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Synthesis, spectral characterization, molecular modeling, thermal study and biological evaluation of transition metal complexes of a bidentate Schiff base ligand

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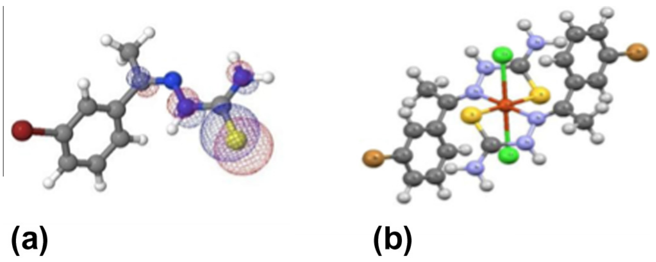
HIGHLIGHTS

- Ligand and Cu(II) and Ni(II) complexes were synthesized.
- Characterized the ligand and complexes by IR, Mass, NMR, UV, EPR, TGA/DTA, etc.
- Molecular modeling and thermal analysis have been provided in support of the structures.
- A distorted octahedral geometry has been assigned for Ni(II) and tetragonal geometry for Cu(II) complexes.
- Synthesized compounds have been screened against bacterial and fungal species in *in vitro* conditions.

GRAPHICAL ABSTRACT



(a) HOMO orbitals of the PM6 geometry optimised structure of the ligand

(b) Geometry optimised structure of Cu(L)2Cl2

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ABSTRACT

Complexes of copper(II) and nickel(II) of general composition $M(L)_2X_2$, have been synthesized [where L = 3-Bromoacetophenone thiosemicarbazone and $X = CH_3COO^-$, Cl^- and NO_3^-]. All the complexes were characterized by elemental analysis, magnetic moments, IR, electronic and EPR spectral studies. The ligand behaved as bidentate and coordinated through sulfur of —C=S group and nitrogen atoms of —C=N group. The copper(II) and nickel(II) complexes were found to have magnetic moments 1.94–2.02 BM, 2.96–3.02 BM respectively which was corresponding to one and two unpaired electrons respectively. The molar conductance of the complexes in solution of DMSO lies in the range of 10–20 Ω^{-1} cm^2 mol^{-1} indicating their non-electrolytic behavior. On the basis of EPR, electronic and infrared spectral studies, tetragonal geometry has been assigned for copper(II) complexes and an octahedral geometry for nickel(II) complexes. The values of Nephelauxetic parameter β lie in the range 0.19–0.37 which indicated the covalent character in metal ligand 'σ' bond. Synthesized ligand and its copper(II) and nickel(II) complexes have also been screened against different bacterial and fungal species which suggested that complexes are more active than the ligands in antimicrobial activities.

Introduction

The past few decades have witnessed a great deal of interest in the chemistry of transition metal Schiff base chelates specially thiosemicarbazones as they are found lots of applications in spectrophotometry [1], as corrosion inhibitors [2], pulse polarography

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[3], as gravimetric reagents [4], in potentiometric studies [5,6], as visual indicators [7]. Great work is done on the biological activities of metal complexes of thiosemicarbazones [8–21]. Antitumoral activity is one of the main findings for thiosemicarbazones and their metal complexes [22]. In comparison to the 4d- or 5d-metal analogs, complexes of first row transition elements find better applications at the cellular level [23]. In view of above applications it is highly desirable to synthesize and characterize 3d transition metal complexes with thiosemicarbazone ligands. In the present paper we report the synthesis, characterization and biological evaluation of Cu(II) and Ni(II) complexes with thiosemicarbazone (L) derived from 3-Bromoacetophenone.

Experimental

Materials and methods

All the chemicals used were of A R grade and procured from Sigma Aldrich, Bangalore, India. Metal salts were purchased from E. Merck, India and were used as received.

