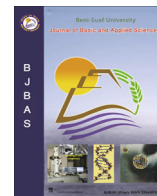


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Synthesis, physicochemical studies and biological evaluation of unimetallic and heterobimetallic complexes of hexadentate dihydrazone ligands



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ABSTRACT

A new coordination unimetallic and heterobimetallic complexes of hexadentate N_2O_4 donor dihydrazone ligands were prepared by the condensation of 4-formyl antipyrine with adipic dihydrazide and succinic dihydrazide. The ligands (**1**) and (**11**) and their complexes thoroughly characterized using various analytical, physical and spectroscopic techniques, which indicate a distorted octahedral geometry around the metal ions. The ESR spectra of solid copper(II) complexes (**2–4**) and (**12–14**) showed axial symmetry with $g_{\parallel} > g_{\perp} > g_e$, indicating distorted octahedral structure and the presence of the unpaired electron in a $d_{(x^2-y^2)}$ orbital with significant covalent bond character. The antimicrobial activity results of the metal compounds (**2–5**), (**7**), (**10**), (**12–15**) and (**17**) show that, all these complexes exhibit inhibitory moderate to mild effects towards *Bacillus subtilis*, *Escherichia coli* and *Aspergillus niger*.

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1. Introduction

Hydrazones play an important role in inorganic, organic, analytical and medicinal chemistry because of their ability to form a large variety of stable compounds and complexes upon coordination with different transition metal ions. Hydrazones have drawn much concern in order to investigate their structures as well as their enormous biomedical activities as: anti-inflammatory (Kajal et al., 2014), antimalarial (Sharma et al., 2014), antitrypanosomal (Carvalho et al., 2004), antibacterial (Rasras et al., 2010), analgesic, antiplatelet (Mashayekhi et al., 2013), antioxidant, antitumor, and antiviral activities (El-Tombary and El-Hawash, 2014). Dihydrazone ligands and their complexes have received increasing attention due to their ease of synthesis, flexibility, versatility, geometry and coordination sites properties (Dey et al., 2014). Due to their versatility as polyfunctional chelating agents towards different metal ions forming homo- or heterobinuclear complexes

(Bacchi et al., 2005) the chemistry of dihydrazone ligands attracted many authors in the last two decades. Complexes contain metal ions, imines and hetero aromatic nitrogen bases may considered as models for substrate metal ion–enzyme interaction (Wang et al., 2014). Chelation causes changes in the biological properties of the ligands and the metal, which cause variety biological activity (Turan et al., 2014). The presence of active azometine $NHN=CH-$ protons in these compounds imparts them a major importance as good candidates for the development of new drugs. Also, the $C=N$ double bond in hydrazones are of major concern, as they act as a pivotal group for synthesis of organic compounds, metal complexes and organocatalysis.

2. Experimental

2.1. Instrumentation and measurements

The starting chemicals were of analytical grade and provided from Merck Company. IR spectra of the solid ligand and complexes recorded on Perkin-Elmer infrared spectrometer 681 or Perkin-Elmer 1430 using KBr disc. The 1H NMR spectra were recorded

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with a JEOL EX-270 MHz FT-NMR spectrometer in DMSO- d_6 as solvent, where the chemical shifts were determined relative to the solvent peaks. Mass spectra of the solid ligands and its metal complexes recorded using JEUL JMS-AX-500 mass spectrometer provided with data system. The molar conductivity of the metal complexes in DMSO at 10^{-3} M concentration measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The molar conductance calculated by equation:

$$\Lambda_m = \frac{V \times K \times g}{Mw \times R} \quad (1)$$

where Λ_m = molar conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$), V = volume of the complex solution (ml), K = cell constant (0.92cm^{-1}), Mw = molecular weight of the complex, g = weight of the complex (gram), R = resistance measured in ohms (Ω). Electronic absorption spectra recorded on a Shimadzu 240 or Perkin Elmer 550 spectrometer using 1-cm quartz cells taking DMSO as solvent. Nujol mull electronic spectra were recorded using whatman filter paper No.1 and referenced against another similar filter paper saturated with paraffin oil. The magnetic susceptibilities of the solid complexes measured in a borosilicate tube with a Johnson Matthey Magnetic susceptibility Balance at room temperature using the modified Gouy method:

$$\mu_{\text{eff}} = 2.84 \sqrt{(\xi_{m,\text{coord}} \times T)} \quad (2)$$

Diamagnetic corrections estimated from Pascal's constant (Lewis and Wilkins, 1960). Thermal gravimetric analysis (TG) carried out on a Perkin Elmer 7 Series from 50 to 1050 °C at a heating rate of 10 °C per minute. The solid ESR spectra of the copper (II) and ruthenium (III) complexes recorded with ELEXSYS E500 Bruker spectrometer in 3-mm Pyrex tubes at 298 K. Diphenylpicrylhydrazide (DPPH) used as a g-marker for the calibration of the spectra. Elemental analyses (CHN) performed in the Analytical Unit within Cairo University, Egypt. Standard analytical methods used to determine the metal ion content (Holzbecher et al., 1976; Svehla, 1979; Vogel, 1989; Welcher, 1958). TLC confirmed the purity of all prepared compounds.

