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Complex formation, thermal behavior and stability competition between Cu(II) ion and Cu⁰ nanoparticles with some new azo dyes. Antioxidant and in vitro cytotoxic activity

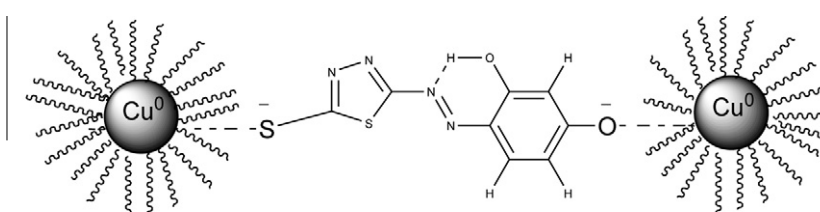
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HIGHLIGHTS

- ▶ Cu(II) complexes of four triazole and thiadiazole-based azo chromophore were synthesized and characterized.
- ▶ The mode of interaction between the synthesized azo ligands and copper nanoparticles was studied.
- ▶ The antitumor and antioxidant activities of the synthesized azo ligands and their Cu(II) azo complexes have been evaluated.

GRAPHICAL ABSTRACT



The mode of interaction between HL⁴ with the surface of colloidal Cu⁰

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ABSTRACT

Four triazole and thiadiazole-based azo chromophores namely [(E)-4-((1H-1,2,4-triazol-3-yl)diazonyl)benzene-1,3-diol.(HL¹), (E)-4-((5-(methylthio)-1H-1,2,4-triazol-3-yl)diazonyl)benzene-1,3-diol.(HL²), (E)-4-((1,3,4-thiadiazol-2-yl)diazonyl)benzene-1,3-diol.(HL³) and (E)-4-((5-mercapto-1,3,4-thiadiazol-2-yl)diazonyl)benzene-1,3-diol.(HL⁴)] were synthesized and characterized by elemental analyses, IR, UV–Vis as well as mass spectroscopy. Cu(II) complexes of the investigated azo dyes have been synthesized and characterized by elemental analyses, IR, electronic and ESR spectra, magnetic susceptibility and thermogravimetric analyses. The bond lengths and bond angles have been calculated to confirm the geometry of the ligands and their Cu(II) complexes. The mode of interaction of the azodyes to copper nanoparticles was described as coordination mode of charged dye molecules on the colloidal Cu⁰ surface through anchoring –OH[−] group. The apparent association constants of the colloidal copper nanoparticles azodye complexes in solution were evaluated using the spectral method and compared with the formation constant of the Cu(II) azo complexes. The antitumor and antioxidant activities of the synthesized azo dyes and their Cu(II) azo complexes have been evaluated.

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Introduction

Metal complexes of azo compounds have remained an attractive area of research for coordination and structural chemists. The importance of the heterocyclic azo dyes may stem from its biological activity and analytical applications [1–6]. Recent years have

a great deal of interest in the synthesis and characterization of azo compounds and their metal complexes [7–13].

Metal complexes of 1,2,4-triazole derivatives are biologically active having nuclease like activity [14], anti-proliferative [15], antibacterial and antifungal activity [16–19], antitumor [20] and anticancer [21]. Also, the chemistry of 1,3,4-thiadiazole derivatives received much attention because of their significant biological activities [22] and anticancer activity [23].

In the present work, we synthesized new four azo dyes compounds (HL¹–HL⁴). The structures of these azo compounds were elucidated by elemental analysis, IR, UV–Vis and mass spectra. The coordination behavior of the investigated azo dyes towards

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Cu(II) ion was studied via the elemental analysis, IR, electronic, ESR spectra, magnetic moment and molar conductance measurements. In addition, the thermal behavior of Cu(II) complexes was studied. The kinetic and thermodynamic parameters for the decomposition steps have been calculated. The mode of interaction between the synthesized azo-compounds and copper nanoparticles in solution was studied. The biological activities (antitumor and antioxidant) of the azo-compounds and their Cu(II) complexes were evaluated.

Experimental

Reagents

All the reagents and solvents were of analytical grade quality. 3-Amino-1H-1,2,4-triazole, 3-amino-5-methylmercapto-1H-1,2,4-triazole, 2-amino-1,3,4-thiadiazole, 2-amino-5-mercapto-1,3,4-thiadiazole, cetyltrimethyl ammonium bromide (CTAB) and 1,3-dihydroxybenzene were purchased from Sigma–Aldrich Co. and were used without further purification.

Physical measurements

Elemental analyses of the azo ligands and their Cu(II) azo complexes were performed with the aid of Perkin–Elmer model 2400 automated analyzer. Infrared spectra for both azo ligands and their Cu(II) azo complexes were recorded on Perkin Elmer 1430 Infrared Spectrophotometer using KBr discs in the range 200–4000 cm^{-1} . Electronic absorption spectra of azo ligands and their Cu(II) azo complexes were recorded in the range 200–700 nm on a Shimadzu Recording UV–Vis spectrophotometer model 240 A with the aid of 1 cm quartz cuvettes. The electronic absorption spectra of the solid Cu(II) azo complexes were recorded using Nujol mull technique [24].