Synthesis of ligand (L)

Hot ethanolic solution of thiosemicarbazide (0.91 g, 0.01 mol) and ethanolic solution of 3-Bromoacetophenone (1.99 mL, 0.01 mol) were mixed. This mixture was refluxed at 60–70 °C for 6 h. On cooling the reaction mixture, cream-colored crystals were precipitated out. They were filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}, (yield 76%, mp 183 °C). Element chemical analysis data are shown in Table 1. The purity of the compounds was checked by elemental analysis and Infra Red (IR) Spectroscopy.

Synthesis of the complexes

A filtered solution of the appropriate metal salt (0.005 mol) in EtOH was mixed with an ethanolic solution (50 mL) of the 3-Bromoacetophenone thiosemicarbazone (0.010 mol). The resulting mixture was stirred under reflux for 2–30 (h), 14 h for $[Cu(L)(CH_3COO)_2]$, 10 h for $[Cu(L)(Cl)_2]$ complex, 30 h for $[Cu(L)(NO_3)_2]$ complex, 3 h for $[Ni(L)(CH_3COO)_2]$ complex, 4 h for $[Ni(L)(Cl)_2]$ complex, 28 h for $[Ni(L)(NO_3)_2]$ complex. On cooling the reaction mixture, colored crystals were precipitated out. These crystals were removed by filtration, washed thoroughly with 50% EtOH and dried under vacuum over P_4O_{10}.

Analysis

The C, H and N were analyzed on Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic moments were measured at room temperature on a Gouy balance using $CuSO_4{\cdot}5H_2O$ as calibrant. Electronic impact mass spectrum was recorded on JEOL, JMS – DX-303 mass spectrometer. ^1H NMR (300 MHz) spectra were recorded on a Bruker Advanced DPX-300 spectrometer using DMSO as a solvent. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra were recorded on Perkin Elmer-137 instrument as KBr pellets. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the Cu(II) complexes were recorded as polycrystalline sample at room temperature on E_4-EPR spectrometer using the DPPH as the g-marker at SAIF, IIT (Bombay). The complexes were modeled by MOPAC 2007 program in gas phase using level of theory at department of Applied Science and Humanities, FET, Mody Institute of Technology and Science Lakshmangarh Rajasthan. Thermal gravimetric analysis was carried out on model DTG60 thermal gravimetric analyzer.

In vitro screening of compounds for antibacterial activity

The antibacterial activity of the ligand and its metal complexes were tested by using paper disc diffusion method [24] against *Xanthomonas campestries* pv. *Campestris* and *Ralstonia solanacearum*. Cultures of these bacteria were obtained from 'Indian Agricultural Research Institute', New Delhi. Filter paper disc treated with DMSO served as control and with streptomycin used as a standard antibiotic. All determination was made in duplicate for each of the compounds. An average of two independent readings for each compound was recorded. The zone of inhibition was calculated in millimeters carefully.

In vitro screening for antifungal property of compounds

The preliminary fungitoxicity screening of the compounds at different concentrations was performed *in vitro* against the test fungi, *Botrytis cinerea*, *Macrophomina phaseolina* and *Phoma glomerata* by the food poison technique [25]. Fungal culture of *B. cinerea* were obtained from Indian Type Culture Collection, Indian Agricultural Research Institute, New Delhi (ITCC No. 6192) and *P. glomerata* was isolated from seeds of *Impatiens glandulifera* received from UK in the Plant Quarantine Division of National Bureau of Plant Genetic Resources, New Delhi for by incubation on blotter. The mycelial growth of fungi (mm) in each Petri plate was measured

Table 1
Analytical data for the ligand and its Cu(II) and Ni(II) complexes.

