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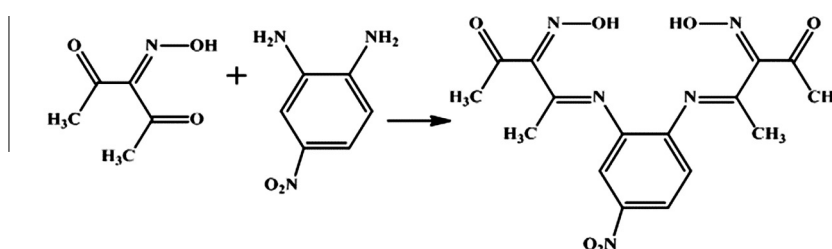
Synthesis, characterization and fungicidal activity of binary and ternary metal(II) complexes derived from 4,4'-((4-nitro-1,2-phenylene)bis(azanylylidene))bis(3-(hydroxyimino)pentan-2-one)

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HIGHLIGHTS

- Novel ligand, binary and ternary metal complexes were synthesized.
- Characterization of the ligand and metal complexes were carried out by various spectral techniques.
- The complexes displayed either a tetragonal distorted octahedral or a square planar geometry.
- The metal complexes are more potent as fungicides than the ligand and the standard antifungal drug "Amphotericin B".

GRAPHICAL ABSTRACT



Preparation of the ligand 4,4'-((4-nitro-1,2-phenylene)bis(azanylylidene))bis(3-(hydroxyimino)pentan-2-one)

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ABSTRACT

Ternary copper(II) and binary copper(II), nickel(II) and cobalt(II) complexes derived from 4,4'-((4-nitro-1,2-phenylene)bis(azanylylidene))bis(3-(hydroxyimino)pentan-2-one) (H_2L) were synthesized and characterized by elemental and thermal analyses, IR, UV–Vis. and 1H NMR spectroscopy, conductivity and magnetic moments measurements. The analytical and spectral data showed that, the ligand acts as dibasic tetradentate or dibasic hexadentate bonding to the metal ion via the two-imine nitrogen, two nitrogen and/or oximate oxygen atoms of deprotonated oxime groups forming five and/or six rings including the metal ions. The complexes adopt either tetragonal distorted octahedral or square planar geometry around metal ions. The ESR spectra of the solid copper(II) complexes are characteristic to d^9 configuration and having an axial symmetry type of a $d_{(x^2-y^2)}$ ground state. The g values confirmed the geometry is elongated tetragonal octahedral geometry with considerably ionic or covalent environment. The antifungal biological activity of the prepared compounds was studied using well diffusion method. The obtained results showed that, the ligand is biologically inactive while its metal complexes were more potent fungicides than the ligand and standard antifungal drug (Amphotericin B).

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Introduction

The chemistry of oxime ligands has become a fascinating area of research over several years because of their ability to stabilize

many different metals in various oxidation states, the development of bioinorganic models, the design of selective receptors for Ca(II) and Ba(II) ions, the development of new oxygen activation catalysis, as well as their structural features which include short intra-molecular hydrogen bonds and packing configurations which occasionally give rise to unusual optical properties[1–3]. As a ligand, the oxime moiety is potentially ambidentate [4] and can

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coordinate either through the nitrogen [5], (Fig. 1-I) or the oxygen atom (II) [6,7]. The vast literature on structural studies of oxime complexes reveals some interesting features of its coordination behavior. It may coordinate to one metal ion through the nitrogen atom and another metal ion through the oxygen atom (Fig. 1-III) forming $\mu_{1,2}$ (N, O) oximate-bridged extended network [8]. In the majority of complexes, only the nitrogen atom coordinates to the metal center, and the oxygen atom does not take part in coordination, although there are quite few examples where both the atoms (oximate nitrogen and oxygen, (Fig. 1-IV) do take part in coordination [9,10]. From a medicinal chemistry point of view, it is found that different oxime ligands and their metal complexes have shown notable bioactivity as chelating therapeutics, drugs, inhibitors of enzymes, intermediates in biosynthesis of nitrogen oxides [11,12], antimicrobial [13], anticancer [14], fungicides [15], bactericides [16], antioxidant [17]. The antibacterial activity of 4-R-arylhydrazone-oximes vanadyl complexes against *Escherichia coli*, *Bacillus*, *Proteus* and *Klebsiella* indicates these compound as potential molecules for drug design [7]. Copper(II), nickel(II) and cobalt(II) complexes of anti- β -ferrocenylethylaminoglyoxime and anti- β -ferrocenyl ethylaminophenylglyoxime showed mild antibacterial activity against *Staphylococcus aureus*, *Streptococcus mutans*, *Enterococcus faecalis*, *E. coli* and *Pseudomonas aeruginosa* [18]. Indirubin-3-oxime induces cell death and apoptosis in human laryngeal carcinoma cells [19]. From another point of view, oxime compounds have been used as efficient chelating agents in analytical chemistry for isolation, separation and extraction of different metal ions [20,21]. In view of the interest and importance of oxime compounds, the work reported herein is focused on synthesis and characterization of new binary copper(II), nickel(II) and cobalt(II) as well as ternary copper(II) oxime complexes derived from 4,4'-(4-nitro-1,2-phenylene)bis(azanylylidene)-bis(3-(hydroxyimino)pentan-2-one). These compounds were characterized by elemental and thermal analyses, spectral, magnetic and conductivity studies as well as thermal analysis (TGA/DTA). The work was extended to study the antifungal activity of the ligand and its metal complexes against *Aspergillus niger* using well diffusion method.

