

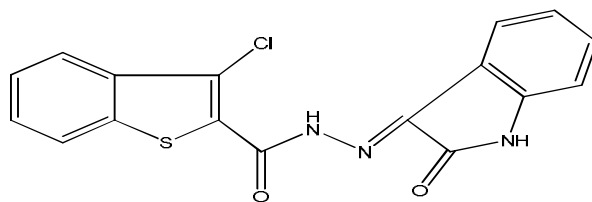
**Synthesis, spectral characterization and antimicrobial activity studies of some complexes of Schiff base derived from (E)-3-chloro-N'-(2-oxoindolin-3-ylidene) benzo[b]thiophene-2-carbohydrazide****Razak Gafoor Sab^{1*}, Fazlur Rahaman² and B.H.M.Mruthyunjayaswamy²**1. Department of Chemistry, HKES SLN College of Engineering, Y-Camp, Raichur-584135, Karnataka, **INDIA**2. Department of Studies and Research in Chemistry, Gulbarga University, Gulbarga-585106, Karnataka, **INDIA**Email: razak_ustaad@rediffmail.comAccepted on 19th May 2014**ABSTRACT**

Complexes of Cu(II), Ni(II), Zn(II), Mn(II), Fe(II), Cd(II) and Hg(II) with the Schiff base derived from 3-chlorobenzo(b)thiophene-2-carbohydrazide and Indoline-2,3-dione has been synthesized and characterized on the basis of elemental analysis, electrical conductance, ESR, XRD, IR, FAB-MASS, ¹HNMR, electronic spectra and magnetic susceptibility measurements. The Schiff base behaves as tridentate ligand coordinating through ONO donor site and forms the complexes of the types ML₂. (H₂O)_n (where, L= Schiff base, M=Metal). The complexes are non-electrolytes, monomers and octahedral in nature. The ligand and its complexes have been screened for their antimicrobial activity.

Keywords: Carbohydrazide, Schiff base, ESR, XRD, Antimicrobial activity.**INTRODUCTION**

Metal complexes with potentially tridentate and tetradentate ligands have evoked much interest in coordination chemistry [1]. Schiff base complexes of transition metals have played a prominent role in the development of coordination chemistry [2]. Several Schiff base metal complexes have been studied because of their industrial and biological applications [3-5]. Schiff bases containing polyfunctional groups offer many practical advantages and unique structural environment for complexation [6]. Carbohydrazide compounds most directly associated with the foundation of organic chemistry are of special interest in view of their use in the synthesis of heterocyclic molecule, analytical chemistry, polymer and pharmaceutical applications. The chemistry of these compounds and some of their derivatives are reviewed by Kurzer and Wilkinson [7]. The hydrazine group of these compounds display normal reactivity towards carbonyl compounds and give rise to a large variety of hydrazone or Schiff bases. It has been well established that these hydrazones are capable of exhibiting keto-enol tautomerism and one of the form is retained when they form complexes with the transition metal ions [8].

In view of these findings and in continuation of our research work on coordination chemistry [9-11], we report here the synthesis, characterization and antimicrobial activity studies of Cu(II), Ni(II), Zn(II), Mn(II), Fe(II), Cd(II) and Hg(II) complexes of Schiff base .



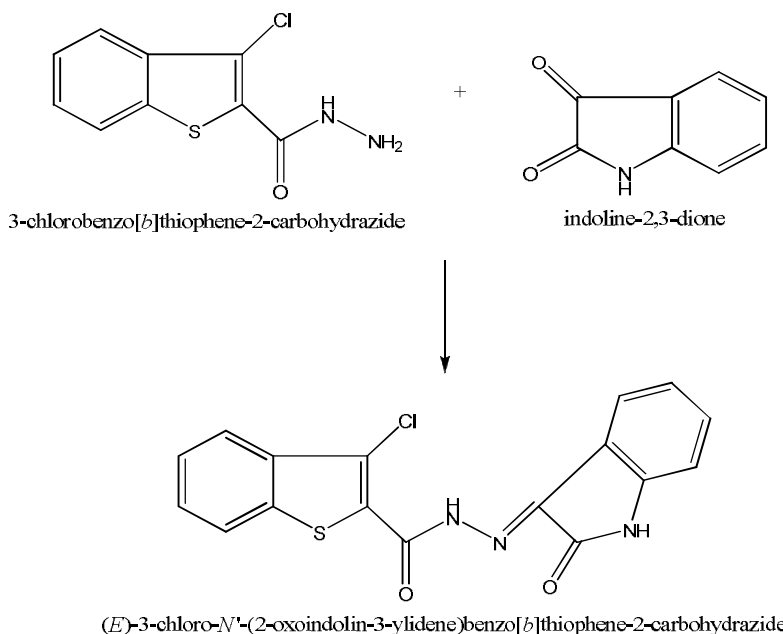
(E)-3-chloro-N'-(2-oxoindolin-3-ylidene)benzo[b]thiophene-2-carbohydrazide

MATERIALS AND METHODS

All the chemicals are of analytical grade. Solvents were dried and distilled before use according to standard procedures. Indoline-2, 3-dione used is of reagent grade and acetic acid used is of an analytical grade.

Synthesis of 3-chloro-N'-[(1E, 2E)-3-phenylprop-2-en-1-ylidene]-1-benzothiophene-2-Carbohydrazide (Ligand L) : A mixture of 3-chlorobenzo (b) thiophene-2-carbohydrazide (0.001mol) and indoline-2, 3-dione (0.001mol) in ethanol (20ml) containing few drops of glacial acetic acid was refluxed for about 5 h on water bath. The reaction mixture was cooled to room temperature; the separated compound was collected by filtration, washed with little alcohol and recrystallized from absolute ethanol (Scheme-1). (m.p.: 211-213 °C).

Synthesis of Cu(II), Ni(II), Zn(II), Mn(II), Fe(II), Cd(II) and Hg(II) complexes : To a hot solution of (E)-3-chloro-N'-(2-oxoindolin-3-ylidene)benzo[b]thiophene-2-carbohydrazide ligand L (0.001 mol) in ethanol (30 ml) was added a solution of the appropriate metal(II) chlorides (0.001 mol) in ethanol (10ml) and the mixture was refluxed for 6-8 h. The resulting solid complex was collected by filtration and washed with hot ethanol and dried in a vacuum over anhydrous calcium chloride in desiccators. (Yield 68-73%).



Scheme 1

The agar diffusion cup plate method was followed for antibacterial and antifungal assay as described in Indian pharmacopeia [13]. Inoculum was prepared from 24 h old culture in nutrient broth. The 100 ppm solutions of the each complex were prepared by dissolving the required quantity of complexes in DMF.

The corresponding ligand **L** was also dissolved in DMF to prepare 100 ppm solution and antibacterial and antifungal activity studies were carried out under similar conditions for comparison. Above solution was further diluted with DMF to prepare of 10 ppm solution. With the help of stainless steel well cutter (6mm), cups were cut out and into each of these cups 100 μ l of each of the solutions of different concentration and control (DMF) were placed separately under aseptic conditions with the help of a sterile micropipette. The plates were then maintained at room temperature (26 °C) for 1 h to allow the diffusion of the solutions into medium and then incubated at 37 °C for antibacterial and antifungal activity *E. coli*, *S. aureus*, *A. niger* and *Candida albicans* respectively.