Compounds	Empirical formulae	Color	M.p.	Yield	Metal	Elemental analysis data (%) found (calculated)			μ_{eff} (BM)
			(°C)	(%)		C	H	N	
Ligand (L)	$C_9H_{10}N_3SBr$	Cream	183	76	–	39.38 (39.85)	3.52 (3.69)	15.39 (15.50)	
$[Cu(L)_2(CH_3COO)_2]$	$CuC_{18}H_{20}N_6S_3O_4$	Dark Green	>260	56	8.37 (8.78)	36.05 (36.49)	3.26 (3.59)	11.28 (11.61)	2.02
$[Cu(L)_2Cl_2]$	$CuC_{18}H_{20}N_6Br_2S_2Cl_2$	Dark Green	>260	57	8.58 (8.77)	32.05 (32.15)	2.87 (2.98)	12.38 (12.50)	1.96
$[Cu(L)_2(NO_3)_2]$	$CuC_{18}H_{20}N_8O_6Br_2S_2$	Green	>260	57	8.59 (8.70)	29.50 (29.61)	2.62 (2.74)	15.21 (15.35)	1.94
$[Ni(L)_2(CH_3COO)_2]$	$NiC_{22}H_{26}N_6S_2Br_2$	Brown	>260	62	8.09 (8.17)	36.62 (36.73)	3.51 (3.62)	11.55 (11.69)	2.96
$[Ni(L)_2Cl_2]$	$NiC_{18}H_{20}N_6O_2Br_2S_2Cl_2$	Green	>260	58	8.64 (8.71)	32.01 (32.06)	2.91 (2.97)	12.35 (12.47)	2.98
$[Ni(L)_2(NO_3)_2]$	$NiC_{18}H_{20}N_8O_6Br_2S_2$	Green	>260	53	8.02 (8.10)	29.73 (29.81)	2.64 (2.76)	15.32 (15.45)	3.02

diametrically and growth inhibition (I) was calculated using the formula: $I\ (\%) = (C - T)/C \times 100$, where I = % inhibition, C = radial diameters of the colony in control, T = radial diameter of the colony in test compound.

Molecular modeling

The ligands and the complexes were modeled by MOPAC 2007 [26] program in gas phase using PM6 level of theory [27]. Selected parts of the complexes not containing the metal ion were preoptimized using molecular mechanics methods. Several cycles of energy minimization had to be carried for each of the molecules. Geometry was optimized using Eigen Vector following. The Root Mean Square Gradient for the molecules were all less than one. Self Consistent Field was achieved in each case. Vibrational analysis was done to check the absence of imaginary frequencies.

Results and discussion

The complexes were synthesized by reacting ligand with the metal ions in 2:1 M ratio in ethanolic medium. The ligand behaves as bidentate and coordinated through sulfur of —C=S group and nitrogen atoms of —C=N group. The analytical data, magnetic moments and spectral analysis agree well with the proposed composition of formed complexes. All the complexes have shown good solubility in DMSO. The molar conductance of the complexes in fresh solution of DMSO lies in the range of 10–20 Ω^{-1} cm^2 mol^{-1} indicating their non-electrolytic behavior. Thus, the complexes may be formulated as $[M(L_2)X_2]$ (where M = Cu(II), Ni(II); L = 3-Bromoacetophenone thiosemicarbazone, $X = CH_3COO^-, Cl^-, NO_3^-$).

Mass spectrum

The peak obtained at 271 corresponding to molecular ion peak $(M)^+$ (Supplementary material). Atomic mass of molecule is calculated as 271 amu for molecular formula ($C_9H_{10}N_3SBr$). An isotopic peak because of Br is also obtained at 273 $(M + 2)^+$. Large number of peaks of varying intensity present in the spectrum correspond the 155, 171, 181, 196, 211, 254 and 256 fragments (Supplementary material) getting generated during the analysis. Other peaks at 73, 113 might be the isotopic peaks because of bromine group.

$$\begin{aligned} M^+ - CH_3 = 256,\ M^+ - NH_3 = 254,\ M^+ - CH_2NS \\ = 211,\ M^+ - NH_2CNSH = 196,\ M^+ - CH_3NHCSNH_2 \\ = 181,\ M^+ - Br = 192,\ M^+ - C_6H_4Br = 171. \end{aligned}$$

^{1}H NMR spectrum of ligand

^{1}H NMR spectrum of ligand (Supplementary material) (L = 3-Bromoacetophenone thiosemicarbazone) (in d_6 – DMSO) exhibits following signals: δ 8.760 ppm (s) (1H, HN—CS), δ 6.461 ppm (s) (2H, H_2N—), δ 1.650 ppm (s) (3H, —CH_3) δ 7.266–7.860 ppm (m) (4H, —Ph—).

