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# Synthesis, spectral characterization and biological evaluation of copper(II) and nickel(II) complexes with thiosemicarbazones derived from a bidentate Schiff base

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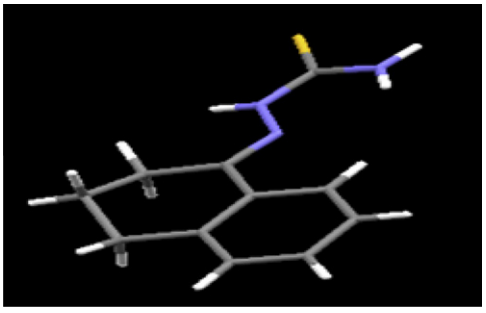
## HIGHLIGHTS

- Synthesized ligand was characterized by single crystal study and other methods.
- Synthesized Cu(II) and Ni(II) complexes with ligand were characterized by different spectroscopic methods.
- Synthesized compounds have been screened against bacterial and fungal species in *In vitro* conditions.
- Ligand was not found to be active against pathogenic bacteria while some of the complexes were found effective.
- All the complexes were found to be more active against fungal pathogens than the parent ligand.

## GRAPHICAL ABSTRACT

Ligand and its Cu(II) and Ni(II) complexes were successfully synthesized, and characterized in the solid state and in solution. The some of the synthesized Cu(II) and Ni(II) complexes have shown an enhanced antimicrobial activities.
Single crystal structure for ligand.



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## ABSTRACT

Complexes of copper(II) and nickel(II) of general composition $M(L)_2X_2$, have been synthesized with the ligand 1-Tetralone thiosemicarbazone (where L = 1-Tetralone thiosemicarbazone and $X = Cl^-, 1/2SO_4^{2-}$). The molar conductance of the complexes in fresh solution of DMSO lies in the range of 10–20 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ indicating their non-electrolytic behavior. Thus, the complexes may be formulated as $[M(L_2)X_2]$. Ligand was characterized by mass, NMR, IR and single crystallographic studies. All the complexes were characterized by elemental analyses, magnetic moments, IR, electronic and EPR spectral studies. The IR spectral data of ligand indicated the involvement of sulfur and azomethine nitrogen in coordination to the central metal ion. The copper(II) and nickel(II) complexes were found to have magnetic moments1.93–1.96 BM and 2.91–2.94 BM corresponding to one and two unpaired electrons respectively. On the basis of molar conductance, EPR, electronic and infrared spectral studies, a tetragonal geometry has been assigned for Cu(II) chloride complex and trigonal bipyramidal to Cu(II) sulfate complex but an octahedral geometry for Ni(II) complexes. Newly synthesized ligand and its Cu(II) and Ni(II) complexes have also been screened against different bacterial and fungal species.



## Introduction

Schiff's bases such as thiosemicarbazones and semicarbazones are important class of compounds which have long attracted attention, owing to their remarkable biological and pharmacological

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properties [1]. Complexes of thiosemicarbazones with transition metals have received attention because of their biological activities including antitumor, antibacterial, fungicidal and ant – carcinogenic properties [2]. The well documented biological activities of several thiosemicarbazones often have been attributed to their ability to form chelates with transition metal ions [3]. These metal complexes, especially those containing copper(II), are more active than the uncoordinated thiosemicarbazone molecules. Copper(II) complexes possess a wide range of biological activity and are among the most potent anti-viral, anti-tumor and anti-inflammatory agents [4]. Metal complexes of Ni(II) are also found to act as a sensor [5].

In view of above applications it is highly desirable to synthesize and characterize transition metal complexes with such 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 1-Tetralone.

## 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 1-Tetralone (1.46 mL, 0.01 mol) was mixed. This mixture was refluxed at 60–70 °C for 4 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 65%, mp 180 °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. Scheme for the synthesis of ligand is given in Fig. 1.