Physical Measurements: IR spectra of the synthesized compounds were recorded as KBr pellets on PERKIN-ELMER Spectrum One FT-IR spectrometer. ¹H NMR spectra were recorded d₆-DMSO as solvent on a Bruker Avance 400 MHz spectrometer. UV-Vis spectra of the complexes were recorded on Elico-SL 164 double beam spectrometer in the range 200-1200 nm in DMF solution (1 × 10⁻³ M). Molar conductance of the complexes were measured in DMF solution at room temperature using an Elico make, Equip-Tranics, Automatic conductivity meter, Model No. EQ667 provided with Elico conductivity Bridge CC-01. FAB-mass spectra of the ligand and Cu(II) complex were obtained on JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon (6kv, 10mA) as the gas. The accelerating voltage was 10kV and the spectrum was recorded at room temperature using meta-nitrobenzyl alcohol (NBA) as a matrix. Elemental analyses were obtained from HERAEUS C, H, N-O rapid analyzer and metal analyses were carried out by following the standard methods [14]. ESR measurements were carried out on a BRUKER BioSpin GmbH spectrometer working at a microwave frequency of 9.157 GHz using DPPH as reference with the field set at 3200 Gauss. Magnetic susceptibility were determined by the Faraday method using a model 300 Lewis coil Force Magnetometer of tesla field strength at room temperature. The instrument was calibrated with Hg[Co(SCN)₄] [15].

Table 1: Analytical, magnetic susceptibility and molar conductance data of ligand **L** and its complexes

| Compounds/ complexes | Mol wt | Calculated/ (Found)(%) | | | | | | Magn. Momen t B.M. | $(\lambda_m)(c$ $m^2\Omega^{-1}$ $mol^{-1})$ | M.P. °C Yield (%) |
|---|-----------|------------------------|------------------|----------------|------------------|----------------|----------------|--------------------------|--|-------------------------|
| | | M | C | H | N | S | Cl | | | |
| C ₁₇ H ₁₀ N ₃ O ₂ ClS | 356 | -- | 57.30 (57.25) | 2.80 (2.79) | 11.79 (11.62) | 8.98 (8.88) | 9.83 (9.89) | -- | 16 | 211-213 (65) |
| [Cu(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 881 | 7.77 (7.72) | 50.43 (50.51) | 2.96 (2.87) | 10.38 (10.28) | 7.91 (7.82) | 8.76 (8.70) | 1.98 | 14 | 256-257 (73) |
| [Co(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 876 | 7.33 (7.28) | 50.74 (50.67) | 2.98 (2.91) | 10.44 (10.37) | 7.96 (7.89) | 8.70 (8.64) | 4.99 | 15 | 275-256 (69) |
| [Ni(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 876 | 7.32 (7.29) | 50.62 (50.98) | 2.97 (2.95) | 10.43 (10.36) | 7.94 (7.88) | 8.80 (8.86) | 2.97 | 15 | 292-293 (69) |
| [Zn(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 883 | 8.00 (7.95) | 50.24 (50.22) | 2.95 (2.91) | 10.35 (10.23) | 7.88 (7.83) | 8.74 (8.71) | Diamag . | 15 | 297-298 (71) |
| [Cd(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 930 | 13.03 (13.08) | 47.49 (47.40) | 2.79 (2.76) | 9.77 (9.68) | 7.45 (7.46) | 8.26 (8.22) | Diamag . | 16 | 295-296 (73) |
| [Hg(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 1018 | 21.11 (21.05) | 43.08 (42.98) | 2.53 (2.99) | 8.87 (8.75) | 6.75 (6.77) | 7.49 (7.52) | Diamag . | 13 | 288-289 (68) |
| [Fe(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 873 | 6.86 (6.81) | 50.93 (50.83) | 2.99 (3.01) | 10.48 (10.39) | 7.99 (7.93) | 8.73 (8.67) | 5.69 | 15 | 285-286 (72) |
| [Mn(C ₁₇ H ₁₀ N ₃ O ₂ ClS) ₂ Cl ₂].2H ₂ O | 872 | 6.85 (6.81) | 50.87 (50.85) | 2.99 (3.01) | 10.50 (10.43) | 8.00 (7.97) | 8.75 (8.69) | 5.81 | 15 | 278-279 (73) |

RESULTS AND DISCUSSION

All the synthesized complexes are coloured and amorphous in nature and stable in air. All these complexes found to be insoluble in common organic solvents but are soluble in solvents such as DMSO and DMF. The analytical data of all the complexes are given in the **Table 1**. Molar conductivity data obtained in DMF suggest that all the complexes are of non-electrolyte type.

IR spectra: The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation (Table.2). The IR spectrum of ligand L showed in Fig.1 a band at 3260 cm^{-1} and 3156 cm^{-1} attributable to $\nu(\text{NH})$ of amide group and indole nitrogen which is observed in the region $3256\text{-}3257\text{ cm}^{-1}$ and $3129\text{-}3157$ in case of all the complexes confirms that the carbonyl group has not undergone enolisation during complexation and thereby both $\nu(\text{NH})$ remain intact in all the complexes. The band due to $\nu(\text{C}=\text{O})$ observed in ligand L at 1660 cm^{-1} , suffers a negative shift of $-12\text{-}35\text{ cm}^{-1}$ and appeared in the region $1625\text{-}1648\text{ cm}^{-1}$ in all the complexes, indicates the involvement of carbonyl oxygen of amide function of hydrazide moiety in the complexation with the metal ion. Another band due to $\nu(\text{C}=\text{O})$ group attached to indole ring observed at 1718 cm^{-1} in case of ligand L has appeared in the region $1706\text{-}1711\text{ cm}^{-1}$ in all the complexes with a negative shift of $07\text{-}12\text{ cm}^{-1}$ confirms the involvement of carbonyl oxygen in the complexation with the metal ion[16]. The band due to $\nu(\text{C}=\text{N})$ which was observed at 1609 cm^{-1} in case of ligand L has shown a negative shift of $14\text{-}52\text{ cm}^{-1}$ in case of all the complexes and appeared in the region $1557\text{-}1595\text{ cm}^{-1}$ proves the involvement of azomethine nitrogen in the complexation with all the metal ions [17].