2.2. Synthesis of ligands (1 and 11)

The hydrazone ligands were prepared by refluxing adipohydrazide (1.74 g, 1 mmol) or succinohydrazide (1.46 g, 1 mmol) dissolved in 20 mL of methanol with (4.32 g, 2 mmol) 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl (4-formyl anti-pyridine) dissolved in 30 mL of methanol (Scheme 1). The mixture heated under reflux for two hour with stirring. After cooling, the formed solid product filtered off, then washed several times with cold methanol and finally dried at room temperature.

(1), **N¹,N⁶-bis((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)methylene) adipohydrazide (H₂L¹)**; Yield 85%, m.p. 278 °C, color is white. *Elemental microanalyses*, Calcd. (%) for ligand (H₂L¹) = C₃₀H₃₄N₈O₄ (FW = 570.7): C, 63.1; H, 6.0; N, 19.6. Found (%) C, 62.9; H, 5.8; N, 19.4. IR data, 3240/3214, 1683, 1647, 1606, 958 cm^{-1} assigned to $\nu(\text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{N})$. ¹H NMR (DMSO- d_6 , 270 MHz). δ = 11.05, 10.90 (s, 2H, NH), 8.00, 7.80 (s, 2H, H-C=N), 7.30–7.50 (m, 10H, CH aromatic), 3.20 (s, 6H, N-CH₃), 2.54 (s, 6H, C-CH₃), 2.49 (t, 4H, CO-CH₂), 1.60 (t, 4H, CH₂-CH₂). The mass spectrum of the ligand (H₂L) revealed molecular ion peak at m/z 569.

(11), **N¹,N⁴-bis((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)methylene) succinohydrazide (H₂L²)**; Yield 85%, m.p. 250 °C, color is white; *Elemental microanalyses*. Calcd. (%) for ligand (H₂L²) = C₂₈H₃₀N₈O₄ (FW = 542.6): C, 62.0; H, 5.6; N, 20.7. Found (%) C, 61.6; H, 5.5; N, 20.0; IR (KBr, cm^{-1}), 3328/3203, 1668, 1650, 1609, 958 cm^{-1} assigned to $\nu(\text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N},$

$\text{N}=\text{N})$. ¹H NMR (DMSO- d_6 , 270 MHz). δ = 11.05, 10.85 (s, 2H, NH), 8.00, 7.80 (s, 2H, H-C=N), 7.30–7.50 (m, 10H, CH aromatic), 3.20 (s, 6H, N-CH₃), 2.55 (s, 6H, C-CH₃), 2.5 (s, 4H, CO-CH₂). The mass spectrum of the ligand revealed molecular ion peak at m/z 542.

2.3. Preparation of unimetallic metal complexes (2–3), (5–10), (12–13), (15–17)

These complexes were prepared by adding salts of Cu(CH₃COO)₂·H₂O, CuCl₂·2H₂O, FeCl₃·6H₂O, Fe(NO₃)₃·9H₂O, RuCl₃·3H₂O, UO₂(CH₃COO)₂·2H₂O, UO₂(NO₃)₂·6H₂O or TiCl₄ (1 mmol, in 20 mL) of absolute ethanol to the ligands suspension (1 mmol, in 20 mL of absolute ethanol) in presence of 1 ml triethylamine. The mixture heated under reflux for four hours with stirring. The resulting solid complexes filtered off on heating, washed several times with hot ethanol and dried over anhydrous CaCl₂. *Elemental microanalyses* for

Complex (2) = [Cu(HL¹)(CH₃COO)(H₂O)₂]; Yield 63%, color is light green, M.P., >300 °C, Λ_m , 6.0 O⁻¹ cm² mol⁻¹. Calcd. (%) (FW 728.27); C, 52.78; H, 5.54; N, 15.39; Cu, 8.73. Found (%): C, 53.1; H, 5.3; N, 15.5; Cu, 8.5. IR data, 3428 (br), 3240/ 3215 1683, 1646/1625, 1603/1584, 1523, 1280, 1019, 1562/1378 (Δ = 184), 674/551, 505 cm^{-1} assigned to $\nu(\text{H}_2\text{O}, \text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{C}-\text{O}, \text{C}-\text{O}, \text{N}-\text{N}, \nu_{\text{s}}\text{CH}_3\text{COO}/\nu_{\text{as}}\text{CH}_3\text{COO}, \text{Cu}-\text{O}/\text{Cu}-\text{O}, \text{Cu}-\text{N})$.