Magnetic moments

The observed magnetic moments of Cu(II) and Ni(II) complexes are given in Table 1. The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry around the metal ion. Room temperature magnetic moment of the Cu(II) complexes lies in the range of 1.94–2.02 BM, corresponding to one unpaired electron. The magnetic moment observed for the Ni(II) complexes lies in the range of 2.96–3.02 BM corresponding to two unpaired electrons [28].

Infrared spectra

The assignments of the significant IR spectral bands of ligand and its Cu(II), Ni(II) complexes are presented in Table 2. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide —NH—C=S functional group. The ν(S—H) band at 2565 cm^{-1} is absent in the IR spectrum of ligand but ν(N—H) band at ca. 3209 cm^{-1} is present, indicating that in the solid state, the ligand remains as the thione tautomer. The position of ν(C=N) band of the thiosemicarbazone appeared at 1585 cm^{-1} is shifted towards lower wave number in the complexes indicating coordination via the azomethine nitrogen [29,30]. This is also confirmed by the appearance of band in complexes in the range of 455–468 cm^{-1}, which has been assigned to the ν(M—N) [31]. A medium band found at 1103 cm^{-1} is due to the ν(N—N) group of the thiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethine nitrogen. The band appearing at ca. 783 cm^{-1} corresponding to ν(C=S) in the IR spectrum of ligand is shifted towards lower wave number. It indicates that thione sulfur coordinates to the metal ion [32]. Thus, it may be concluded that the ligand behaves as bidentate chelating agent coordinating through azomethine nitrogen and thiolate sulfur [33].

Anions

The IR spectra of Cu(II) and Ni(II) acetato complexes showed the medium intensity bands at 1471–1490 and 1327–1340 cm^{-1}, assigned to ν_a(C—O) and ν_s(C—O), respectively. The difference between these two frequencies is ~144–150 cm^{-1}, which strongly supported that both acetate ions are coordinated to the metal ion in a unidentate fashion [32] (Fig. 1). The infrared spectrum of the Cu(II) and Ni(II) nitrato complexes showed ν_5 = 1384–1410, ν_1 = 1279–1320, ν_2 = 1073–1023 and $\Delta(\nu_5 - \nu_1)$ = 105–90 cm^{-1} indicating monodentate nature of nitrate group [34].

Table 2
Important infrared spectral bands (cm^{-1}) and their assignments.

Compounds	Assignments					Bands due to anions
	ν(N—H)	ν(C=O)	ν(C=N)	ν(C=S)	ν(M—N)	
$[Cu(L)_2(CH_3COO)_2]$	3165		1491	782	440	ν_{as}(OAc) = 1471, ν_s(OAc) = 1327, $\Delta\nu$ = 144 cm^{-1} indicating monodentate nature of acetate group [29]
$[Cu(L)_2Cl_2]$	3147		1557	781	439	
$[Cu(L)_2(NO_3)_2]$	3169		1592	783	460	ν_5 = 1384, ν_1 = 1279, ν_2 = 1073 and $\Delta(\nu_5 - \nu_1)$ = 105 cm^{-1} indicating monodentate nature of nitrate group [29]
$[Ni(L)(CH_3COO)_2]$	3286	1658	1545		482	ν_{as}(OAc) = 1490, ν_s(OAc) = 1340, $\Delta\nu$ = 150 cm^{-1} indicating monodentate nature of acetate group
$[Ni(L)Cl_2]$	3195	1686	1570		437	
$[Ni(L)(NO_3)_2]$	3194	1676	1567		454	ν_5 = 1410, ν_1 = 1320, ν_2 = 1021and $\Delta(\nu_5 - \nu_1)$ = 90 cm^{-1} indicating monodentate nature of nitrate group

