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Synthesis and characterization of new nano complexes acetophenon dithiocarbamate and study of their biological properties

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ABSTRACT

The dithiocarbamate (DTC) ligands have also proven to be excellent compounds due to their extensive applications as fungicides, pesticides, vulcanization accelerators. Most of these applications are based on complexation properties of DTC ligands with metal ions, especially with transition metal ions. DTC ligands readily form chelates with all transition metal ions through its two donor sulfur atoms. The secondary diamine ligands, used as starting material for the preparation of the metal complexes, were obtained in 80% yield by condensation of acetophenon with 1,6-hexamethylenediamine in methanol followed by reduction of the Schiff base with $NaBH_4$ in methanol. One-pot synthesis from this amine, carbon disulfide, triethylamine and $CoCl_2.6H_2O$ gave colorless precipitates. The ultrasonic treatment applied for preparation nanoparticles. The antibacterial activity of nanoparticles derivatives tested against microorganism and compared with non-nano conditions. The resulting nanoparticles were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM).

INTRODUCTION

Dithiocarbamate-containing coordination compounds are well known and have been widely studied because of their wide biological, industrial, agricultural and chemical applications[1-9]. The dithiocarbamates can be used as nitrogen-oxygen trapping agents[1], chelating agents of heavy metals[2-4], vulcanizers, fungicides, lubricants and catalysts. They have also been used in medicine since the dithiocarbamate moeity has been found in a variety of biologically active molecules[5-9].

In this view, we have synthesized complex with dithiocarbamate. The ultrasonic treatment applied for preparation of dithiocarbamate nanoparticles. The complexes have been charactersized by elemental analysis, FT-IR spectra, NMR (^1H and ^{13}C). The antifungal activities of synthesized compounds were studied *Candida albicans*, *Aspergillus flavus*, *Aspergillus nigar*.

EXPERIMENTAL

Materials and general methods

The reagents and solvents were of analytical grade. 1,10- Phenanthroline, amine, carbon disulfide were purchased from Merck Company. ^1H and ^{13}C NMR measurments were recorded on a Bruker 300 spectrometer (300 and 75 MH, respectively) in $CDCl_3$ using TMS as the internal reference. IR spectra of the compounds as KBr-disks were recorded in the range of 400 – 4000 cm^{-1} with a Mattson 1000 FT spectrometer. Melting points of sulfonamide derivatives were determined on a Gallenkamp melting point apparatus and are uncorrected Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert

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Company with monochromatized Cu Kα radiation. A multiwave ultrasonic generator (Sonicator-3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/ transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W. The microdilution broth method was used to determine the antibacterial activity of compounds against the bacteria: *C. albicans ATCC 10231, A. flavus* ATCC *9170, A. nigar ATCC 16404*.

Synthesis of complex

1,6-Hexamethylenediamine (3.95 g) and two equivalents of acetophenon (8.17 g) were dissolved in ethanol (25 mL) and the solution was refluxed for 30 min. After evaporation of the solvent the diaimine was obtained in form of yellow oil. *N,N'*-bis[α-methyl(phenyl) methylene] hexanediamine (7.94 g) was dissolved in methanol and the solution was cooled to 0 °C. Sodium borohydride (3.17 g) was added under stirring and the mixture was allowed to react over night. The prouduct was washed with water and dichloromethane. After filtration the solvent was evaporated to obtain a withe oil that was identified as the product. *N,N*-bis α-methyl(benzyl)methanediamine (0.51 g), triethylamine (0.05 mL) and carbon disulfide (0.26 g) were dissolved in methanol (5 mL) and stirred for 5 h. $CoCl_2.6H_2O$ (0.41 g) was dissolved in 3 ml of methanol and added to the solution. A green powder precipitated that was filtered and recrystallized from chloroform (Figure 1).

Spectra data

N,N'-bis[α-methyl(phenyl) methylene] hexanediamine

IR (KBr−cm^{-1}) υ (C-N), 1203.33; υ (=C-H), 3062.35; υ (CH_2), 3857.53 - 2968.79; υ (C=C), 1577.65; υ (CH_3), 1367.15, υ (C-H, out-of-plane), 761.62; υ (out-of-plane ring bend) 701.01. ^{1}H−NMR ($CDCl_3$, TMS, 300 MHz) : δ(ppm) 2.59 (s, 6H, CH_3), 7.35 - 7.95 (m, 10H, C_6H_5), 2.20 - 2.29 (t, 4H, NCH_2), 1.80 - 1.82(d, 4H, NCH_2CH_2), 1.53 (s, 4H, $NCH_2CH_2CH_2$).

N,N-bis α-methyl(benzyl)methanediamine

IR (KBr −cm^{-1}) υ (N-H) 3400; υ (C-N), 1206.06; υ (CH_3), 1364.63, υ (C-H, out-of-plane), 736.03; υ (out-of-plane ring bend) 698.23. ^{1}H−NMR ($CDCl_3$, TMS, 300 MHz): δ(ppm) 7.22-7.34 (m, 10H, -C_6H_5), 4.81 - 4.87 (m, 6H, CH_3), 3.60 - 3.74 (m, 4H, NCH-C_6H_5), 2.54 - 2.59 (m, 4H, NCH_2), 2.317 - 2.47 (m, 2H, N-H), 1.45 - 1.47 (d, 4H, NCH_2CH_2), 1.32 - 1.34 (t, 4H, $NCH_2CH_2CH_2$).