Complex (3) = [Cu(HL¹)Cl(H₂O)₂]; Yield 70%; color is light gray, M.P., 250 °C; Λ_m , 3.0 O⁻¹ cm² mol⁻¹. Calcd. (%) (FW = 704.66); C, 51.13; H, 5.03; N, 15.90; Cl, 5.03, Cu, 9.02. Found: C, 51.1; H, 5.2; N, 16.0; Cl, 4.5; Cu, 8.7; IR data, 3421 (br), 3241/3215, 1683, 1647/1631, 1603/1560, 1515, 1287, 1012, 658/ 501, 477, 380 cm^{-1} assigned to $\nu(\text{H}_2\text{O}, \text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{C}-\text{O}, \text{C}-\text{O}, \text{N}-\text{N}, \text{Cu}-\text{O}/\text{Cu}-\text{O}, \text{Cu}-\text{N}, \text{Cu}-\text{Cl})$.

Complex (5) = [Fe(HL¹)Cl₂(H₂O)]·H₂O; Yield 60%, color is Dark brown, M.P., >300 °C, Λ_m , 21.8 O⁻¹ cm² mol⁻¹. Calcd. (%) (FW 732.42); C, 49.20; H, 4.8; N, 15.03; Fe, 7.62; Cl, 9.68. Found: C, 49.5; H, 4.8; N, 15.0; Fe, 7.2; Cl, 8.88. IR data, 3420 (br), 3195, 1677, 1646/1635, 1590/ 1570, 1523, 1300, 1015, 605/554, 490, 349 cm^{-1} assigned to $\nu(\text{H}_2\text{O}, \text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{C}-\text{O}, \text{C}-\text{O}, \text{N}-\text{N}, \text{Fe}-\text{O}/\text{Fe}-\text{O}, \text{Fe}-\text{N}, \text{Fe}-\text{Cl})$.

Complex(6) = [Fe(HL¹)(NO₃)₂(H₂O)]·2H₂O; Yield 61%, color is dark brown, M.P., >300 °C, Λ_m , 26.2 O⁻¹ cm² mol⁻¹. Calcd. (%) (FW 803.53); C, 44.84; H, 4.89; N, 17.43; Fe, 6.95. Found: C, 44.6; H, 4.7; N, 17.5; Fe, 6.5. IR data, 3424 (br), 3243/3200, 1670, 1645/1636, 1596/1566, 1493, 1273, 1022, 1456/1380/875 (Δ = 7.6), 670/575, 461, cm^{-1} assigned to $\nu(\text{H}_2\text{O}, \text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{C}-\text{O}, \text{C}-\text{O}, \text{N}-\text{N}, \text{NO}_3, \text{Fe}-\text{O}/\text{Fe}-\text{O}, \text{Fe}-\text{N})$.

Complex (7) = [(UO₂)(HL¹)(CH₃COO)]·2H₂O; Yield 67%, color is orange, M.P., >300 °C, Λ_m , 4.5 O⁻¹ cm² mol⁻¹. Calcd. (%) (FW = 934.74); C, 41.12; H, 4.31; N, 11.99; UO₂, 28.89. Found: C, 41.2; H, 4.4; N, 11.7; UO₂, 28.1. IR data, 3427 (br), 3241/3203, 1682, 1642/1630, 1596/1565, 1503, 1298, 1022, 1537/1360 (Δ = 177), 631/503, 470, 909 cm^{-1} assigned to $\nu(\text{H}_2\text{O}, \text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{C}-\text{O}, \text{C}-\text{O}, \text{N}-\text{N}, \nu_{\text{s}}\text{CH}_3\text{COO}/\nu_{\text{as}}\text{CH}_3\text{COO}, \text{U}-\text{O}/\text{U}-\text{O}, \text{U}-\text{N}, \text{U}=\text{O})$.

Complex (8) = [(UO₂)(HL¹)(NO₃)]·H₂O; Yield 74%, color is orange, M. P., >300 °C, Λ_m , 25.2 O⁻¹ cm² mol⁻¹. Calcd. (%) (FW = 901.67); C, 39.98; H, 3.69; N, 13.98; UO₂, 29.95. Found (%): C, 40.3; H, 3.9; N, 13.6; M, 29.3. IR data, 3524 (br), 3241/3200, 1682, 1641/1633, 1594/1568, 1532, 1246, 1021, 1461/1384/867 (Δ = 77), 634/506, 462, 909 cm^{-1} assigned to $\nu(\text{H}_2\text{O}, \text{NH}, \text{C}=\text{O}^{\text{a}}, \text{C}=\text{O}^{\text{b}}, \text{C}=\text{N}, \text{N}=\text{C}-\text{O}, \text{C}-\text{O}, \text{N}-\text{N}, \text{NO}_3, \text{U}-\text{O}/\text{U}-\text{O}, \text{U}-\text{N}, \text{U}=\text{O})$. ¹H NMR (DMSO- d_6 , 270 MHz). δ = 10.89 (s, 1H, NH), 8.10, 9.20 (s, 2H, H-C=N), 7.30–7.55 (m, 10H, CH aromatic), 3.32 (s, 6H, N-CH₃), 2.57 (s, 6H, C-CH₃), 2.49 (t, 4H, CO-CH₂), 1.77 (t, 4H, CH₂-CH₂).

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