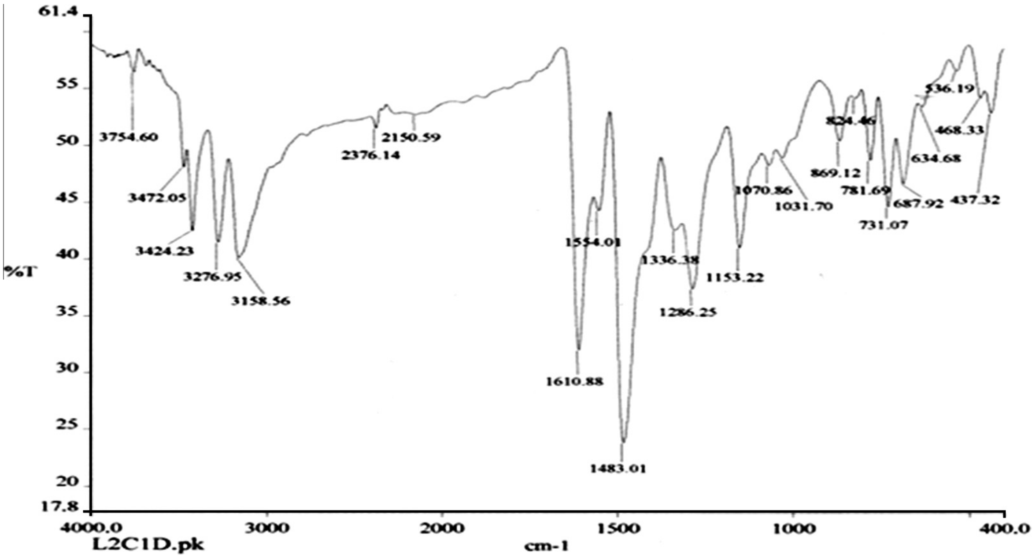


Fig. 1. IR spectra of $[Cu(L)_2(CH_3COO)_2]$ complex.

Electronic spectra

The electronic spectra of the Cu(II) complexes showed three bands in range of 9728–10,560, 16,271–18,622 and 27,322–35,211 cm^{-1} which can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively, corresponding to tetragonal geometry [35]. Electronic spectra of Ni(II) complexes showed bands in the region of 9488–9653, 10,787–11,121 and 20,576–21,459 cm^{-1}. An examination of these bands indicates that the complexes have an octahedral geometry and might possess D_{4h} symmetry [36]. The ground state of Ni(II) in an octahedral coordination is $^3A_{2g}$. Thus, these bands may be assigned to the three spin allowed transitions [37,38] and the fourth one may be considered as a charge transfer band, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions, respectively corresponding to an octahedral geometry of Ni(II) complexes.

Ligand field parameters

Various ligand field parameters were calculated and listed in Table 3. The values of Dq have been calculated from transition energy ratio diagram [39]. Our results are in agreement with the same type of complexes reported earlier [40]. The Nephelauxetic parameter β was readily obtained by using the relation $\beta = B$ (complex)/B (free ion), where B (free ion) for Ni(II) is 1041 cm^{-1} [41]. The values of β lie in the range 0.19–0.37. These values indicated the covalent character in metal ligand 'σ' bond.

Electronic paramagnetic resonance spectra

EPR spectra of Cu(II) complexes were recorded at room temperature as polycrystalline sample, on X band at frequency of 9.1 GHz under the magnetic-field strength of 3000G. The analysis of spectra of Cu(II) complexes (Supplementary material) gives $g\| = 2.098$–2.298, $g\perp = 2.08$–2.234 and $G = 1.27$–2.62 (Table 4). The trend $g\| > g\perp > 2.0023$ observed for the complex indicates that unpaired electron is localized in $dx^2 - y^2$ orbital of the Cu(II) ion and the spectral features are a characteristic of axial symmetry. Thus, a tetragonal geometry is confirmed for the aforesaid complex [42]. $G = (g\| - 2)/(g\perp - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. According to Hathaway, if $G > 4$, the exchange interaction is negligible, but $G < 4$ indicates considerable exchange interaction in the solid complexes. The "G" value for Cu(II) complexes reported in this paper, is <4 indicating the exchange interaction in solid complexes [43].

