–	–	–
MnL <sub>2</sub>	Light brown	737.75	54.56 (55.35)	14.85 (15.19)	8.24 (8.69)	–	6.95 (7.45)	11.53
CoL <sub>2</sub>	Red	741.75	54.05 (55.03)	15.12 (15.11)	7.95 (8.65)	–	6.89 (7.95)	19.68
NiL <sub>2</sub>	Dark brown	741.51	54.82 (55.07)	14.92 (15.11)	8.95 (8.65)	–	8.2 (7.92)	14.62
CuLCl	Black	440.41	47.85 (46.36)	13.02 (12.72)	7.82 (7.28)	7.45 (8.05)	15.23 (14.43)	9.82
ZnLCl	Yellow	442.27	45.23 (46.17)	13.10 (12.67)	7.67 (7.25)	7.99 (8.02)	13.82 (14.79)	10.56

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

L	MnL <sub>2</sub>	CoL <sub>2</sub>	NiL <sub>2</sub>	CuLCl	ZnLCl	Tentative assignment
3330 br	–	–	–	–	–	v(N-O-H)
3410 s	3390 s	3375 s	3370 s	3362 s	3354	v(NH)
3275 s	3265 s	3269 s	3274 s	3270 s	3275 s	v(NH <sub>2</sub> )asym
3169 s	3172 m	3180 s	3142 s	3169 s	3170 s	v(NH <sub>2</sub> )sym
2930 m	2939 m	2935 w	2936 m	2938 m	2930 w	v(C-H)
1707 s	1648 s	1647 s	1645 s	1648 s	1647 s	v(C=O)
1658 s	1596 s	1597 s	1599 s	1600 s	1595 s	v(C=N) azomethine
1595 m	1575 m	1573 m	1574 m	1575 m	1574 m	v(C=N) oximino
946 m	976 m	978 m	979 m	972 m	980 m	v(N-N)
990 m	1010 m	1009 m	1012 m	1027 m	1015 m	v(N-O)
608 s	608 m	609 s	608 s	609 m	608 s	v(C=S)
–	550 m	570 m	605 m	610 m	590 m	v(M-O)
–	510 m	515 m	518 m	520 m	513 m	v(M←O)
–	430 m	445 m	448 m	457 m	460 m	v(M←N)
–	–	–	–	395 m	385 m	v(M-Cl)

L = 2-Amino-N'-[(1E,2Z)-2-(hydroxyimino)-1-phenylethylidene]-4,5,6,7-tetrahydro-1-benzothioephene-3-carbohydrazide.

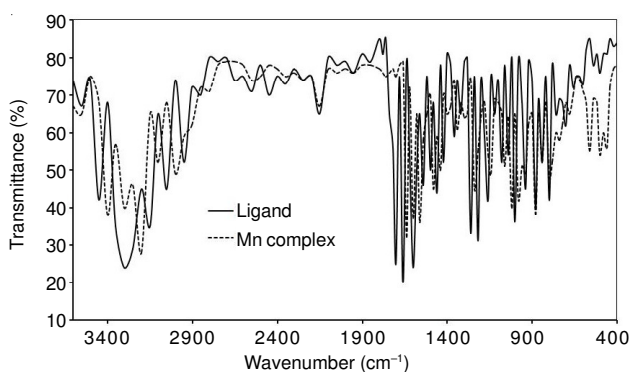


Fig. 1. Infrared spectrum of ligand and MnL<sub>2</sub> complex

coordination of the azomethine group in the metal. The (N-OH) oxime OH signal observed in the spectrum of the ligand at 11.8  $\delta$  is rapidly exchanged with D<sub>2</sub>O. The absence of the signal due to (NOH) in the complexes indicates the deprotonation and coordination of ligand with metal ion through oxygen atom. Two multiplets centered at 2.6-2.7  $\delta$  and doublet at 1.2  $\delta$  in the ligand and metal complexes are due to different hydrogen atom of the tetrahydro benzo thiophene ring. A signal at 7.96  $\delta$  due to NH<sub>2</sub> proton is unaltered on complexes and thus clearly indicates the non involvement of the NH<sub>2</sub> group in complex formation. Phenyl group of phenylethylidene is seen as complex multiplets between 7.8-8.0  $\delta$ . A singlet at 9.95  $\delta$  is attributed to NH proton which is unaffected in the metal ions complexes.

