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Spectroscopic evaluation for VO(II), Ni(II), Pd(II) and Cu(II) complexes derived from thiosemicarbazide: A special emphasis on EPR study and DNA cleavage

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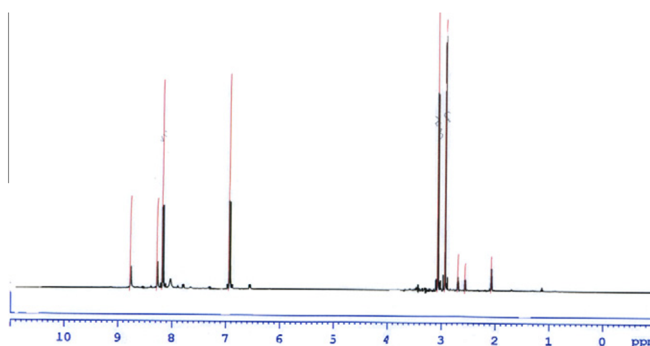
HIGHLIGHTS

- Bivalent complexes was prepared.
- The coordination behavior of the ligand was concerned.
- The EPR spectra is supporting the geometry.
- The biological investigation was carried out.

GRAPHICAL ABSTRACT

The ^{1}HNMR spectrum of the used free ligand in complexation.



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ABSTRACT

Some thiosemicarbazide complexes were prepared and deliberately investigated by all allowed tools. The ligand coordinates as a mono negative bidentate towards VO(II) and Ni(II) as well as a neutral bidentate towards Pd(II) and Cu(II) ions. Electronic spectral data beside the magnetic measurements facilitate the structural geometry proposal. EPR spectra of Cu(II) and VO(II) complexes were recorded in their solid state. Spin Hamiltonian parameters and molecular orbital coefficient for Cu(II) and VO(II) complexes were calculated and supporting the octahedral geometry of Cu(II) complex and a square pyramidal for VO(II) one. The biological activity investigation was studied by the use of all prepared compounds. The VO(II) and Cu(II) complexes display the susceptible biotoxicity against a gram-positive bacterium. Also, Cu(II) complex displays the same toxicity against gram-negative bacteria used. The effect of all compounds on DNA were photographed. A successive degradation for the DNA target was observed with Pd(II) and Ni(II) complexes beside their original ligand.

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Introduction

Organic compounds containing oxygen, nitrogen and sulfur as donors are extensively studied [1]. Recently, their complexes cover several areas ranging from general considerations of the effect of sulfur and electron delocalization in transition metal complexes in the potential biological activity. Namely, thiosemicarbazide (TSC), N^1H_2—N^2H—$C^3(S)$—N^4H_2, behaves as a bidentate ligand coordinates through the terminal N^1 and S atoms, the remaining N atoms (the hydrazine N^2 and thioamide N^4) form the hydrogen bonding donor pair, suitably oriented for the interaction with the

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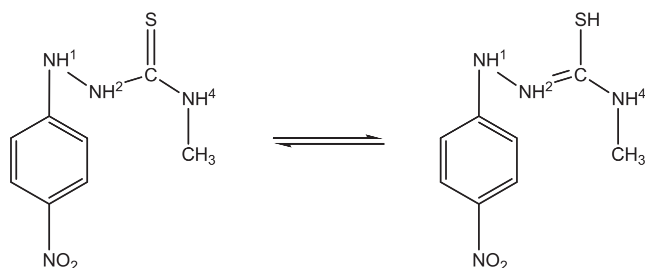

Fig. 1. The thione–thiol forms of 1-(4-nitrophenyl)-4 methyl thiosemicarbazide (HNPMT).

acceptor pair, i.e. oxygen atoms of the dicarboxylate anion [2]. This work is considered a continuation for our work. Previously, we prepared a series of complexes using variable thiosemicarbazides and thiosemicarbazones derivatives [3–16]. A distinguish biological activity was recorded for most investigated complexes especially with the presence of N, S and O heteroatom's. This is the cause for continuing the work in the same area. In this paper, we concerned with the preparation of a series of VO(II), Ni(II), Pd(II) and Cu(II) complexes with a new derivative of thiosemicarbazide. EPR parameters of VO(II) and Cu(II) complexes were calculated to serve in the structural investigation. Also, the biological effect of all prepared compounds was studied towards different bacteria as well as, towards the DNA degradation.