Complex

IR (KBr−cm^{-1}) υ (C-N), 1492.69; υ $(CS_2)_{as}$, 1238.02; υ $(CS_2)_s$, 949.61; υ (C-N), 1128.65; υ (C-H, out-of-plane), 720.97; υ (out-of-plane ring bend) 609.03; υ (Co-S), 330. ^{1}H−NMR (DMSO-d_6, TMS, 300 MHz): δ(ppm) 7.081 - 7.162 (m, 20H, 4 C_6H_5), 0.815 - 3.99 (br, 8H, 4 $CH_2C_6H_5$; 8H, 4 NCH_2; 8H, 4 NCH_2CH_2; 8H, 4 $NCH_2CH_2CH_2$; 6H, CH_3).

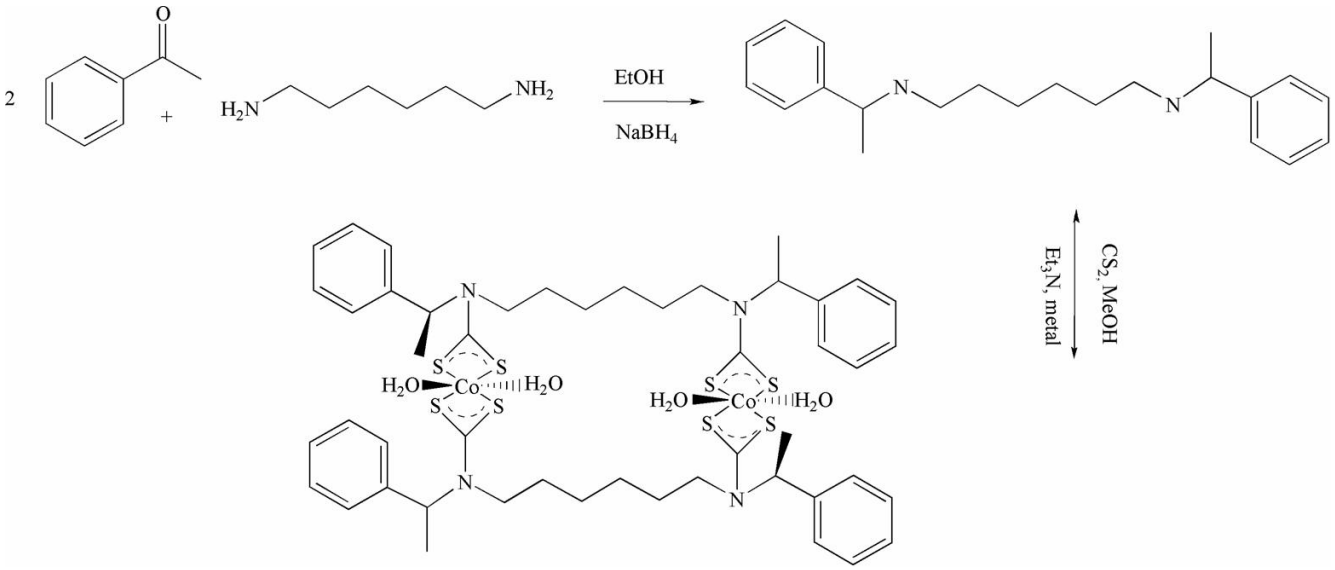

Figure 1 : The structure of complex

^{13}C-NMR (DMSO-d_6, TMS, 300 MHz): δ(ppm) 19, 20.5, 26.5, 28.5, 50, 57.5, 128, 129, 130, 205.

Synthesis of dithiocarbamate nanoparticles

Ultrasonic device was employed to improve the dispersibility of the complex dithiocarbamate nanoparticles dispersed in aqueous solutions. To prepare the complex dithiocarbamate precursor amount of ligand with concentrations of 2M was added to the 1M solution $CoCl_2.6H_2O$ was added to the solution. Then the suspension was ultrasonically irradiated with a high-density ultrasonic probe immersed directly into the solution. The obtained suspension was allowed to age for 90 min. The precipitate was separated from mother liquor by using a centrifuge at 4000 rpm for 1 min, and at least 2 cycles of washing (using 25 °C deionised water) and centrifuging were required to removal of the residual impurities. The final product was dried at 50 °C in a vacuum system. The working parameters of the ultrasonic device were 70 kHz and 50 W/cm^2.

Characterization of nanoparticles

X-ray diffraction (XRD) technique was used to determine the ingredients of the sample. The average crystallite size of the as-prepared dithiocarbamate complex nanoparticles is about 50 nm, according to the Debye-scherrer formula: $D = 0.9\lambda/ \beta \cos \theta$ (Figure 2). The morphology of nanoparticles was observed using a scanning electron microscopy (Figure 3).

