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Syntheses, spectroscopic characterization, thermal study, molecular modeling, and biological evaluation of novel Schiff's base benzil bis(5-amino-1,3,4-thiadiazole-2-thiol) with Ni(II), and Cu(II) metal complexes

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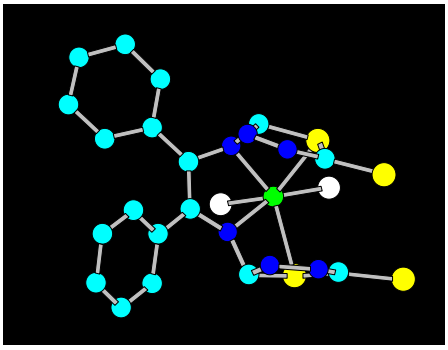
HIGHLIGHTS

- Synthesis, characterization and Molecular modeling of novel Schiff's base ligand and complexes.
- Complexes possessed octahedral, tetragonal, square pyramidal, and tetrahedral geometry.
- Thermal data suggested that metal complexes were more stable than free ligand.
- *In vitro* antimicrobial activity of ligand and its complexes were screened.
- Complexes were found more biologically sensitive than ligand.

GRAPHICAL ABSTRACT

Synthesized ligand behaves as tetradentate and coordinates to metal ion through sulfur atoms of thiol ring and nitrogen atoms of imine group. Ni(II), and Cu(II) complexes were synthesized with this nitrogen–sulfur donor (N_2S_2) ligand. Geometry optimized structure of [Cu(L)Cl_2] complex.



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ABSTRACT

Novel Schiff's base ligand, benzil bis(5-amino-1,3,4-thiadiazole-2-thiol) was synthesized by the condensation of benzil and 5-amino-1,3,4-thiadiazole-2-thiol in 1:2 ratio. The structure of ligand was determined on the basis of elemental analyses, IR, ^{1}H NMR, mass, and molecular modeling studies. Synthesized ligand behaved as tetradentate and coordinated to metal ion through sulfur atoms of thiol ring and nitrogen atoms of imine group. Ni(II), and Cu(II) complexes were synthesized with this nitrogen–sulfur donor (N_2S_2) ligand. Metal complexes were characterized by elemental analyses, molar conductance, magnetic susceptibility measurements, IR, electronic spectra, EPR, thermal, and molecular modeling studies. All the complexes showed molar conductance corresponding to non-electrolytic nature, expect [Ni(L)]$(NO_3)_2$ complex, which was 1:2 electrolyte in nature. [Cu(L)(SO_4)] complex may possessed square pyramidal geometry, [Ni(L)]$(NO_3)_2$ complex tetrahedral and rest of the complexes six coordinated octahedral/tetragonal geometry. Newly synthesized ligand and its metal complexes were examined against the opportunistic pathogens. Results suggested that metal complexes were more biological sensitive than free ligand.

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Introduction

Schiff's bases and their transition metal complexes were playing an important role in the development of coordination chemistry [1,2]. Schiff's base metal complexes were studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas [3]. Schiff's bases had a chelating structure and were in demand because they were straight forward to prepare [4]. In Azomethine derivatives, the C=N linkage was essential for biological activities like antifungal [5], antibacterial [6], antitumour [7], antimalarial [8], antiviral [9,10], etc. The synthesis of Schiff's base ligand incorporating 1,3,4-thiadiazole ring as amine was attracted widespread attention due to their diverse pharmacological properties such as antimicrobial, analgesic, and anti-hepatitis B viral activities [11]. Thiadiazole derived Schiff's bases showed analgesic, and inflammatory activities also [12]. In recent years, a number of research articles had been published on transition metal complexes derived from 5-amino-1,3,4-thiadiazole-2-thiol and its derivatives which contain aza, oxo-aza, and thio-aza donor atoms [13,14]. The present report deals with synthesis, spectroscopic characterization, thermal study, and biological evaluation of Ni(II), and Cu(II) complexes with tetradentate ligand, which was derived from benzil and 5-amino-1,3,4-thiadiazole-2-thiol.

Experimental details

Materials

All chemicals used were commercial products and used as supplied. 5-Amino-1,3,4-thiadiazole-2-thiol, and benzil were of AR grade and procured from Alfa Aesar, Heysham, England and Sigma Aldrich, Bangalore, India. Metal salts were purchased from E. Merck, India and were used as received. All used solvents were of spectroscopic grade.