Table 2: IR spectral data (cm^{-1}) of ligand L and its complexes

| Compounds/ complexes | $\nu(\text{OH}/\text{H}_2\text{O})$ | $\nu(\text{NH}/\text{NH})$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{N})$ | Thiophene Ring vib. | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{Cl})$ |
|--|-------------------------------------|----------------------------|--------------------------|--------------------------|------------------------|--------------------------|--------------------------|---------------------------|
| $\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS}$ | -- | 3260/3156 | 1718/1660 | 1609 | 1503 | -- | -- | -- |
| $[\text{Cu}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3427 | 3257/3150 | 1710/1648 | 1573 | 1514 | 498 | 405 | 320 |
| $[\text{Co}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3423 | 3245/3136 | 1710/1635 | 1587 | 1512 | 497 | 411 | 321 |
| $[\text{Ni}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3424 | 3257/3157 | 1710/1647 | 1558 | 1514 | 496 | 404 | 316 |
| $[\text{Zn}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3422 | 3256/3155 | 1710/1646 | 1557 | 1513 | 496 | 404 | 317 |
| $[\text{Cd}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3430 | 3257/3150 | 1711/1645 | 1562 | 1514 | 496 | 401 | 320 |
| $[\text{Hg}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3444 | 3256/3129 | 1706/1625 | 1595 | 1511 | 497 | 405 | 311 |
| $[\text{Fe}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3423 | 3256/3150 | 1711/1646 | 1562 | 1513 | 497 | 403 | 315 |
| $[\text{Mn}(\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{ClS})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | 3426 | 3257/3157 | 1710/1647 | 1558 | 1514 | 495 | 405 | 315 |

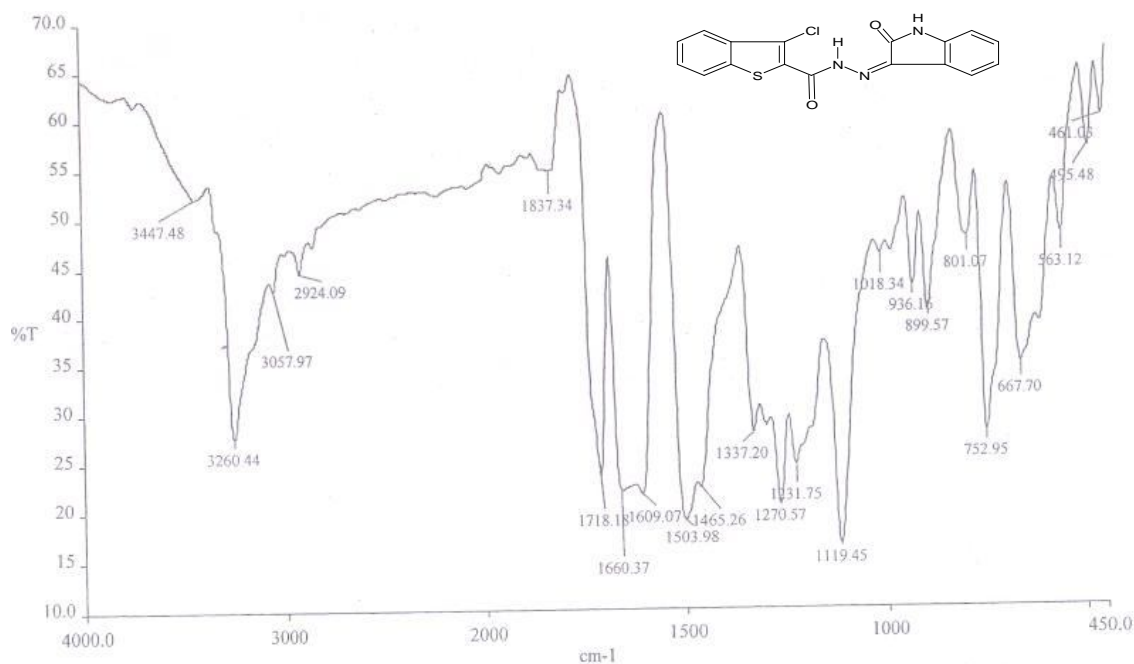


Fig.1 IR spectra of the ligand L

The appearance of a new broad band in the region $3422\text{--}3444\text{ cm}^{-1}$ in all the complexes indicates the presence of lattice water [18]. The characteristic vibration of the benzo(b)thiophene moiety observed at 1503 cm^{-1} in case of ligand L has appeared at about the same region $1511\text{--}1513\text{ cm}^{-1}$ in all the complexes which rules out the possibility of involvement of benzo(b)thiophene ring sulfur in the coordination with the metal ions [19]. Skeletal vibrations of metal-oxygen and metal-nitrogen bonds of the complexes can be precisely assigned in the Far IR region. Appearance of a new set of bands in case of all the complexes under study, due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations is the direct evidence for complexation. The bands observed in the region $495\text{--}498\text{ cm}^{-1}$ and $401\text{--}405\text{ cm}^{-1}$ are assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively.

Electronic spectra: The electronic spectra of Cu(II), Ni(II) and Mn(II), complexes of the ligand L were recorded in DMF solution at 10^{-3} molar concentration. The electronic spectra of Ni(II) complex under the present investigation exhibited three bands at 10511 cm^{-1} , 16114 cm^{-1} and 24373 cm^{-1} respectively, in DMF solution. These bands are assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$ transitions respectively. The band around $\sim 10516\text{ cm}^{-1}$ is attributable to a d-d component of the Ni(II) complex as reported by earlier workers [20]. The light green colored Cu(II) complex exhibits a broad asymmetric band in the region $16584\text{--}13269\text{ cm}^{-1}$ with maxima at 14546 cm^{-1} in a distorted octahedral geometry [21]. The broadness of the band may be due to dynamic Jahn-Teller distortion and is assigned to ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transitions. The electronic spectra of Mn(II) complex is expected to show four spin allowed transition. The four narrow absorption bands approximately four narrow absorption bands approximately around 18500 cm^{-1} , 24650 cm^{-1} , 29000 cm^{-1} and 31750 cm^{-1} were assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{G})(\nu_1)$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g({}^4\text{G})(\nu_2)$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g({}^4\text{D})(\nu_3)$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{P})(\nu_4)$ transition respectively for octahedral Mn(II) complex[22]. In the Mn(II) complex of the ligand L under present study has exhibited four absorption bands at 18218 , 23854 , 26949 and 31734 cm^{-1} , which corresponds ν_1 , ν_2 , ν_3 and ν_4 transitions respectively suggesting octahedral geometry for the Mn(II) complex.

¹H NMR Spectral Studies

¹H NMR Spectrum of the ligand L: ¹H NMR spectrum of ligand L showed in Fig.2 a fine singlet due to amide proton of CONH function at $\delta 10.86\text{ ppm}$ (1H, s). The eight aromatic protons of benzothiofuran

and phenyl ring have appeared in the region δ 6.84-7.88 ppm (m, 8H) as a multiplet. Proton on nitrogen of the indole has appeared as a singlet at δ 14.09 ppm (s, 1H).