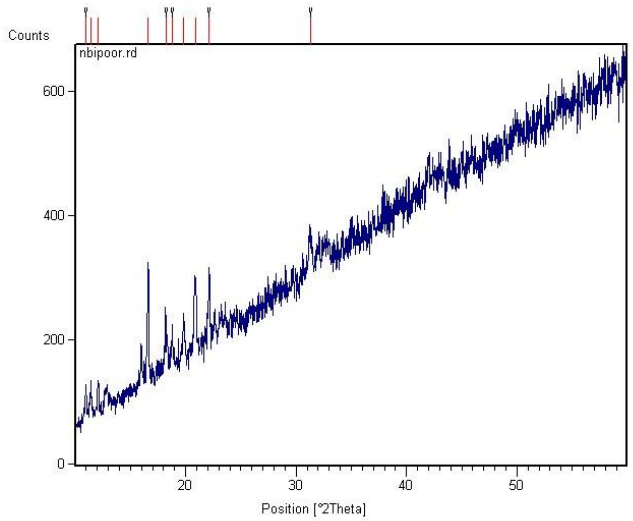

Figure 2 : The XRD pattern of complex dithiocarbamate nanoparticles.

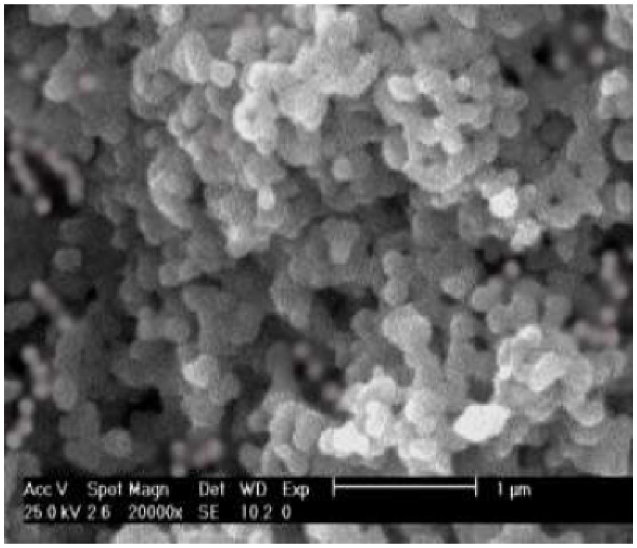

Figure 3 : SEM photographs of the sample dithiocarbamate (the scale bar is 1 µm).

In vitro antibacterial activity

The compounds have been screened in vitro against *Escherichia coli, Klebsiella pneumoniae* and *Staphylococcus aureus, Bacillus subtilis* Various methods are available for the evaluation of the antibacterial activity of different types of drugs. However, the most widely used method consists in determining the antibacterial activity of the complex is to add it in known concentrations to the cultures of the test organisms.

Disc diffusion assay

Method of paper disc diffusion 60µgr concentration solution of dithiocarbamate was prepared, and the antibacterial activity of the dithiocarbamate against *Escherichia coli, Klebsiella pneumoniae* and *Staphylococcus aureus* and *Bacillus subtilis* was studied. The bacterium suspension concentration was controlled as 5×10^5–5×10^6 cfu/ml; the diameters of filter paper were 5 mm, and for the experiments, flat plates were incubated at 30-35°C (bacterium) for 18-24 h. Their inhibition diameter (including filter paper) was measured with a vernier caliper.

In vitro antibacterial study

In the antibacterial study (TABLE 1) of some synthesized complexes was tested against pathogenic bacterial strains such as *Escherichia coli, Klebsiella pneumoniae* and *Staphylococcus aureus* and *Bacillus subtilis* using the disc diffusion method. Gentamycin was used as reference drug for bacteria. In general, the

compounds showed significant antibacterial activity and the bacterial strains with the zone of inhibition.

TABLE 1

No.	Complexes	Zone of inhibitation (mm)			
		Escherichia coli	Klebsiella pneumoniae	Staphylococcus aureus	Bacillus subtilis
1	dithiocarbamate complex	18	18	17	17
2	Nano dithiocarbamate complex	23	23	20	20

DISCUSSION

In this research project an attempt has been made to build the complex dithiocarbamate and while separating them, this compound would be recognized with the use of spectroscopic techniques. The synthesis of this substance would be significant from the perspective of separation and production. Furthermore, this substance by having the unique property of ultrasonic waves are transformed into nano by the use of ultrasonic device. The size of particles were measured by using the current relations and methods like XRD and SEM. In addition, the antibacterial and antifungal properties of this substance were studies both in normal and nano conditions. When complex dithiocarbamate is transformed into nano form the proportion of surface to volume will be increased. The increase in the surface of particles decreases the surface pressure and causes the distant change among the particles or even the distance among the atoms of particles. The change in the distance among atoms of particles and high proportion of surface to volume in nano particles will have the same impact on the properties of substances. Therefore, the synthesized nano particles of dithiocarbamate have the capability of being antibacterial and antifungal in comparison to their normal forms. The dithiocarbamte nanoparticles is of antibacterial and antifungal activities more than bulk (non-nano) forms.

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