Synthesis of Schiff's base ligand

An ethanolic solution of 5-amino-1,3,4-thiadiazole-2-thiol (2 mol, 2.664 g) was heated for 15 min. and then added to hot ethanolic solution of benzil (1 mol, 2.102 g) with continuous stirring and the reaction solution was refluxed for 5 h at 60 °C. It was allowed to stay at room temperature and kept in refrigerator overnight. On cooling, the yellow color solid product was precipitated out. It was filtered off, washed several times with cold ethanol, distilled water and then dried in vacuum over P_4O_{10}. Synthesis of ligand is given in Scheme 1 (Supplementary Material).

Synthesis of metal complexes

A hot ethanolic solution of the corresponding metal salt, (except sulfate which was taken in aqueous medium) (0.001 mol) was mixed with hot ethanolic solution of Schiff's base ligand (0.001 mol) and content refluxed for 10–12 h at temp. 85–90 °C. pH (5–7) was adjusted by adding of 2–3 drops of aqueous ammonia. The corresponding colored complexes were separated out by filtration, washed thoroughly with ethanol, distilled water and dried under vacuum over P_4O_{10}.

Analytical and physical measurements

Elemental study (CHN) was analyzed on Carlo-Erba 1106 elemental analyzer. 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. IR spectra were recorded on FT-IR spectrum BX-II spectrophotometer in CsI pellet. The electronic spectra were recorded in DMSO on Shimadzu UV–visible mini-1240 spectrophotometer. Electronic impact mass spectrum was recorded on JEOL, JMS-DX-303 mass spectrometer. ^{1}H NMR spectra was recorded on a Bruker Advanced DPX-300 spectrometer using DMSO-d_6 as a solvent at IIT Delhi. EPR spectra of all complexes were recorded at room temperature (RT) on E_4-EPR spectrometer using the DDPH as the g-marker at SAIF, IIT Bombay. Thermo gravimetric analysis was carried out in dynamic nitrogen atmosphere (30 mL/min) with a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzer. Molecular modeling of ligand and its metal complexes was performed using Hyperchem. 7.51 version.

Molecular modeling

3D molecular modeling of the proposed structure of ligand and its metal complexes was performed using Hyperchem. 7.51 version. This version was used to calculate energy and other parameters like bond angles, bond lengths by Molecular Mechanics, MM plus force field. Hydrogen atoms were omitted for the sake of clarity. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries. Several cycles of energy minimization had to be carried for each molecule. Vibration analysis was done to check the absence of imaginary frequencies.

Antibacterial screening

The antibacterial screening of ligand and its metal complexes was tested against some bacteria *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa,* and *Klebsiella pneumonia* by using paper disk diffusion method [15]. Base plates were prepared by pouring 10 mL of autoclaved Muller Hinton agar into sterilized Petri dishes (9 mm diameter) and allowing them to settle. Molten autoclaved Muller Hinton that was kept at 38 °C was incubated with a broth culture of used bacteria species. Prepared plates were incubated for 24–30 h and the inhibition zones (mm) were measured around each disk carefully. As organism grows, it forms a turbid layer, except in the region where the concentration of antibacterial agent was above the minimum inhibitory concentration, and a zone of inhibition was seen. The solutions of tested compounds were prepared in DMSO.

Antifungal screening

The Poison food Technique was applied to examine fungicidal investigations of synthesized ligand and its metal complexes against some fungi *Rhizoctonia solani, Sclerotium rolfsii, Macrophomina phaseolina, Fusarium oxysporum,* and *Aspergillus niger*. DMSO and Fluconazole were employed as a control and standard fungicide, respectively. The inhibition of the mycelial growth of fungi was expressed in percentage and determined from the growth in the test plate relative to the respective control plate as given below:

$$I(\%) = (CT)/C \times 100,$$

where I = % Inhibition, C = Radial diameters of the colony in control, T = Radial diameter of the colony in test compound.

Results and discussion

Metal complexes were synthesized by mixing the hot ethanolic solution of ligand with ethanolic solution of the corresponding metal salt in 1:1 ratio. The Schiff's base ligand behaved as a