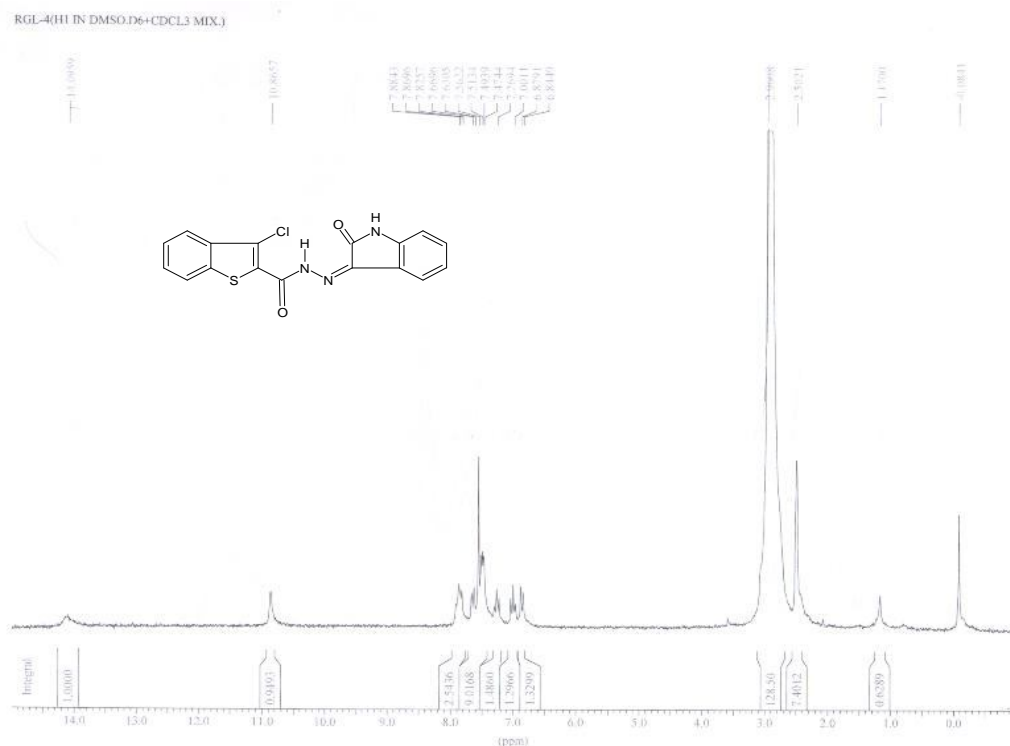


Fig.2 ^1H NMR spectra of the ligand **L**

^1H NMR spectrum of Zn(II) complex of the ligand **L:** In the ^1H NMR spectra of Zn(II) complex the eight aromatic protons were observed in the region δ 6.86-7.64 ppm (m, 8H) as a multiplet. Proton of the amide NH function gave signal at δ 10.86 ppm (s, 1H) in ligand **L** appeared at δ 11.04 ppm (s, 1H). Signal due to proton of indole nitrogen appeared at δ 14.08 ppm (s, 1H). When the ^1H NMR spectra of the ligand **L** and the Zn(II) complex are compared, it was observed that the signals of the protons of different functionalities of the ligand **L** have been shifted towards the downfield region confirming the coordination of the ligand to the Zn(II) ion.

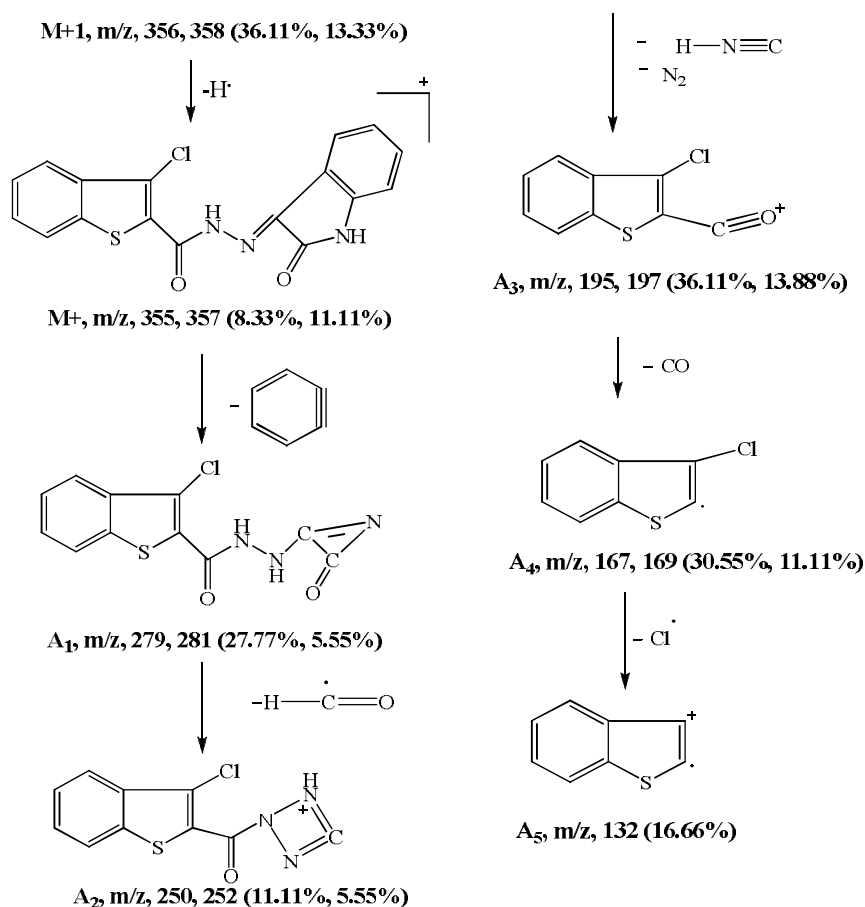
^1H NMR spectrum of Cd(II) complex of the ligand **L:** In the ^1H NMR spectra of Cd(II) complex the eight aromatic protons were observed in the region δ 6.89-7.63 ppm (m, 8H) as a multiplet. Proton of the amide NH function which was resonated at δ 10.86 ppm (s, 1H) in ligand **L** appeared at δ 11.14 ppm (s, 1H). Signal due to proton on indole nitrogen was resonated at δ 14.09 ppm (s, 1H) as singlet in ligand **L** appeared at δ 14.04 ppm (s, 1H). When the ^1H NMR spectra of the ligand **L** and the Cd(II) complex are compared, it was observed that the signals of the protons of different functionalities of the ligand have been shifted towards the downfield region confirming the coordination of the ligand to the Cd(II) ion.

FAB-mass spectral analysis: FAB-Mass spectrum of ligand **L** displayed M^{+1} peak at 356, 358 (36.11%, 13.33%) which on losing a hydrogen radical gave molecular ion peak recorded at m/z 355, 357 ($\text{M}+1 - \text{H} = \text{M}^+$, 8.33%, 11.11%). This on the expulsion of benzene molecule gave a fragment ion peaks at 279, 281 ($\text{M}^+ - \text{C}_6\text{H}_6 = \text{A}_1$, 27.77%, 5.5%) which on further loss of HCO radical followed by simultaneous loss of hydrogen, cyanide radical and nitrogen molecule gave fragment $\text{H}^+ \text{N} \equiv \text{C}$ ions recorded at m/z 250, 252 ($\text{A}_1 - \text{HCO} = \text{A}_2$, 11.11%, 5.55%) and m/z 195, 197 ($\text{A}_2 - \text{H}^+$, CN^+ , $\text{N}_2 = \text{A}_3$, 36.11%, 13.88%) respectively. Fragment ion peak of 195, 197 on sequential expulsion of CO molecule and chloride radical gave fragment

ion recorded at m/z 167, 169 (A_3 - CO= A_4 , 30.55%, 11.11%) and m/z 132 (A_4 - C_6H_4 = A_5 , 16.66%) respectively (**Scheme-2**).