Experimental

Preparation of the ligand

The ligand was prepared by refluxing solution of 4-nitrophenyl hydrazine (3.02 gm; 20 mmol) with methyl isothiocyanate (1.46 gm; 20 mmol) in absolute EtOH. The reaction mixture was refluxed for 3 h and then left to cool. Pale yellow crystals were separated. The product was filtered off, washed several times with ethanol and then kept to dry in a desiccators over $CaCl_2$. The analytical and spectral data proposed the structure in Fig. 1. ^{1}HNMR spectrum (Fig. 2) displays the following data: $\delta = 8.76$ (s, 1H, NH^1); $\delta = 8.27$ (s, 1H, NH^2 or SH); $\delta = 8.716$ (s, 1H, NH^4); $\delta = 6.81$–6.94 (m, 4H, Ph); $\delta = 3.07$ (s, 3H, CH_3) and $\delta = 2.93$ for DMSO and may assert on the following structure.

Preparation of the metal complexes

The metal complexes were prepared by adding stoichiometric quantities of (2 mmol) the metal salt, $VOSO_4{\cdot}2.5{\cdot}H_2O$, $PdCl_2$, $Cu(NO_3)_2{\cdot}3H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ to a hot solution of the ligand (2 mmol, 0.45 gm) in absolute EtOH. A direct change in the color was observed by a sudden addition. The mixture was refluxed for 3 h till the precipitate is formed. To ensure the isolation of pure complexes the resulting solid were filtered immediately, washed several times with hot EtOH and kept in a vacuum desiccators over $CaCl_2$.

Antimicrobial activity and genotoxicity

The ligand and its complexes were screened for their antimicrobial activity using the cup-diffusion technique [17] against *Bacillus* sp. as gram positive and *Klebsiella* sp. and *Proteus* sp. as gram negative bacteria. 0.2 ml of the tested substance (10 μg/ml) was placed in specified cup made in the nutrient agar medium on which a culture of the tested bacteria has been spread to produce uniform growth. After 24 h incubation at 37 °C, the diameter of inhibition zone was measured as mm. A solution of Calf thymus DNA (2 mg) was dissolved in 1 ml of distilled water to a final concentration of 2 g/l. Stock concentrations of the ligand and their complexes were prepared by dissolving 2 mg/ml in DMSO. An equal volume of each compound and DNA were mixed thoroughly and kept at room temperature for 2–3 h. The effect of chemicals on the DNA were analyzed by agarose gel electrophoresis. 2 μl of loading dye was added to 15 μl of the DNA-chemical mixture before being loaded into the wall of an agarose gel. The loaded DNA-chemical mixtures were fractionated by electrophoresis, visualized by UV and photographed.

Equipment and analysis

C, H and N content of the ligand and its complexes were determined at the Microanalytical Unit of Cairo University, Egypt. The metal content was determined by standard methods [18]. The IR spectra were recorded as KBr disc on a Mattson 5000 FTIR Spectrophotometer. The UV–Vis spectra of the complexes were recorded on UV_2 Unicam Spectrophotometer. The ^{1}HNMR spectrum of the ligand, in d_6 DMSO, was recorded on a Varian Gemini Spectrophotometer (200 MHz). The EPR spectra of the Cu(II) and VO(II) complexes (as a powder) at 300 k were recorded on a Bruker EMX Spectrometer working in the x-band (9.78 MH) with 100 kHz modulation frequency, 1 mw microwave power and 4G modulation amplitude. The magnetic measurements were carried out on a Johnson Matthey magnetic balance, UK. The effective magnetic moments were evaluated by applying $\mu_{eff} = 2.828\sqrt{X'_M T}$, where X_M is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the ligand. The X-ray powder diffraction analyses were carried out using Rigku Model

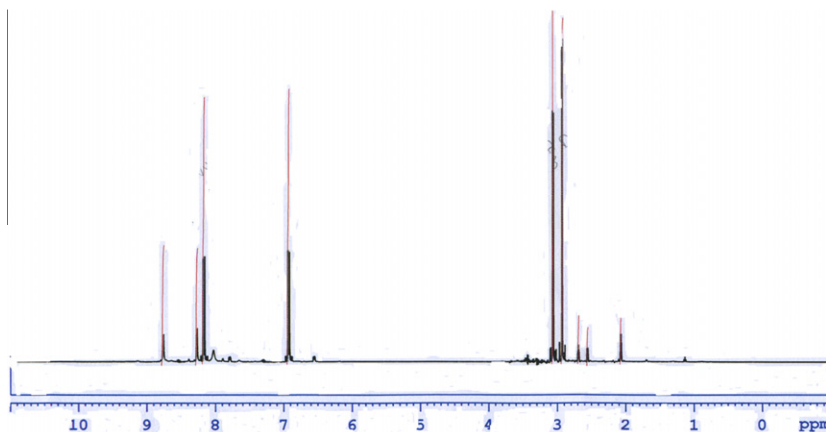

Fig. 2. The ^{1}HNMR spectrum of HNPMT ligand.

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