The electronic absorption spectrum of the ligand in DMF showed three band at 270, 320 and 340 nm the first one may

be assigned to intraligand  $\pi \rightarrow \pi^*$  transition which is nearly unchanged on complexation, where as the second and third band may be assigned to the  $n \rightarrow \pi^*$  and charge transfer transition of the azomethine and carbonyl group<sup>21,22</sup>. It is found that these band were shifted to lower energy on complexation, indicating participation of these group in coordination with the metal ions. In addition, the spectra of the complexes showed new bands observed in the 400-380 nm range which may be attributed to the charge transfer transitions.

The electronic spectra of Mn(II) complex shows absorption band at 17900, 24980 and 28750  $\text{cm}^{-1}$  assigned to the transition  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4E_g(G)$ , respectively indicating octahedral geometry<sup>23</sup>, which is supported by magnetic moments value of 5.82 BM. The electronic spectrum of Co(II) show absorption band at 7697, 14560 and 20100  $\text{cm}^{-1}$  attributed to the transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(v_1)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(v_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(v_3)$ , respectively. This confirms octahedral geometry for the Co(II) complex<sup>24,25</sup>. The magnetic moment value of 4.75 BM is found to be well within the range as expected for octahedral Co(II) complexes. Ni(II) complex exhibit three absorption band 10090, 16250 and 24560  $\text{cm}^{-1}$ , which may be assigned to the  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(v_3)$  transition, respectively indicating octahedral geometry<sup>23-25</sup>. The magnetic moment value of 2.92 BM supports octahedral geometry. The square planar Cu(II) complexes are expected to show the transition  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  but band due to these transition usually overlap to give one broad absorption band<sup>24</sup>. The electronic spectrum of

Cu(II) complex exhibits a broad band centered at 18850  $\text{cm}^{-1}$  indicating a distorted square planar geometry around the Cu(II) ion. The magnetic moment of Cu(II) complex 1.69 BM indicating the presence of one unpaired electron. 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 tetra-coordinated Zn(II) complexes. It has been reported that tetra-coordinated Zn(II) complexes, preferred tetrahedral geometry<sup>25</sup>.

Various ligand field parameters<sup>26-28</sup> were calculated for the complexes are listed in Table-3. The results are in agreement with the respective position of anion in spectrochemical series. The nephelauxetic parameter  $\beta$  were readily obtained by using relation  $\beta = B(\text{complex})/B(\text{free ion})$  where B (free ion) for Mn(II) is 786, for Co(II) is 1120 and for Ni(II) is 1041  $\text{cm}^{-1}$  the values of  $\beta$  lies in the range of 0.67-0.89. The value indicates the appreciable covalent character of metal-ligand sigma bond (Table-3).

The EPR spectrum of Cu(II) complex was recorded in DMSO at LNT. The g and A value obtained are  $g_{\parallel} = 2.313$ ,  $g_{\perp} = 2.162$  and  $A_{\parallel} = 145$  G. The trend  $g_{\parallel} > g_{\perp}$  observed for this complex, indicates that unpaired electron is most likely in the  $d_{x^2-y^2}$  orbitals of the copper(II) ion and the special features are characteristic of axial symmetry<sup>29</sup> further  $g_{av} = 2.21$  and  $\alpha^2 = 0.83$  the value of  $\alpha^2$  indicate the covalent nature of the metal-ligand bonding.

Thermal decomposition of the complexes was studied by TG technique in nitrogen atmosphere. There is no weight loss up to 180 °C and this ruled out the presence of any water molecule in the complexes. The thermogram of Mn(II) complex indicated that it was stable upto 210 °C. Thermal decomposition took place in the temperature range of 210-520 °C. First TG loss was observed in 210-300 °C with the loss of amino substituted thiophene moiety  $2\text{C}_8\text{H}_{10}\text{SN}$  (theo 41.27 % exp, 42.82 %) followed by an exotherm at 256 °C. Second TG loss was in the temperature range of 350-430 °C with a loss of phenyl group  $2\text{C}_6\text{H}_5$  (theo 20.63 % exp, 20.46 %) followed by an exotherm at 382 °C. Third TG loss for Mn(II) complex occurred in the temperature range of 450-510 °C with a loss of remaining ligand moiety  $2\text{CONH}$ ,  $2\text{C}_2\text{N}_2\text{H}$  and (O) followed by an exotherm at 468 °C, the residue left was of weight correspond to MnO (theo 9.61 % exp, 9.16 %). The thermogram of Co(II) complex indicated that it was stable upto 180 °C. Thermal decomposition took place in the temperature range of 180-520 °C. First TG loss was observed in 180-280 °C with the