Table 3
Electronic spectral bands (cm^{-1}) and ligand field parameters of the complexes.

Complexes	γ_{max} (cm^{-1})	ε ($L\,mol^{-1}\,cm^{-1}$)	ν_2/ν_1	Dq (cm^{-1})	B (cm^{-1})	β	LFSE ($KJ\,mol^{-1}$)
$[Cu(L)_2(CH_3COO)_2$	10,040, 18,622, 27,322	52, 90, 150	1.85				
$[Cu(L)_2Cl_2]$	10,560, 18,653,	57, 94, 134	1.76				
$[Cu(L)_2(NO_3)_2]$	9728, 10,787, 35,211	38, 82, 126	1.11				
$[Ni(L)_2(CH_3COO)_2$	9653, 11,123, 21,459	31, 54, 121	1.15	965	242	0.23	138.553
$[Ni(L)_2Cl_2]$	9506, 11,050, 20,576	28, 46, 137	1.16	951	207	0.19	136.446
$[Ni(L)(NO_3)_2]$	9488, 10,787, 23,474	47, 89, 148	1.13	949	387	0.37	136.187

Table 4
EPR Spectral data and bonding coefficient parameters of Cu(II) complexes.

Complexes	g_{II}	$g\perp$	g_{iso}	k_{II}	$k\perp$	α	β	G
$[Cu(L_2)_2(CH_3COO)_2]$	2.298	2.234	2.255	0.914	0.956	0.914	1.046	1.27
$[Cu(L_2)_2Cl_2]$	2.21	2.08	2.123	0.951	0.975	0.951	1.026	2.625
$[Cu(L_2)_2(NO_3)_2]$	2.098	2.051	2.067	0.396	0.63	0.396	1.588	1.922

Molecular modeling

In case of ligand (L) it is noticed that the HOMO orbitals (−8.68466 eV) are located on the substituent of the phenyl group while the LUMO orbitals (−0.72565 eV) on the phenyl group. Computed dipole moment is 5.356 Debye. N—N bond lengths are 1.37 A, N—C 1.39, 1.36 A, C═S 1.68 A, C═N 1.31 A and C—Br 1.91 A (Supplementary material).

In the Cu(II) complexes with ligand the two sulfa amido ligands occupying the equatorial position and the Cl^-/nitrate are in the apical position bound trans fashion in a distorted octahedral geometry (Supplementary material). The bond lengths and angles are close to those reported in literature [44]. The copper atom lies on the mean plane of the two chelating nitrogen and two chelating oxygen atom. The two phenyl groups on the ligands are exactly parallel to each other. The chelating part of the ligand adopts a distorted pentagonal arrangement with the metal centre as one of the apices. The important bond distances and angles are summarized in Tables 5 and 6 for the copper complexes. Attempts to optimize the $[Cu(L)_2(CH_3COO)_2]$ and Ni(II) complexes were not successful.