FAB-Mass spectrum of Cu(II) complex of ligand **L** showed a molecular ion peak $M+1$ at m/z 849, 851, 853 (5.5%, 13.3%, 2.7%), which is equivalent to its molecular weight. The molecular ion $M+1$ by the expulsion of $2H_2O$ molecules gave fragment ion A_1 at m/z 813, 815, 817 ($M+ - 2H_2O = A_1$, 19.44%, 25.00%, 7.7%). The fragment ion A_1 by the loss of two chloride atoms gave a peak at m/z 742, 744, ($A_1 - 2Cl_2 = A_2$, 19.44%, 25.00%). which on further elimination of two $C_9H_4ClISON$ molecule simultaneously gave fragment ion A_2 at m/z 324 ($A_1 - 2C_9H_4ClISON = A_2$, 5.5%) The IR, and Mass spectral data of the Cu(II) complex is in conformity with its structure **Scheme-3**.

Magnetic Susceptibility data: The magnetic susceptibility measurements of the complexes were performed at room temperature (Table 1). The reported magnetic moment values for various Ni(II) complexes are in the range for octahedral complexes are 2.83-4.0 B.M [23]. In the present investigation the observed magnetic moment value for Ni(II) complex is 2.97 B.M. The present Cu(II) complex has a magnetic moment value 1.98 B.M. The reported values for the mononuclear Cu(II) complexes having no major spin interactions is in the range 1.75-2.20 B.M [24, 25]. Thus the present Cu(II) complex is devoid of any spin interactions with distorted octahedral geometry. For Mn(II) and Fe(II) complexes the observed magnetic moment value is 5.68 BM and 5.91 BM respectively which are characteristic of octahedral geometry. The Zn(II), Cd(II) and Hg(II) complexes showed a diamagnetic behavior having a d^{10} system which is as expected.



Scheme-2

ESR spectrum: The X-band ESR spectrum of the powder Cu(II) complex was recorded at room temperature using DPPH as a reference standard. One unpaired electron in Cu(II) complex with ${}^2B_{1g}$ as ground state lies in $d_{x^2-y^2}$ orbital and follows the trend $g_{\parallel} > g_{\perp} > g_e$ ($g_e = 2.0036$ -free ion value). The observed $g_{\parallel} = 2.36$ and $g_{\perp} = 2.07$ values of the Cu(II) complex under the present study followed the same trend $g_{\parallel} > g_{\perp} > g_e$ which suggest that the presence of unpaired electron in $d_{x^2-y^2}$ orbital giving octahedral geometry [26]. This is also in agreement with its electronic spectral data for octahedral geometry. The observed $G = 5.14$ for the complex under present study evidenced the monomeric nature of the complex [27]. This fact is further supported by the absence of a band corresponding to $\Delta M_s = \pm 2$ transition [28] in the observed ESR spectrum which is characteristic of monomeric complex.

X-ray diffraction studies: The ligand **L** showed in **Fig.3** and its Cu(II) complex showed in **Fig.4** have characterized by powder XRD studies with a view to find the type of the crystal system. The ligand **L** and its Cu(II) complex are chosen for powder XRD study. The XRD data of ligand **L** and its Cu(II) complex are given in the **Table 3** and **4** respectively. There are 25 reflections (2θ) between 5.61802° and 54.04807° with maximum at $2\theta = 10.0072^\circ$ and $d = 8.83158 \text{ \AA}$ whereas Cu(II) complex consists of 13 reflections with maxima at $2\theta = 5.68672^\circ$ corresponding to the value of $d = 15.52807 \text{ \AA}$. The interplanar spacing (d) has been calculated from the positions of intense peaks using Bragg's relation $n\lambda = 2d \sin\theta$ (where $\lambda =$ wavelength of X-ray used $\text{CuK}\alpha = 1.5406 \text{ \AA}$). The observed and calculated values of d are quite consistent (**Table 3** and **4**). The unit cell calculations have been carried out for the cubic system [29, 30]. The cell parameters have been calculated by using the equation for cubic system, $\sin^2 \theta = \lambda^2/4a^2 (h^2+k^2+l^2)$, where $\lambda^2/4a^2$ is common factor. In the present case ligand **L** and Cu(II) complex have $\lambda^2/4a^2 = 0.00247$ and 0.00248 respectively. The $h^2+k^2+l^2$ values are given in the **Table 3** and **4**. The presence of forbidden number 7, 15, and 60 in case of ligand **L** and 7 and 31 Cu(II) complex indicate that they may belong to hexagonal or tetragonal system [31, 32].

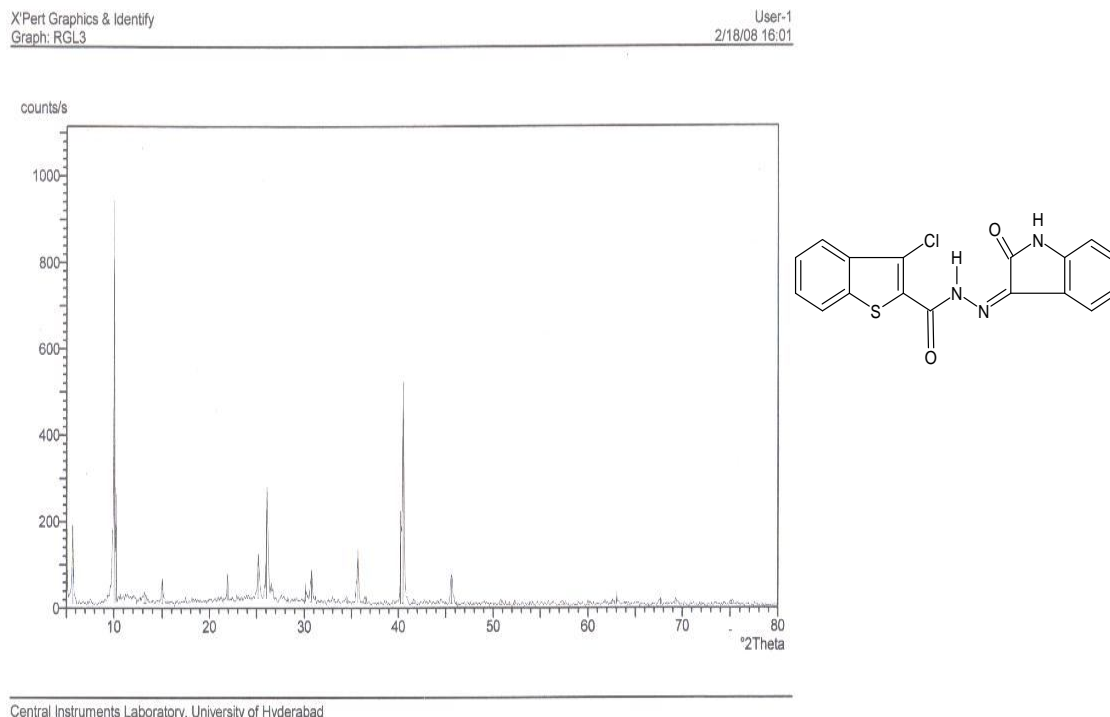
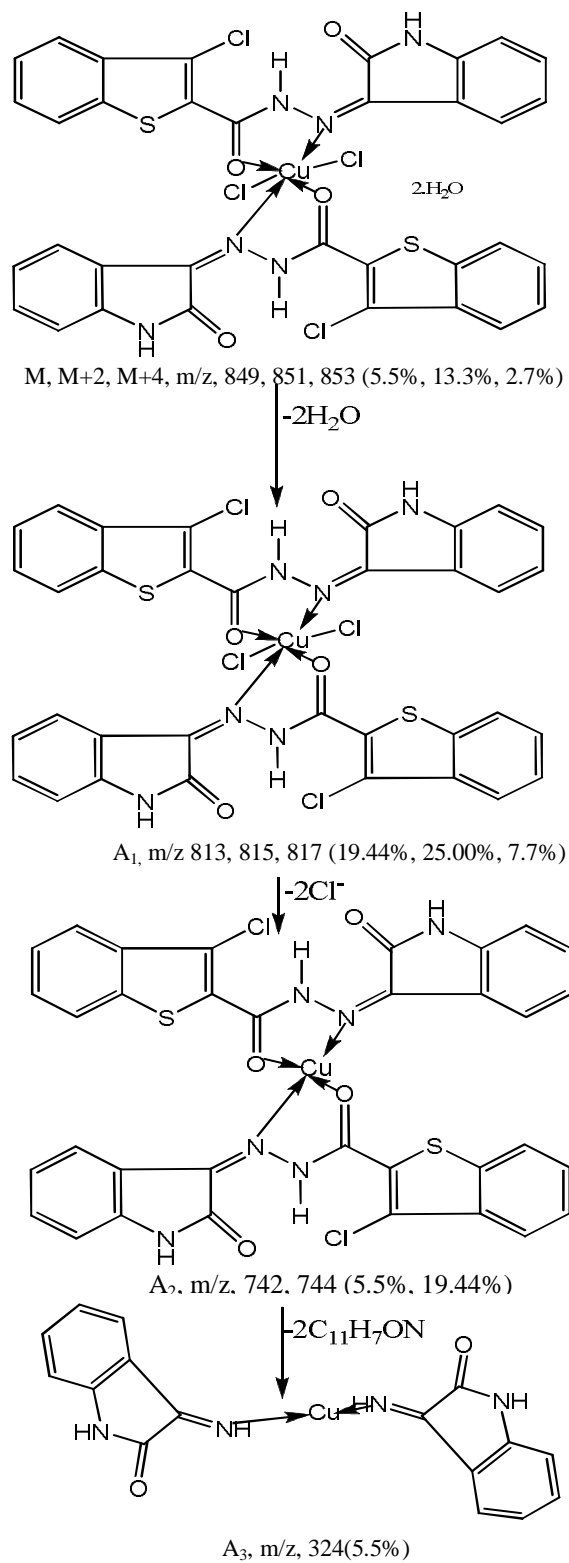


