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Studies on chalcone derivatives: Complex formation, thermal behavior, stability constant and antioxidant activity

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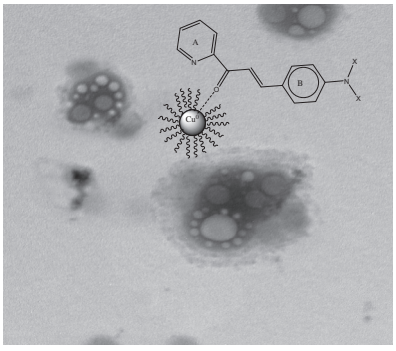
HIGHLIGHTS

- Spectroscopic studies of copper(II):chalcones complexes.
- Thermal decomposition of Cu(II) complexes.
- Initial geometry optimizations for Cu(II) complexes.
- Interaction between chalcones and the surface of copper nanoparticles.
- Antioxidant activity of chalcones.

GRAPHICAL ABSTRACT

The interaction between chalcones ligands and colloidal copper nanoparticles may occurred through the carbonyl group as a result of contribution of the other group in intermolecular hydrogen bond with nitrogen atom of pyridinyl group besides the great steric hindrance with hetero ring. TEM image for the complex formation between DEAPP and Cu nanoparticles. The inserted scheme suggests the mode of interaction between DMAPP and DEAPP with the surface of colloidal Cu^0.



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ABSTRACT

The chalcone 3-[4′-dimethylaminophenyl]-1-(2-pyridyl) prop-2-en-1-one (DMAPP) and 3-(4′-diethylaminophenyl)-1-(2-pyridinyl) prop-2-en-1-one abbreviated as DEAPP have been synthesized and characterized with IR, ^{1}H NMR, ^{13}C NMR spectroscopic techniques as described previously (El-Daly et al., 2008; Gaber et al., 2009; El-Sayed, 2013). By using UV visible spectroscopy method the mole fraction ratio for copper with DMAPP and DEAPP complexes were determined and it was found to be 1:1. The stability constants of this complex have been determined by Job's method. The stability constant (K_f) of copper with DMAPP and DEAPP complexes in universal buffer pH = 3.2 was determined to be 9.9×10^4 and 5.2×10^4 respectively. The effect of Cu(II) ion on the emission spectrum of the free chalcone is also assigned. Adherence to Beer's law and Ringbom optimum concentration ranges are determined. The thermal decomposition of the metal complexes is studied by TGA technique. The kinetic parameters like activation energy, pre-exponential factor and entropy of activation are estimated. The structure of complexes was energetically optimized through molecular mechanics applying MM^+ force field coupled with molecular dynamics simulation. 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 chalcone to copper nanoparticles was studied. The apparent association constants of the colloidal copper nanoparticles: chalcone complexes in solution were evaluated using the spectral method and compared with the

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formation constant of the Cu(II) chalcone complexes. Antioxidant activity of these chalcones was evaluated by using 1,1′-diphenyl-2-picrylhydrazyl (DPPH·) radicals scavenging method, which showed that the antioxidant activity of DMAPP has higher value than the DEAPP. Semi-empirical study results showed that DMAPP have higher dipole moment than DEAPP [1].

Introduction

Chalcones are open chain flavonoids, valuable intermediates in the synthesis of many active pharmaceutical drugs like biosynthesis of flavonoids. Chalcones represent an essential group of natural as well as synthetic products and some of them possess wide range of pharmacological activity such as antibacterial [2], antitumor [3], anticancer [4], antitubercular [5], anti-inflammatory [6], antioxidant [7], antimalarial [8] and anti-leishmanial. Chalcones and their derivatives are of high interest materials due to their antioxidant properties [9]. Chalcone molecules have variety of pharmacological activities, attracted medicinal chemists therefore several strategies have been developed to synthesize [10]. Chalcones with substituents that increase the electron density of the B ring, such as methoxy, butoxy or dimethylamine groups, did not show significant activity in the inhibition of nitrite production [11]. Chalcone is a strong antioxidant, their ability to act as free radical acceptors; the metal complexing properties of these molecules may make some contribution to their total activity. The presence of reactive α, β-unsaturated keto group in chalcones is found to be responsible for their biological activity. Introduction of metal ion into chalcone compounds can bring about significant changes in biological effects [12,13]. As metal chelators, the flavonoids play an important role in both the bioavailability and toxicity of a variety of metals. The complexation of Al(III) by quercetin reduces the overload of aluminum in the diet, a metal which has been implicated in neurological and bone disorders [14,15]. Transition metal ions are found in several bacterial species and are reported to play an important role in different enzymatic and physiological reactions, the interaction of chalcones with metal ions may also change the antioxidant properties and also biological effects of the chalcones [16]. In this work, we have attempted spectroscopic study on the oxidation and the coordination aspects of DMAPP and DEAPP in the presence of Cu(II) ion, and the mode of interaction of these ligands with the surface of colloidal copper nanoparticles in solution (see Fig. 1).