The mass spectra of azo compounds were recorded using Shimadzu Qp-2010 plus. Magnetic susceptibilities of the prepared solid Cu(II) azo complexes were measured at room temperature at 25 °C on Sherwood Scientific Magnetic Susceptibility Balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The ESR spectra of powdered samples of Cu(II) azo complexes were recorded at room temperature with the aid of JEOL JES-FE2XG Spectrometer equipped with an E101 micro wave bridge. The magnetic field was calibrated with diphenyl picrylhydrazide (DPPH). The conductance measurements for the prepared solid Cu(II) azo complexes were recorded with the aid of Hana model 1331 conductometer. The thermal analysis (TGA–DrTGA) was performed using Shimadzu TG-50 thermal analyzer up to 800 °C at a heating rate 10 °C min^{-1} in an atmosphere of N_2 . The morphology of the prepared copper nanoparticles was investigated using JEOL-JEM-100SX electron microscope. The particle size and size distributions were obtained by image analyses. The antitumor activity of investigated azo compounds ($\text{HL}^1\text{–HL}^4$) and their Cu(II) azo complexes were evaluated against Ehrlich Ascites Carcinoma cells. Also, the antioxidant assay for some synthesized azo ligand and their Cu(II) azo complexes was performed.

Synthesis of the azo ligands ($\text{HL}^1\text{–HL}^4$) and their Cu(II) azo complexes

Synthesis of azo compounds

Azo dyes ($\text{HL}^1\text{–HL}^4$) Fig. 1, were synthesized by coupling the diazonium salt of 3-Amino-1H-1,2,4-triazole, 3-amino-5-methylmercapto-1H-1,2,4-triazole, 2-amino-1,3,4-thiadiazole, 2-amino-5-mercapto-1,3,4-thiadiazole with 1,3-dihydroxybenzene at –5 to 0 °C. The precipitated solids were filtered off, washed several times with bidistilled water, purified by further recrystallization from hot ethanol to give the pure azo ligands and finally dried in

desiccator over anhydrous CaCl_2 . The analytical and physical data of the synthesized azo compounds were presented in Table 1.

Preparation of Cu(II) azo complexes

The solid Cu(II) azo complexes were prepared in molar ratio 1:1 by dropwise addition of 50 mL hot ethanolic Cu(II) acetate solution (1 mmol) to the azo-compounds (1 mmol) in 50 mL of hot ethanol, whereupon suspensions of the Cu(II) azo complexes resulted. The reaction mixture was then heated at ~50 °C under refluxed for 4–5 h. TLC plates were used to detect the reaction finishing. The precipitated solids were collected by filtration, washed several times with bidistilled water and then dried in desiccator over anhydrous CaCl_2 . The analytical and physical data of the synthesized complexes were presented in Table 1.

Synthesis of copper nanoparticles

Cu nanoparticles were synthesized as previously described [20] by reduction of Cu^{+2} to Cu^0 . 10 ml of 0.003 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ prepared in isopropanol (IPA) solution was added dropwise to 10 ml of 0.09 M of cetyltrimethylammonium bromide/isopropanol (CTAB/IPA) solution. The reaction mixture was stirred vigorously giving a violet colloid absorbing at 560 nm. The appearance of a violet color indicated the presence of copper nanoparticles [25]. CTAB was used as catalyst for the reduction of Cu^{2+} with IPA and as stabilizer to protect Cu nanoparticles from oxidation.

Molecular modeling

An attempt to gain a better insight on the molecular structure of the ligands and their complexes, geometry optimization and conformational analysis has been performed by the use of MM + force-field as implemented in hyperchem 8.0 [26]. Semi empirical method PM3 is then used for optimizing the full geometry of the system using Polak–Ribiere (conjugate gradient) algorithm and Unrestricted Hartree–Fock (UHF) is employed keeping RMS gradient of 0.01 kcal/mol.

Results and discussion

Study of the azo ligands ($\text{HL}^1\text{–HL}^4$)

U.V–Vis spectra

The electronic absorption spectra of 5×10^{-5} M azo ligands ($\text{HL}^1\text{–HL}^4$) in methanol showed three main absorption bands. The first band appeared around 210 nm assigned to the moderate energy $\pi\text{--}\pi^*$ electronic transition within the phenyl moiety represented the (${}^1\text{L}_a \rightarrow {}^1\text{A}$) state. The second band observed in the range 250–310 nm attributed to low energy $\pi\text{--}\pi^*$ electronic transition of the heterocyclic moiety and phenyl ring corresponded to the (${}^1\text{L}_b \rightarrow {}^1\text{A}$) state. The third band appeared within the range 380–470 nm derived from n to π^* electronic transition involving the whole electron system and charge transfer interaction within the molecule.

Solvent effect on UV–Vis spectra

The electronic absorption spectra of 10^{-5} M azo ligands ($\text{HL}^1\text{–HL}^4$) under investigation were also recorded in Ethanol, Di-methylformamide, Acetonitrile, Methylene chloride and *n*-Heptane.

The plot of charge transfer energy (E_{CT}) against the solvent parameters such as dielectric constant (**D**) given by Suppan [27], refractive index relation **F(n)** of Bayliss and Mac Rae, Dimroth and Reichardt's **E_T(30)**, Kosower's **Z**, Kamlet and Taft's π^* solvatochromic scales, α scale of acidity and β scale of basicity, gave non

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