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Synthesis, spectroscopic, anticancer and antibacterial studies of Ni(II) and Cu(II) complexes with 2-carboxybenzaldehyde thiosemicarbazone

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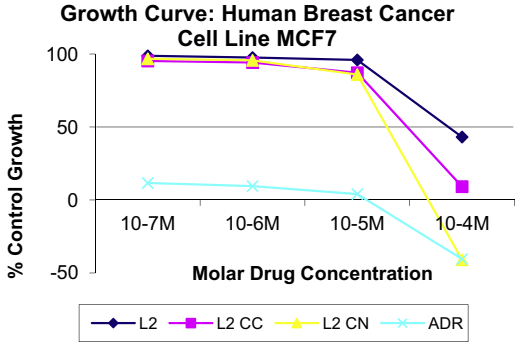
HIGHLIGHTS

- Synthesis and spectral characterizations of novel Schiff base ligand (2CBTS).
- Preparation and spectral studies of Ni(II) and Cu(II) complexes of 2CBTS.
- Antibacterial screening of ligand, Ni(II) and Cu(II) complexes.
- Anticancer studies of 2CBTS and its Cu(II) complexes against MCF 7.

GRAPHICAL ABSTRACT

Tridentate Schiff base ligand 2-carboxybenzaldehyde thiosemicarbazone (L) and its Ni(II) and Cu(II) complexes were synthesized and characterized with spectral data. Synthesized complexes have a composition of $M(L)X(H_2O)_2$ (where M = Ni(II), Cu(II) and X = Cl^-, NO_3^-, CH_3COO^-). Spectral studies reveals, an octahedral geometry for Ni(II) and a tetragonal geometry for Cu(II) complexes. Compounds were screened for anticancer studies against MCF-7 and calculated minimum inhibitory concentration and also for antibacterial activity using Kirby–Bauer single disk susceptibility test.



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ABSTRACT

Ni(II) and Cu(II) complexes of 2-carboxybenzaldehyde thiosemicarbazone (L) were synthesized and investigated by their spectral and analytical data. These newly synthesized complexes have a composition of $M(L)X(H_2O)_2$ (where M = Ni(II), Cu(II) and X = Cl^-, NO_3^-, CH_3COO^-) and (L) is the tridentate Schiff base ligand. The ligand and its complexes have been characterized on the basis of analytical, molar conductivity, magnetic susceptibility measurements, FT-IR, ESR, ^1H NMR and electronic spectral analysis. All the compounds were non-electrolytic in nature. On the basis of spectral studies an octahedral geometry has been assigned for Ni(II) and a tetragonal geometry for Cu(II) complexes. The ligand and its metal complexes were screened for their anticancer studies against human breast cancer cell lines MCF-7 and calculated minimum inhibitory concentration and also for antibacterial activity using Kirby–Bauer single disk susceptibility test.

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Introduction

The preparation of a novel ligand is the most important step in the development of metal complexes which exhibit unique properties and reactivity. Since the electron donor properties of ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies. The chemistry of thiosemicarbazones has received considerable attention in view of their variable bonding modes, promising biological applications, structural diversity and ion-sensing ability [1].

Thiosemicarbazone ligands derived from the combination of thiosemicarbazide and an aldehyde or ketone, are a useful ligand group for obtaining coordination spheres with mixed N/S donors. Interest in these ligands has been driven, in part, by potentially beneficial biological activities of ligands and their metal complexes, including, antifungal, antimicrobial, anticancer, fungicide, bacteriocide, anti-inflammatory and antiviral activities [2–7]. The inhibitory action of these compounds is attributed to their chelating properties [8–12].

In this present investigations, we report the synthesis, spectral studies of Schiff base thiosemicarbazone ligand of 2-carboxybenzaldehyde (2CBTS) and its Ni(II) and Cu(II) complexes. The compounds were also screened for their anticancer and antibacterial activities.