### *Synthesis of the complexes*

The complexes were prepared by the general method: A filtered solution of the appropriate metal salt (0.005 mol) in EtOH or water in case of sulfato complexes (25 mL) was mixed with a solution of the 1-Tetralone thiosemicarbazone (0.010 mol) in EtOH (50 mL) and the resulting mixture was stirred under reflux for 2–36 h (h) (8 h for $[Cu(L)_2Cl_2]$, 2 h for $[Cu(L)_2SO_4]$ complex, 7 h for $[Ni(L)_2Cl_2]$ complex, 36 h for $[Ni(L)_2SO_4]$) complex. For $[Cu(L_2)Cl_2]$ complex pH was maintained at 6 by adding aqueous ammonia. The crystals formed were removed by filtration, washed thoroughly with 50% EtOH and dried under vacuum over $P_4O_{10}$.

### *Analysis*

The C and H and S were analyzed on Carlo–Erba 1106 elemental analyzer. The Nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities 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. Proton ($^1H$) NMR spectra were recorded on Hitachi FT-NMR model R-600 spectrometer using DMSO as a solvent. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra (CsI) were recorded on FTIR spectrum BX-II spectrophotometer. 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. The molecular weights of complexes were determined croscopically in benzene.

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

| Compounds | Emperical formulae | Color | M.p. (°C) | Yield (%) | Metal | Elemental analysis data (%) Found (calculated) | | | | $\mu_{eff}$ (BM) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | S | |
| Ligand (L) | $C_{11}H_{13}N_3S$ | Cream | 180 | 65 | | 59.70 (60.27) | 6.06 (5.94) | 19.04 (19.18) | 14.97 (14.61) | |
| $[Cu(L_2)Cl_2]$ | $CuC_{22}H_{26}N_6S_2Cl_2$ | Dark green | >290 | 64 | 11.01 (11.09) | 46.43 (46.11) | 4.12 (4.54) | 14.98 (14.67) | 11.65 (11.91) | 1.93 |
| $[Cu(L_2)SO_4]$ | $CuC_{22}H_{26}N_6S_3O_4$ | Turquoise green | >290 | 68 | 10.36 (10.62) | 44.47 (44.17) | 4.08 (4.38) | 14.66 (14.05) | 15.89 (16.07) | 1.96 |
| $[Ni(L_2)Cl_2]$ | $NiC_{22}H_{26}N_6S_2Cl_2$ | Light green | >290 | 63 | 10.11 (10.33) | 46.68 (46.50) | 4.23 (4.61) | 15.10 (14.80) | 11.41 (11.28) | 2.91 |
| $[Ni(L_2)SO_4]$ | $NiC_{22}H_{26}N_6S_3O_4$ | Dark green | >290 | 66 | 9.45 (9.89) | 44.87 (44.53) | 4.23 (4.41) | 14.55 (14.16) | 16.42 (16.20) | 2.94 |

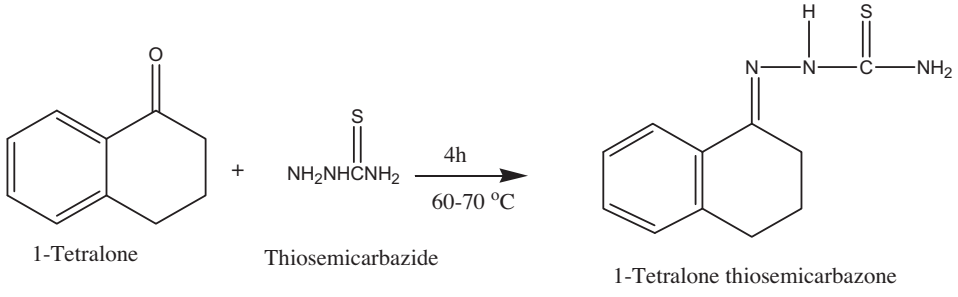


**Fig. 1.** Synthesis and structure of ligand (L).