loss of  $2\text{C}_8\text{H}_{10}\text{SN}$  (theo 41.32 % exp 40.62 %) followed by an exotherm at 248 °C. Second TG loss was in the temperature range of 320-410 °C with a loss of phenyl moiety  $2\text{C}_6\text{H}_5$  and  $2\text{CONH}$  group (theo 32.13 % exp, 31.46 %) followed by an exotherm at 395 °C. Third TG loss for Co(II) complex occurred in the temperature range of 440-550 °C with a loss of remaining ligand moiety  $2\text{C}_2\text{N}_2\text{H}+(\text{O})$  followed by an exotherm at 485 °C. The residue left was of weight correspond to CoO (theo 10.10 % exp, 10.94 %). The thermogram of Ni(II) complex indicated that it was stable upto 205 °C. Thermal decomposition took place in the temperature range of 205-475 °C. First TG loss was observed in 205-330 °C with the loss of substituted thiophene moiety  $2\text{C}_8\text{H}_{10}\text{SN}$  and phenyl molecule  $2\text{C}_6\text{H}_5$  (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  $2\text{C}_8\text{H}_6\text{N}_2+(\text{O})$  (theo 52.08 % exp, 53.20 %) followed by an exotherm at 265 °C. The residue left was of weight correspond NiO (theo 10.07 % exp, 10.32 %). The thermogram of Cu(II) complex indicated that it was stable upto 200 °C. Thermal decomposition took place in the temperature range of 200-480 °C. First TG loss was observed in 200-350 °C with the loss of  $\text{C}_8\text{H}_{10}\text{SN}$  and  $\text{C}_6\text{H}_5$  (theo 39.83 % exp, 38.20 %) followed by an exotherm at 275 °C. Second TG loss was in the temperature range of 410-480 °C with a loss of remaining ligand fragments CONH and  $\text{C}_2\text{N}_2\text{H}(\text{O})$  (theo 29.86 % exp, 28.70 %) followed by an exotherm at 464 °C. The residue left was of weight correspond to CuO (theo 18.06 % exp 18.10 %). The thermogram of Zn(II) complex indicated that it was stable upto 195 °C. Thermal decomposition took place in the temperature range of 195-450 °C. First TG loss was observed in 195-360 °C with the loss of  $\text{C}_8\text{H}_{10}\text{SN}$  and  $\text{C}_6\text{H}_5$  (theo 52.30 % exp, 51.82 %) followed by an exotherm at 338 °C. Second TG loss was in the temperature range of 410-450 °C with a loss of remaining ligand fragments CONH,  $\text{C}_2\text{N}_2\text{H}$  and (O) (theo 29.29 % exp, 28.95 %) followed by an exotherm at 419 °C. The residue left was of weight correspond to ZnO (theo 18.41 % exp, 19.23 %). The TGA/DTA data of complexes are given in Table-4.

The kinetic parameters such as activation energies ( $E^*$ ), enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ) and free energy change of decomposition ( $\Delta G^*$ ) were evaluated graphically by employing the Coats-Redfern relation<sup>30</sup>:

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

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

Complex	Absorbion band ( $\text{cm}^{-1}$ )	Tentative assignment	Magnetic moment (BM)	Dq	B ( $\text{cm}^{-1}$ )	$\beta$	$\nu_2/\nu_1$	LFSE (kJ/mol)
MnL <sub>2</sub>	17900	${}^6A_{1g} \rightarrow {}^4T_{1g}(\text{G})$	4.92	1790	538.6	0.685	1.396	0
	24980	${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{G})$						
	28750	${}^6A_{1g} \rightarrow {}^4E_g(\text{G})$						
CoL <sub>2</sub>	7694	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$	4.52	843.7	870	0.896	2.096	80.64
	14560	${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$						
	20000	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$						
NiL <sub>2</sub>	10090	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$	3.18	1009	702.6	0.675	1.610	144.63
	16250	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$						
	24560	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$						