Experimental

Materials and methodologies

All the chemicals used were of AR grade, procured from Alfa/Aesar and Aldrich. Solvents used were of analytical grade. IR spectra (KBr pellets) were recorded in the region 4000–400 cm^{-1} on a FT-IR spectrum BX-II spectrophotometer. ^1H NMR spectrum was recorded with a model Bruker Advance DPX-300 spectrometer operating at 300 MHz using DMSO-d_6 as a solvent and TMS as an internal standard. EPR spectra of Cu(II) complexes were recorded as polycrystalline sample and in the DMSO solution, at room temperature (RT) on E_4-EPR spectrometer using the DPPH as the *g*-marker. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini-1240 spectrophotometer. Magnetic moment measurements (Gouy balance) were made at room temperature using $CuSO_4{\cdot}5H_2O$ as a calibrant.

Synthesis and characterization of ligand (L)

A solution of thiosemicarbazide (1.822 g, 0.02 mol) in 15 mL absolute ethanol was heated for 10 min in the presence of a few drops of acetic acid to make a clear solution. To this a hot solution of 2-carboxybenzaldehyde (3.00 g, 0.02 mol) in absolute ethanol (15 mL) was added drop wise with constant stirring. The resulting mixture was refluxed for 30 min and cooled overnight at 0 °C. The off white product (Scheme 1) so formed was filtered, washed with cold ethanol, and dried under vacuum over P_4O_{10}, Yield was 65.0%. Melting Point observed was 188 °C.

Preparation of the complexes

A hot ethanolic solution (~15 mL, 0.001 mol) of ligand was taken in a round bottom flask and heated for about 10 min at 70 °C to make the solution clear. Then hot ethanolic solution (~15 mL, 0.001 mol) of the corresponding metal salt was added with continuous stirring and then refluxed for about 12–15 h. On cooling at room temperature, the solid product was precipitated out. The resulting solid product was filtered, washed several times with ethanol, and dried in vacuum over P_4O_{10}.

Biological studies

Anticancer activity

The sulphorhodamine B (SRB) assay is used for cell density determination, based on the measurement of cellular protein content. The method described here has been optimized for the toxicity screening of compounds to adherent cells in a 96 well format. After an incubation period, cell monolayers are fixed with 10% (wt/vol) trichloroacetic acid and stained for 30 min, after which the excess dye is removed by washing repeatedly with 1% (vol/vol) acetic acid. The protein-bound dye is dissolved in 10 mM tris base solution for OD determination at 510 nm using a microplate reader. The results are linear over a 20-fold range of cell numbers and the sensitivity is comparable to those of fluorometric methods.

Antibacterial activity

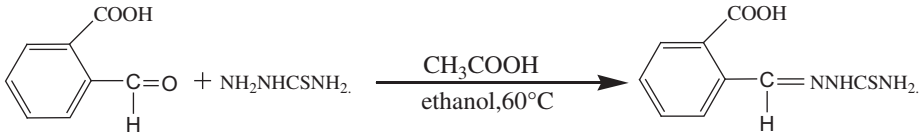
The ligand and its metal complexes were screened for their antibacterial activity against gram positive and gram negative bacteria *Escherichia coli* and *Bacillus cereus* respectively. Antibacterial activity was performed by using the Kirby–Bauer single disk susceptibility test (13, 14).

Results and discussion

All complexes were prepared by reaction of metal salt with ligand. The molar conductivities at room temperature of 10^{-3} M solutions of complexes in DMSO were in range of 13–18 Ω^{-1} cm^2 mol^{-1} corresponding to non-electrolytes. The metal complexes were sparingly soluble in water, ethanol, acetone and most of the organic solvents but completely soluble in DMSO and DMF. Higher melting point of the metal complexes than the free ligand indicated the stability of the complexes. The analytical data revealed that all complexes possessed 1:1 metal to ligand stoichiometry based on elemental analysis, the complexes were assigned the composition as shown in Table 1.

IR spectra

The main assignments of IR absorption bands of the ligand and its metal complexes are given in Table 2. The IR spectrum of free ligand shows ν(C=N) azomethine band at 1606 cm^{-1} [14] and band at 786 cm^{-1} due to ν(C=S) [15] (Fig. 1). On complexation, the position of these bands is shifted towards lower frequency



Scheme 1. Synthesis and structure of 2-carboxybenzaldehyde thiosemicarbazone ligand(L).