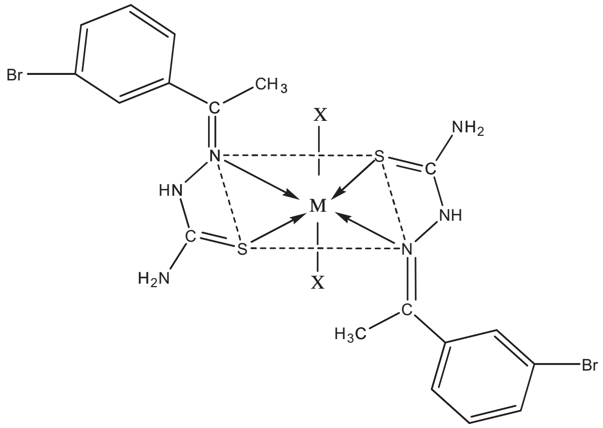
Thermal analysis

The thermal stability of Cu(II) complex is studied by controlling heating rates 10 °C per minute under nitrogen atmosphere. Thermogram of Cu(II) complex is stable up to 250 °C, indicated the absence of lattice water as well as coordinated water. Generally in TG lattice water loses at low temperature region between 60–120 °C, where as coordinated water requires 120–250 °C. Absence of water molecule in Cu(II) complex is supported by the DTA curve, which represents weight loss by endothermic bands. The DTA of copper complex has no endothermic band in the range of 60–250 °C. Endothermic bands present at high temperature in DTA of Cu(II) complex is due to loss of organic molecules and finally metal may converts into its oxide [45,46]. In addition to endothermic bands, the DTA curves of the complex also show exothermic bands. These bands appear at high temperature and represent phase transition, oxidation and/or decomposition of the complex.

On the basis of above discussion following structures (Fig. 2) can be proposed for the synthesized complexes.

Antimicrobial studies

The antimicrobial screening data show that the compounds exhibit antimicrobial properties and it is also important to note that some of the metal chelates exhibit more inhibitory effects than the parent ligands. The increased activity of the metal chelates can be explained on the basis of chelation theory [47].



(Where X = Cl^-, NO_3^-, CH_3COO^- and M=Cu^{2+}, Ni^{2+})

Fig. 2. Proposed structures of Cu(II) and Ni(II) complexes.

Antibacterial activity

The data presented in Table 7 indicated that some of the complexes showed better activities against *Xanthomonas campestris* pv. *campestris (Xc)* as well as *R. solanacearum (Rs)* than the parent ligand. Ligand did not show any activity against these two bacterial pathogens. The complex $[Cu(L)_2(CH_3COO)_2]$ was found to be most active against both the bacterial pathogens at all concentrations i.e. 250, 500 and 1000 μg ml^{-1} but Streptomycin (standard) showed better activities than the complexes at all concentrations. Complex $[Ni(L)_2(CH_3COO)_2]$ and $[Ni(L)_2(NO_3)_2]$ showed activity only at highest concentrations against *X. campestris*. Other testing compounds did not show the activities against pathogen *X. campestris*.

The results also indicated that the complex $[Cu(L)_2(CH_3COO)_2]$ showed best activities against bacteria *R. solanacearum*.

With bacteria *R. solanacearum* the order of activity was found in order:

Streptomycin (standard) > $[Cu(L)_2(CH_3COO)_2]$ > $[Cu(L)_2(Cl)_2]$ > $[Ni(L)_2(CH_3COO)_2]$ > $[Ni(L)_2(NO_3)_2]$ > $[Cu(L)_2(NO_3)_2]$ > $[Ni(L)_2(Cl)_2]$.

In vitro screening for antifungal property of compounds

From Table 8, it is evident that the activity of the ligand increased with increased concentration for the fungus *B. cinerea* (Supplementary material). The activity order for fungus *B. cinerea* was found to be:

$[Cu(L)_2(CH_3COO)_2]$ > $[Cu(L)_2(NO_3)_2]$ > $[Cu(L)_2(Cl)_2]$ > $[Ni(L)_2(Cl)_2]$ > $[Ni(L)_2(NO_3)_2]$ > $[Ni(L)_2(CH_3COO)_2]$ > Ligand > Bavistin i.e. Cu(II) complexes > Ni(II) complexes > Ligand > Bavistin.

For fungus *Macrophomina phaseolena* the activity order was:

Table 5
Selected bond lengths (A°).

Ligand	Cu—N(lig)	Cu—S(lig)	Cu—O(nitrate)	Cu—Cl	Cu—(SNSN mean plane distance)
$[Cu(L)_2Cl_2]$	1.95, 1.95	2.07, 2.07	–	2.65, 2.65	0
$[Cu(L)_2(NO_3)_2]$	1.94, 1.94	2.03, 2.03	2.06, 2.06	–	0

Table 6
Selected bond angles (°).