Experimental

Materials

All reagents employed for the preparation of the ligands and their complexes were of the analytical grade available and used without further purification. 4-nitrobenzene-1,2-diamine was provided from Aldrich company (assay 99%); DMSO (assay 99.7%); absolute ethanol (assay $\geq 99.8\%$). Metal salts were provided from SIGMA-ALDRICH company; $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (assay $\geq 99\%$), $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (assay $\geq 99\%$), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (assay $\geq 99.995\%$). 2-hydroxy benzaldehyde (assay $\geq 98\%$), acetyl acetone provided from Sigma company (assay $\geq 99\%$) and dehydroacetic acid (assay $\geq 98\%$). 3-(hydroxyimino) pentane-2,4-dione was prepared by a published method [22]. The purity of all prepared compounds was confirmed by TLC.

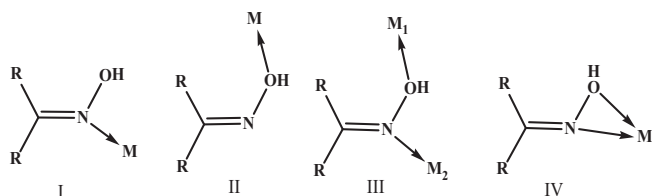


Fig. 1. Mode of coordination of oxime moiety.

Instrumentation and measurement

The ligand and its metal complexes were analyzed for C, H and N at the Microanalytical center, Cairo University, Egypt. Standard analytical methods were used to determine the metal ion content [23–25]. FT-IR spectra of the ligand and its metal complexes were measured using KBr discs by a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400–4000 cm^{-1} . Electronic spectra in the 200–900 nm regions were recorded on a PerkinElmer 550 spectrophotometer. The thermal analysis (TG) was carried out on a Shimadzu DT-30 thermal analyzer from room temperature to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Magnetic susceptibilities were measured at 25 $^{\circ}\text{C}$ by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant [26]. The magnetic moments were calculated from the equation:

$$\mu_{\text{eff.}} = 2.84 \sqrt{\chi_M^{\text{corr.}} \cdot T}$$

The molar conductance of 10^{-3} M solution of the complexes in DMSO was measured at 25 $^{\circ}\text{C}$ with a Bibby conductometer type MCI. The resistance measured in ohms and the molar conductivities were calculated according to the equation:

$$\Lambda_M = \frac{V \times K \times g}{Mw \cdot \Omega}$$

where Λ_M = molar conductivity/ $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, V = volume of the complex solution/mL, K = cell constant ($0.92/\text{cm}^{-1}$), Mw = molecular weight of the complex, g = weight of the complex/g, Ω = resistance/ Ω . ^1H NMR spectrum was obtained on BRUKER 400 MHz spectrometers. Chemical shifts (ppm) are reported relative to TMS. ESR measurements of solid complexes at room temperature were made using a Varian E-109 spectrophotometer, with DPPH as a standard material. TLC is used to confirm the purity of the compounds.

Synthesis of ligand

The ligand, (H_2L) was prepared by dropwise addition of (153 mg, 1.0 mmol) 4-nitrobenzene-1,2-diamine dissolved in 20 mL of absolute ethanol to an ethanolic solution of (hydroxyimino)pentane-2,4-dione (258 mg, 2.0 mmol), (Fig. 2). The mixture was stirred and refluxed for three hours, then left to cool to room temperature. The solid product was filtered off, washed with cold ethanol, followed by recrystallization from ethanol and finally dried under vacuum over anhydrous CaCl_2 . $\text{C}_{16}\text{H}_{17}\text{N}_5\text{O}_6$ (FW = 375.34), Yield: 88%, 3.3 gm, Color: Dark yellow, m.p. = 178, *Elemental Anal.* Calc.: C, 51.20; H, 4.57; N, 18.66. Found: C, 50.98; H, 4.60; N, 18.45. IR, (KBr, cm^{-1}): 2520–3550 (br) $\nu(\text{OH})$, 1673 $\nu(\text{C}=\text{O}_{\text{Acetyl}})$, 1620 $\nu(\text{C}=\text{N}_{\text{imine}})$, 1572 $\nu(\text{C}=\text{N}_{\text{oxime}})$, 1087, 1000 $\nu(\text{N}-\text{OH})$; ^1H NMR (DMSO- d_6 , 400 MHz): 7.90–8.09 ppm (s & d, 3 H, aromatic protons), 2.51 (s, 6 H, (2 $\text{O}=\text{C}-\text{CH}_3$)), 2.49 (s, 6H, ($\text{N}=\text{C}-\text{CH}_3$)). The oxime protons (N–OH) were not observed due to the broadening of signal resulted from the participation of the oxime protons in the intra- and intermolecular hydrogen bonding.

Synthesis of metal complexes

General procedures

Preparation of copper (II) complexes (2–5). Synthesis of complexes (2–4) were carried out by refluxing a hot ethanolic solution of metal acetate (1 mmol) with a hot ethanolic solution of the ligand (1 mmol) for three hours with continuous stirring. The obtained precipitate were filtered off, washed with ethanol and dried in

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