Fig.3. X-ray powder diffraction studies of ligand **L**



Scheme -3

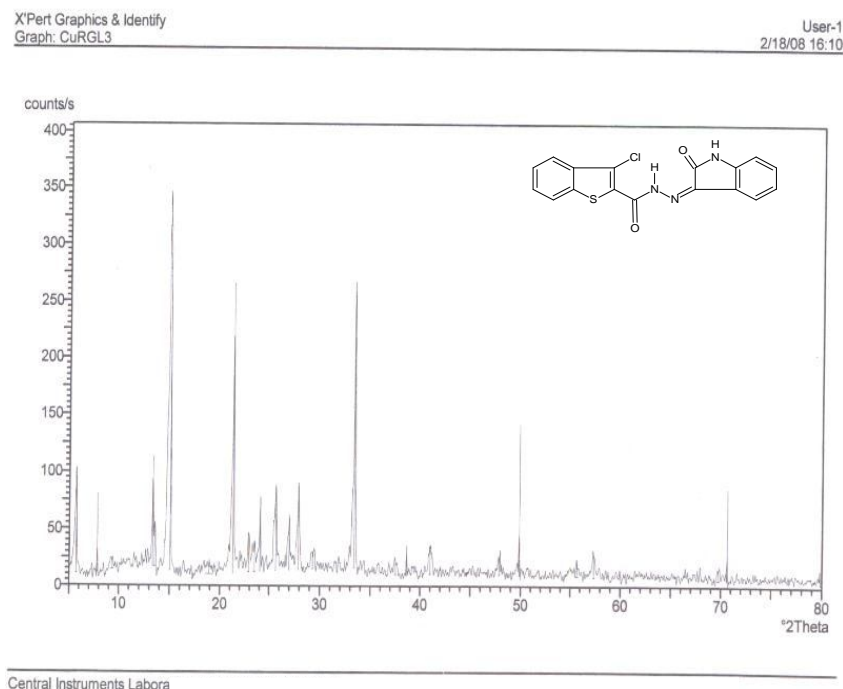


Fig.4. X-ray powder diffraction studies of Cu(II) complex of the ligand L

Table 3: Powder X-ray diffraction data of the Ligand L

| Peak | 2θ | θ | sinθ | sin ² θ | h k l | Relative intensity (%) | d | | h ² +k ² +l ² | a in Å |
|------|---------|---------|---------|--------------------|-------|------------------------|---------|---------|--|--------|
| | | | | | | | Calc. | Obsr. | | |
| 1 | 5.61802 | 2.80901 | 0.04900 | 0.002401 | 100 | 14.63 | 15.7200 | 15.7178 | 1 | 15.72 |
| 2 | 6.77584 | 3.38792 | 0.05909 | 0.003491 | 100 | 23.38 | 13.0357 | 13.0344 | 1 | 15.41 |
| 3 | 8.10377 | 4.05188 | 0.07065 | 0.004991 | 110 | 23.11 | 10.9027 | 10.9012 | 2 | 15.41 |
| 4 | 10.0072 | 5.00363 | 0.08721 | 0.007605 | 111 | 100 | 8.8324 | 8.8315 | 3 | 15.24 |
| 5 | 13.6107 | 6.80535 | 0.10545 | 0.011111 | 210 | 11.33 | 6.5004 | 6.5004 | 5 | 15.32 |
| 6 | 14.6753 | 7.33765 | 0.12771 | 0.016309 | -- | 92.51 | 6.3147 | 6.0311 | 7 | 15.95 |
| 7 | 15.5387 | 7.76937 | 0.13518 | 0.018273 | 220 | 97.68 | 5.6981 | 5.6979 | 8 | 15.83 |
| 8 | 17.9148 | 8.95741 | 0.15570 | 0.024242 | 310 | 8.95 | 4.9472 | 4.9471 | 10 | 15.49 |
| 9 | 18.7779 | 9.38895 | 0.16313 | 0.026611 | 311 | 21.61 | 4.7218 | 4.7217 | 11 | 15.58 |
| 10 | 20.0143 | 10.0071 | 0.17377 | 0.030196 | 222 | 10.77 | 4.4327 | 4.4327 | 12 | 15.24 |
| 11 | 20.4218 | 10.2109 | 0.17727 | 0.031424 | 320 | 7.47 | 4.3453 | 4.3451 | 13 | 15.50 |
| 12 | 21.7735 | 10.8867 | 0.18886 | 0.035668 | -- | 8.93 | 4.0785 | 4.0783 | 15 | 15.4 |
| 13 | 23.1106 | 11.5553 | 0.20031 | 0.094001 | 322 | 29.92 | 3.8454 | 3.8453 | 17 | 15.66 |