Ligand	N(lig)—Cu—N(lig′)	S(lig)—Cu—S(lig′)	O(nit)—Cu—O(nit′)	Cl—Cu—Cl′	N(lig)—Cu—S(lig)	N(lig)—Cu—S(lig′)
$[Cu(L)_2Cl_2]$	180.0	179.9	–	179.9	84.2, 84.2	95.9, 95.9
$[Cu(L)_2(NO_3)_2]$	180	180	179.3	–	84.1, 84.1	95.9, 95.9

Table 7
Antibacterial screening data of the ligand and its Cu(II) and Ni(II) complexes.

Compounds	Diameter of inhibition zone (mm) (conc. in μgml−1)					
	Xanthomonas campestris pv. *Campestris*			*Ralstonia solanacearum*		
	250	500	1000	250	500	1000
Ligand (L)	0	0	0	0	0	0
$[Cu(L)_2\ (CH_3COO)_2]$	19.05	20	26.8	16.5	21.5	25.3
$[Cu(L)_2(Cl)_2]$	0	0	0	11	11	15.1
$[Cu(L)_2(NO_3)_2]$	0	0	0	0	0	12
$[Ni(L)_2(CH_3COO)_2]$	0	0	14.1	0	14	11
$[Ni(L)_2(Cl)_2]$	0	0	0	0	0	11
$[Ni(L)_2(NO_3)_2]$	0	0	12	0	12	14
Streptomycin (standard)	19	22	26	26	30	Not tested
Solvent (DMSO)	0	0	0	0	0	0

Table 8
Antifungal screening data of the ligands and its Cu(II) and Ni(II) complexes.

Compounds	Fungal inhibition (%) (conc. in $\mu g\ ml^{-1}$)											
	Botrytis cinerea				*Macrophomina phaseolina*				*Phoma glomerata*			
	500	800	1000	1500	500	800	1000	1500	500	800	1000	1500
Ligand (L)	45.83	54	61	75	−5.4	74.7	–	70	39.04	48	63	69
$[Cu(L)_2\ (CH_3COO)_2]$	–	72	71.4	100	–	48.3	59.6	87.3	–	62	66.2	96
$[Cu(L)_2(Cl)_2]$	–	58	66	100	–	–	0.5	80.1	–	61	55	80
$[Cu(L)_2(NO_3)_2]$	–	64	78	100	–	52.4	68.8	78.4	Not tested			
$[Ni(L)_2(CH_3COO)_2]$	–	48	69	100	–	65.7	73.5	90.36	–	72	78	100
$[Ni(L)_2(Cl)_2]$	–	42	76	100	–	62.8	79.5	100	–	64	78	100
$[Ni(L)_2(NO_3)_2]$		55	69	100	–	53.2	72.0	100	–	67	94	100
Bavistin (standard)	−25	0	0	0	58.44	78.7	98	100	76.19	100	100	100

Bavistin > $[Ni(L)_2(Cl)_2]$ > $[Ni(L)_2(NO_3)_2]$ > $[Cu(L)_2(CH_3COO)_2]$ > $[Ni(L)_2(CH_3COO)_2]$ > $[Cu(L)_2(Cl)_2]$ > $[Cu(L)_2(NO_3)_2]$ > Ligand.

Here Ni(II) complexes were found to be more active than Cu(II) complexes except $[Cu(L)_2(CH_3COO)_2]$.

With the fungus *P. glomerata* the order of activity was Bavistin (standard) > $[Ni(L)_2(CH_3COO)_2]$ > $[Ni(L)_2(NO_3)_2]$ > $[Ni(L)_2(Cl)_2]$ > $[Cu(L)_2(CH_3COO)_2]$ > $[Cu(L)_2(Cl)_2]$ > Ligand. i.e. Bavistin > Ni(II) complexes > Cu(II) complexes > Ligand.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.04.114.

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