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 <sub>2</sub> ]	210-300	42.82 (41.27)	2C <sub>8</sub> H <sub>10</sub> S N	256 (exo)
	350-430	20.46 (20.63)	2C <sub>6</sub> H <sub>5</sub>	382 (exo)
	450-510	27.56 (28.49)	2CONH+2C <sub>2</sub> N <sub>2</sub> H+(O)	468 (exo)
	> 510 (Residue)	9.16 (9.61)	MnO	
[CoL <sub>2</sub> ]	180-280	40.62 (41.32)	2C <sub>8</sub> H <sub>10</sub> S N	248 (exo)
	320-410	31.46 (32.13)	2C <sub>6</sub> H <sub>5</sub> + 2CONH	395 (exo)
	440-520	16.98 (16.45)	2C <sub>2</sub> N <sub>2</sub> H + (O)	485 (exo)
	> 520 (Residue)	10.94 (10.10)	CoO	
[NiL <sub>2</sub> ]	205-330	61.62 (62.40)	2C <sub>8</sub> H <sub>10</sub> S N + 2C <sub>6</sub> H <sub>5</sub>	265 (exo)
	380-475	28.06 (27.53)	2CONH + 2C <sub>2</sub> N <sub>2</sub> H + (O)	448 (exo)
	> 475 (Residue)	10.32 (10.07)	NiO	
[CuLCl]	200-350	53.20 (52.08)	C <sub>8</sub> H <sub>10</sub> S N + C <sub>6</sub> H <sub>5</sub>	275 (exo)
	410-480	28.70 (29.86)	CONH + C <sub>2</sub> N <sub>2</sub> H + (O)	464 (exo)
	> 480 (Residue)	18.10 (18.06)	CuO	
[ZnLCl]	195-360	51.82 (52.30)	C <sub>8</sub> H <sub>10</sub> S N + C <sub>6</sub> H <sub>5</sub>	338 (exo)
	410-450	28.95 (29.29)	CONH + C <sub>2</sub> N <sub>2</sub> H + (O)	419 (exo)
	> 450 (Residue)	19.23 (18.41)	ZnO	

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  $\text{kJ mol}^{-1}$ ,  $\theta$  is the heating rate and  $(1-(2RT/E^*)) \approx 1$ . 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 ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ) and the free energy of activation ( $\Delta G^*$ ) were calculated using the following equation:

$$\Delta S^* = 2.303 R \log (Ah/kT) \quad (2)$$

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

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

where  $k$  and  $h$  are the Boltzmann and Plank constants, respectively. The calculated values  $E^*$ ,  $A$ ,  $\Delta S^*$ ,  $\Delta H^*$  and  $\Delta G^*$  for the decomposition steps are given in Table-5.

The correlation coefficient of the Arrhenius plots of the thermal decomposition 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 calculated values of the activation energy of the complexes are relatively low indicating autocatalytic effect of the metal ions on the thermal decomposition of the complexes<sup>31,32</sup>. The negative

values for entropy of activated complexes (except third decomposition step of MnL<sub>2</sub> and second decomposition step of CuLCl and ZnLCl complexes) have more ordered or more rigid structure than the reactants or intermediate and the reaction are slower than normal<sup>33</sup>. These values are comparable with other observation<sup>34,35</sup>. The order of stability of complexes on the basis of activation energy is NiL<sub>2</sub> > MnL<sub>2</sub> > CoL<sub>2</sub> > CuLCl > ZnLCl (on the basis of first decomposition stage) and ZnLCl > CuLCl > NiL<sub>2</sub> > MnL<sub>2</sub> > CoL<sub>2</sub> (on the basis of second decomposition stage).