| | | | | | | | | | | |
|----|---------|---------|---------|---------|-----|-------|--------|--------|----|-------|
| 14 | 25.1705 | 12.5852 | 0.21789 | 0.04747 | 420 | 7.43 | 3.5351 | 3.5351 | 20 | 15.65 |
| 15 | 25.8672 | 12.9336 | 0.22382 | 0.05009 | 421 | 8.60 | 3.4415 | 3.4414 | 21 | 15.58 |
| 16 | 26.4865 | 13.2432 | 0.22908 | 0.05247 | 332 | 9.55 | 3.3624 | 3.3624 | 22 | 15.47 |
| 17 | 28.1141 | 14.0570 | 0.24288 | 0.05899 | 430 | 21.17 | 3.1714 | 3.1713 | 25 | 15.50 |
| 18 | 29.4946 | 14.7473 | 0.25455 | 0.06479 | 333 | 12.73 | 3.0260 | 3.0259 | 27 | 15.58 |
| 19 | 31.2917 | 15.6458 | 0.26969 | 0.07273 | 521 | 9.09 | 2.8561 | 2.8561 | 30 | 15.33 |
| 20 | 34.0748 | 17.0374 | 0.29299 | 0.08584 | 442 | 6.34 | 2.6290 | 2.6289 | 36 | 15.60 |
| 21 | 38.5352 | 19.2676 | 0.32998 | 0.10888 | 542 | 2.86 | 2.3343 | 2.3343 | 45 | 15.42 |
| 22 | 41.1665 | 20.5832 | 0.35156 | 0.12359 | 711 | 7.23 | 2.1910 | 2.1909 | 51 | 15.63 |
| 23 | 44.7729 | 22.3864 | 0.38085 | 0.14504 | -- | 1.41 | 2.0225 | 2.0225 | 60 | 15.49 |
| 24 | 47.3935 | 23.6967 | 0.40189 | 0.16151 | 733 | 3.14 | 1.9166 | 1.9166 | 67 | 15.55 |
| 25 | 54.0480 | 27.0240 | 0.45436 | 0.20644 | 921 | 1.78 | 1.6953 | 1.6952 | 86 | 15.67 |

Table 4: Powder X-ray diffraction data of Cu (II) complex of the Ligand L

| Peak | 2 θ | θ | sin θ | sin $^2\theta$ | h k l | Relative intensity (%) | d | | h 2 +k 2 +l 2 | 'a' in Å |
|------|------------|----------|--------------|----------------|-------|------------------------|---------|----------|------------------------|----------|
| | | | | | | | Calc. | Obser. | | |
| 1 | 5.68672 | 2.8434 | 0.04960 | 0.00246 | 100 | 95.20 | 15.5298 | 15.52807 | 1 | 15.52 |
| 2 | 10.0791 | 5.0395 | 0.08784 | 0.00771 | 111 | 7.13 | 8.76912 | 8.76878 | 3 | 15.20 |
| 3 | 13.1754 | 6.5877 | 0.11472 | 0.01316 | 210 | 100.00 | 6.71443 | 6.71421 | 5 | 15.01 |
| 4 | 14.6931 | 7.3465 | 0.12786 | 0.01635 | -- | 11.38 | 6.02440 | 6.02391 | 7 | 15.93 |
| 5 | 15.6006 | 7.8003 | 0.13572 | 0.01842 | 220 | 24.25 | 5.67550 | 5.67548 | 8 | 15.49 |
| 6 | 18.2270 | 9.1135 | 0.15839 | 0.02508 | 310 | 3.83 | 4.86318 | 4.86315 | 10 | 15.37 |
| 7 | 23.0181 | 11.5090 | 0.19952 | 0.03980 | 400 | 6.31 | 3.86065 | 3.86061 | 16 | 15.44 |
| 8 | 25.1837 | 12.5918 | 0.21800 | 0.04752 | 331 | 8.47 | 3.53339 | 3.53332 | 19 | 15.40 |
| 9 | 26.5461 | 13.2730 | 0.22959 | 0.05271 | 421 | 9.45 | 3.35502 | 3.35498 | 21 | 15.37 |
| 10 | 28.3793 | 14.1896 | 0.24513 | 0.06009 | 422 | 14.81 | 3.14233 | 3.14230 | 24 | 15.39 |
| 11 | 31.8716 | 15.9358 | 0.27456 | 0.07538 | -- | 3.33 | 2.80550 | 2.80550 | 31 | 15.62 |
| 12 | 34.3975 | 17.1987 | 0.29568 | 0.08743 | 442 | 6.83 | 2.60511 | 2.60505 | 36 | 15.63 |
| 13 | 41.4116 | 20.7058 | 0.35356 | 0.12500 | 711 | 7.12 | 2.17864 | 2.17858 | 51 | 15.55 |

APPLICATIONS

Antimicrobial activity: Antimicrobial activity was carried out by the cup-plate method [33]. The ligand L and its Cu(II), Ni(II), Zn(II), Mn(II), Fe(II), Cd(II) and Hg(II) complexes have been tested for their antibacterial and antifungal activities. Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 hour [34-37]. It was observed that the maximum inhibition effect was observed in Cu(II), Mn(II) and Hg(II) against against *E. coli* and *S. aureus* and the least inhibition effect was observed in the complexes of Ni(II), Zn(II), Fe(II) and Cd(II) whereas in ligand L was found to be comparatively less active. This indicates the complexation of metal ions with the ligand L will effect on enhanced antibacterial activity of complexes.

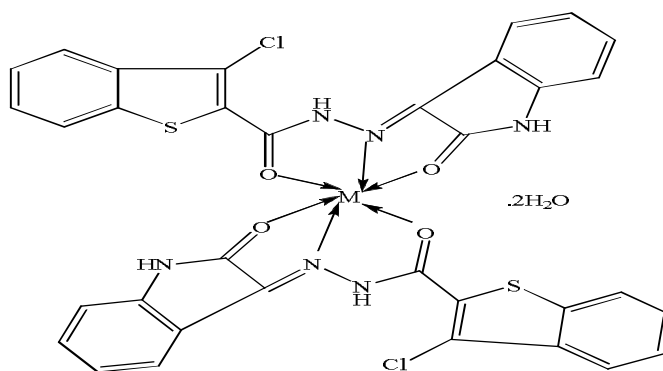
The results of the antimicrobial activity with zone of inhibition have been presented in **Table 5**. The antifungal activity results of the ligand and its above complexes revealed that the ligand L showed moderate activity against *A. niger* and *Candida albicans*. The Cu(II), Ni(II) and Zn(II) complexes showed good antifungal activity against both *A. niger* and *Candida albicans* whereas Fe(II), Mn(II), Cd(II) and Hg(II) complexes showed moderate activity against both *A. niger* and *Candida albicans* compared to the standard drug Grisofulvin against *A. niger* and *Candida albicans* respectively at the same concentrations as that of the test compounds.

