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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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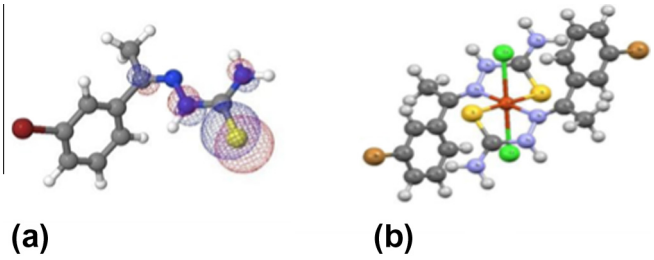
HIGHLIGHTS

- 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. (°C)	Yield (%)	Metal	Elemental analysis data (%) found (calculated)			μ_{eff} (BM)
						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