Experimental

Materials

All reagents and solvents were of analytical grade quality. 2-acetyl pyridine, 4-dimethyl amino benzaldehyde, 4-diethyl amino benzaldehyde, and cetyltrimethyl ammonium bromide (CTAB) were purchased from Sigma–Aldrich Co. and were used without further purification. Solvents used were spectroscopic grade and were preliminarily checked for the absence of absorbing or fluorescent impurities within the scanned spectral ranges. 3-(4′-dimethylaminophenyl)-1-(2-pyridinyl) prop-2-en-1-one abbreviated as DMAPP and 3-(4′-diethylaminophenyl)-1-(2-pyridinyl) prop-2-en-1-one abbreviated as DEAPPP were synthesized as described previously [1]. The used metal ions were of high purity grade acetate salts.

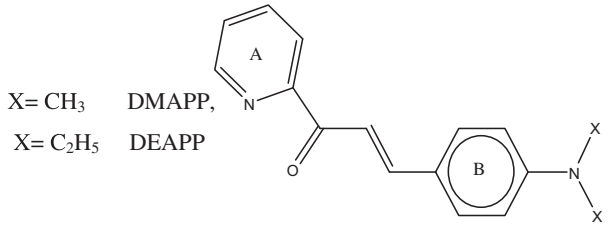

Fig. 1. The structure of chalcone ligands.

Synthesis of metal complexes

A solution of copper acetate (0.01 mol) in ethanol (10 ml) was mixed with a solution of the chalcone (0.01 mol) in the same solvent (30 ml) and the resulting mixture was stirred under reflux for ≪12 h where upon the complexes precipitated after cooling. The solid complexes were then filtered off, washed several times with ethanol, dried and kept in desiccators over dried silica gel. The analytical and spectral data are collected in Table 1.

Synthesis of copper nanoparticles

Cu nanoparticles were synthesized as previously described [17] by reduction of Cu^{2+} to Cu^0. 10 ml of 0.003 M $Cu(NO_3)_2{\cdot}3H_2O$ 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 [18]. CTAB was used as catalyst for the reduction of Cu^{2+} with IPA and as stabilizer to protect Cu nanoparticles from oxidation.

Instrumentation

Microanalyses of C, H and N were made using Heraeus CHN elemental analyzer. The IR spectra were recorded as KBr disks on a Perkin Elmer 1430 spectrophotometer in the 4000–200 cm^{-1} range. The electronic absorption spectra of 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):chalcone complexes were recorded using Nujol mull technique [19,20]. The X-band ESR spectra of the complexes were recorded at room temperature on a JOEL-X-band spectrometer equipped with an E 101 microwave bridge. Diphenyl picryl hydrazide free radical (DPPH) was used as internal standard ($g = 2.0023$).

The fluorescence measurements were recorded with the aid of Shimadzu RF-510 spectrofluorometer. Excitation, emission bandwidth, scan rate and excitation wavelength are 10 nm, 100 nm/min and 370 nm, respectively. Magnetic susceptibilities were measured by employing the Faraday balance technique. The equipment was calibrated with $Hg[Co(CNS)_4]$. Diamagnetic corrections were made from Pascal constants. The thermal analysis (TGA) was carried out using computerized Shimadzu TG-50 thermal analyzer up to 800 °C at a heating rate 10 °C/min. in an atmosphere of N_2.

Determination of the stability constant

Job's method was used to determine the stoichiometric ratio for the reaction between chalcone and Cu(II) ion. A method of