Table 5: Antimicrobial screening data of the ligand L and its complexes

| Test Compound | Antibacterial Activity (Zone of Inhibition in mm) | | Antifungal Activity (Zone of Inhibition in mm) | |
|---------------|--|------------------|---|--------------------|
| | <i>E. coli</i> | <i>S. aureus</i> | <i>A. niger</i> | <i>C. albicans</i> |
| L | 12 | 11 | 13 | 15 |
| Cu | 16 | 17 | 17 | 16 |
| Co | 12 | 13 | 15 | 11 |
| Ni | 13 | 11 | 18 | 19 |
| Zn | 14 | 12 | 19 | 20 |
| Cd | 12 | 11 | 15 | 15 |
| Hg | 17 | 18 | 14 | 15 |
| Mn | 18 | 16 | 15 | 14 |
| Fe | 14 | 15 | 14 | 15 |
| Streptomycin | 20 | 22 | -- | -- |
| Grisofulvin | -- | -- | 24 | 23 |
| DMF(Control) | 02 | 02 | 02 | 02 |
| (Bore size) | 08 | 08 | 08 | 08 |

CONCLUSIONS

In the present investigation the ligand L acts as tridentate ligand coordinating through ONO. The analytical data of complexes suggested the 1:2 type stoichiometry for all the complexes $[ML_2] \cdot (H_2O)_n$. Ligands as well as its complexes were found to be less active against bacteria *E.coli* and *S.aureus* whereas moderately active against fungi *A.niger* and *C. albicans*. All the complexes showed enhanced antimicrobial activity compared to their ligand. On the basis of elemental analysis, UV-Vis, magnetic susceptibility data, IR, NMR, FAB mass and ESR the following structures are proposed for the present complexes.



M= Cu(II), Ni(II), Zn(II), Mn(II), Fe(II), Cd(II) and Hg(II)

ACKNOWLEDGEMENTS

The authors are thankful to the Chairman, Department of Chemistry, Gulbarga University, Gulbarga for providing laboratory facilities. Central University, Hyderabad, STIC Kochi and CDRI Lucknow for ¹HNMR, ESR, Mass, FAB-Mass, XRD and elemental data.

REFERENCES

- [1] U.G.Deshpandey & J.R.Shah, *J. Macromol. Sci. Chem*, **1983**, 20, 355.
- [2] F.A.Cotton, *Prog. Inorg. Chem*, **1966**, 7, 83.
- [3] H.Hitoshi, N.Tamao, A.Hideyuke, F.Manabu & M.Takayuki, *Polyhedron*, **1997**, 16, 3787.
- [4] T.Punniyamurthy, S.J.S.Karla & J.Iqbal, *Tetrahedron Lett*, **1995** 36, 8497.
- [5] S.S.Chavan & P.P.Hanakare, *J. Indian Chem. Soc.*, **2005**, 82, 494.
- [6] Z.H.Chohan, M.Praveen & A. G. Haffer, *Synthesis Acad. Inorg. Metal-Org. Chem*, **1998**, 28, 1673.
- [7] F.Kurzer and K.S.Kale, *Ind. J. Chem.*, **1980**, 19A, 486.
- [8] N.S.Dixit and C.C.Patel, *J. Indian Chem. Soc.*, **1997**, 54, 176.
- [9] B.H.M.Mruthyunjayaswamy, Y.Jadegoud, B.Omkar Ijare, G. Somanath Patil and M. Shreeshaaila Kudari., *Trans. Met. Chem*, **2005**, vol. 30, 234-242.
- [10] B.H.M.Mruthyunjayaswamy, Y.Jadegoud, B.Omkar Ijare, *J. Braz. Chem. Soc.*, **2005**, 16(4), 783-789.
- [11] Fazlur Rahaman, Basavaraj Hiremath, S.M.Basavarajaiah, B.H.M Jayakumarswamy, and B.H.M.Mruthyunjayaswamy, *J. Ind.Chem society.*, **2008**, 85, 381-386.
- [12] Fazular Rahaman, Ijare O B, Jadegoud Y & Mruthyunjayaswamy B H M, *J. Coord. Chem*, **2009**, 1, 1.
- [13] Indian pharmacopoeia, 3rd Edition, New Delhi, **1985**, Appendix IV p. 90.
- [14] A.I.Vogel, A Text book of Quantitative Organic Analysis, **1962**, 3rd Edition, ELBS Longmans Green and Co. Ltd.
- [15] E.Knoevengal, **1898**, Ber.31, 730-737.
- [16] Ayse Ercag, Sema Oztürk Yildirim, Mehmet Akkurt, Mahmure Ustün Ozgur, W.Frank Heinemann, *Chinese Chemical Letters*, **2006**, 17(2), 243-246.
- [17] C.J.Connor, E.S.Sinn, E.J.Cukaskas and B.S.Deaver, *Inorg. Chim. Acta.*, **1979**, 32, 29.
- [18] Rajesh Malhotra, Sudhir Kumar, Jyoti, Hari Ram Singal and Kuldip Singh Dhindsa, *Indian J. Chem.*, **2000**, 39A, 421.

- [19] C.N. R. Rao "Chemical Applications of Infrared Spectroscopy" Academic Perss.New York **1963**.
- [20] K.C.Satpathy, B.B.Jal and R.Mishra, *Trans. Met. Chem.*, 9, 8 (1984).
- [21] Koji Abe, Kanako Matsufuji, Masaki Obha and Hishashi Okawa, *Inorg. Chem.*, **2002**, 41, 4461.
- [22] D. Nicolas, J.C.Bailar Jr, H.J.Emelens & R.S.Nyloms, *Comprehensive Inorganic Chemistry 5th edition*.
- [23] M.Ketan Patel, N.H.Patel, N.Patel and M.N.Patel, *J. Indian. Council Chemists.*, **2000**, 17, 19.
- [24] H.Hathaway, D.E.Billing; *Coord.Chem.Rev.*, **1970**, 6, 143.
- [25] R.J.Dudley and B.J.Hathway, *J. Chem. Soc.* **1970**, Sec. A, 1725.
- [26] Sulekha Chandra and K.Gupta, *Transition Metal Chem.*, **2002**, 27, 196-197.
- [27] M.I.Melnik, Potocnak, L. Macoskora, D. Miklos and C. Holloway, *Polyhedron*, **1996**, 15, 2159.
- [28] B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **1970**, 5, 1.
- [29] B.D.Cullity, *Elements of X-ray Diffraction*, **1978**, Addison-Wesley Pub. Co.
- [30] N.F.M.Henry, H.Lipson and W. A.Wooster, *Interpretation of X-ray Diffraction Photography*, London, Macmillon, **1959**, 179.
- [31] M.J.Burger; *X-ray Crystallography.*, New York, Willey, **1953**, 100.
- [32] M.M.Woolfson; *An Introduction to X-ray Crystallography.*, Cambridge, Cambridge University Press, **1980**, 125.
- [33] A.L.Barry; *The Antimicrobial Susceptibility Test.*, Principles and Practices, **1976**, 4th Edition, ELBS, 180-193.
- [34] L. Ahmed, Z. Mohammed, F. Mohammed, *J. Ethnopharmacol.*, **1998**, 62, 183-193.
- [35] S. N. Padhy, S. B. Mahato, N. L. Dutta, *Phytochem.*, **1973**, 12, 217-221.
- [36] M. H. Moinuddin Khan, Fasiulla, J. Keshavayya and K. R. Venugopala Reddy. *Russian Journal of Inorganic chemistry*, **2008**, 53(1), 66-77.
- [37] M. H. Moinuddin Khan, K. R. Venugopala Reddy and J. Keshavayya. *Inorganic chemistry: An Indian Journal.*, **2008**, 3(1), 36-43.