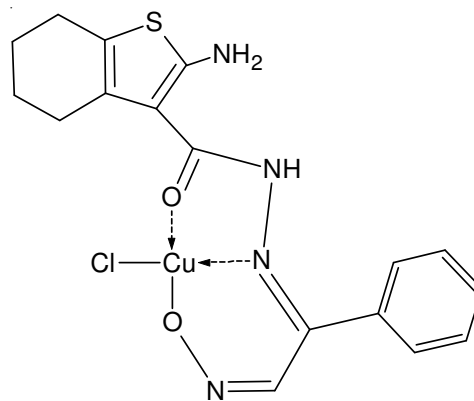


Fig. 2. Structure of [CuLCl] complex

TABLE-5  
KINETIC DATA ON COMPLEXES

Complexes	Temp. range (K)	$E^*$ ( $\text{kJ mol}^{-1}$ )	$A$ ( $\text{s}^{-1}$ )	$\Delta S^*$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )	$\Delta H^*$ ( $\text{kJ mol}^{-1}$ )	$\Delta G^*$ ( $\text{kJ mol}^{-1}$ )	$r$
[MnL <sub>2</sub> ]	483-573	95.12	$4.16 \times 10^8$	-84.68	90.72	135.52	0.979
	623-703	149.95	$1.26 \times 10^{11}$	-38.97	144.07	169.60	0.998
	723-783	258.22	$1.47 \times 10^{16}$	57.03	237.79	195.53	0.957
[CoL <sub>2</sub> ]	453-553	81.30	$2.12 \times 10^7$	-109.32	76.97	133.92	0.978
	593-683	96.42	$5.26 \times 10^6$	-122.97	90.87	173.01	0.989
	713-793	169.60	$5.49 \times 10^{10}$	-47.21	163.30	199.09	0.998
[NiL <sub>2</sub> ]	478-603	97.29	$2.43 \times 10^8$	-89.31	92.81	140.16	0.969
	653-748	186.68	$1.39 \times 10^{13}$	-0.66	180.96	181.17	0.979
[CuLCl]	472-623	66.19	$2.21 \times 10^5$	-147.66	61.63	142.55	0.989
	683-753	198.28	$4.47 \times 10^{13}$	8.88	192.16	185.61	0.988
[ZnLCl]	468-633	40.09	$4.74 \times 10^2$	-199.68	35.01	157.01	0.985
	683-723	258.22	$5.65 \times 10^{18}$	107.09	252.46	178.36	0.995

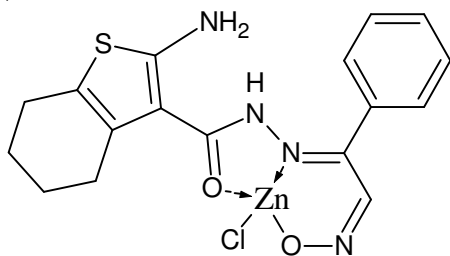
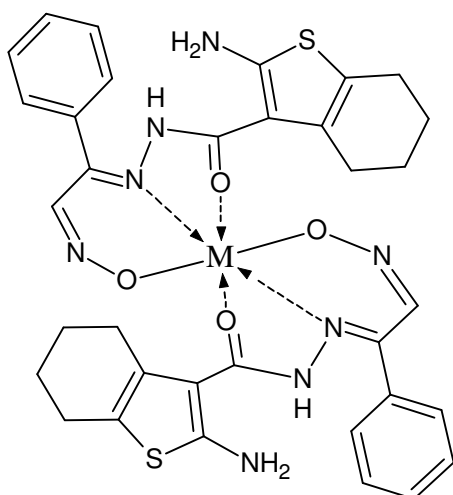


Fig. 3. Structure of [ZnLCl] complex

Fig. 4. Structure of [ML<sub>2</sub>] complex: M = Mn(II), Co(II) and Ni(II) ion

## Conclusion

From the present investigation it has been observed that a new ligand = 2-amino-N'-[(1E,2Z)-2-(hydroxyimino)-1-phenylethylidene]-4,5,6,7-tetrahydro-1-benzothiophene-3-carbohydrazide form a complex with metal ions like Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The data suggested that the ligand behaves as a monobasic tridentate ligand towards the central metal ion with an ONO donor atom sequentially. The physico-chemical data suggested distorted square planer geometry of Cu(II) complex, tetrahedral geometry of Zn(II) complex and octahedral geometry for the Mn(II), Co(II) and Ni(II) complexes.

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