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Fourier Transform Infrared and Raman spectra, DFT: B3LYP/6-311G(d, p) calculations and structural properties of bis(diethyldithiocarbamate)copper(II)

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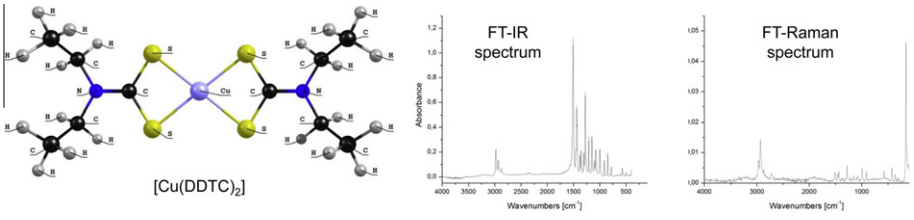
HIGHLIGHTS

- Synthesis of bis(diethyldithiocarbamate)Cu(II) was carried out.
- The FT-IR and Raman spectra of $[Cu(DDTC)_2]$ were carried out.
- The calculations and spectra interpretation have been based on the DFT/B3LYP method.

GRAPHICAL ABSTRACT



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ABSTRACT

Theoretical and experimental bands have been assigned for the Fourier Transform Infrared (FT-IR) and FT-Raman spectra of the bis(diethydithiocarbamate)Cu(II) complex, $[Cu(DDTC)_2]$. The calculations and spectra interpretation have been based on the DFT/B3LYP method, infrared and Raman second derivative spectra, and band deconvolution analysis. To better assign the metal–ligand normal modes in the spectral region of low energy, the deviation percentage of the geometrical parameters was used, with values from the interpretation of the normal modes of L matrix. Results indicate a planar structure around the Cu(II) cation. The calculated infrared and Raman spectra, based on the proposed geometrical structure of the bis(diethyldithiocarbamate)copper(II) complex, agreed with the experimental spectra.

Introduction

Copper complexes have been strongly associated from their wide range of biological activity, including their potential use as antimicrobial, antiviral, anti-inflammatory, antitumor agents, enzyme inhibitors, or chemical nucleases [1]. The works of Stier et al. [2], Antholine et al. [3], and Saryan et al. [4], studied the reactions of bis(thiosemicarbazonato)copper(II) complexes with tumor cells and mitochondria; the inhibition of tumor cell transplantability by iron and copper complexes of 5-substituted 2-formyl pyperidine thiosemicarbazones; and a comparative cytotoxic and biochemical effects of alpha-N-heterocyclic carboxaldehyde thiosemicarbazones, respectively. In these studies the mechanism of copper(II) complexes in their antitumor action involve inhibition of the enzyme ribonucleotide reductase, and according to Karon and Benedict [5], also involve creation of lesions in DNA strands.

Due to the pharmacological activity of the thiosemicarbazides and thiosemicarbazones [6,7] as well as the antitumor response of thiosemicarbazones, in which the Cu(II) complexes have the greatest activity [8,9], the 2-methylthiosemicarbazide copper(II) nitrate was synthesized and a further structural study was carried out by Valdés-Martínez et al. [10]. However, the work of Valdés-

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Martínez contains no information about the vibrational spectra. A vibrational analysis on the Ni(II) thiosemicarbazide complexes and their deutero isotopomers was reported by Geetharani and Sathyamarayana [11], who, to simplify the normal coordinate treatment, considered only half the structure of the complex $Ni(Htsc)_2Cl_2$, where Htsc means thiosemicarbazide.

Téllez et al. [12], to elucidate tentative assignments of metal–ligand modes of thiosemicarbazide complexes, did a structural study and a assignment of the normal vibrations of 2-ethylthiosemicarbazide copper(II) nitrate, $[Cu(MeTSC)_2(NO_3)_2]$ through the *ab initio* DFT: pBP86/DN** procedure, and through normal coordinate analysis (NCA). In the vibrational calculations, the elongated Cu—ONO_2 bonds of the nitrate groups were considered in the C=S and C=N tautomers of the complex. DFT calculations revealed that the infrared spectra can be well interpreted through the C=N tautomer. The observed combination bands at 1763.0 and 1754.0 cm^{-1} were an indication that the —NO_3 groups act as monodentate ligands. Calculations confirmed the experimental assignment of the infrared spectrum.

Although the $[Cu(DDTC)_2]$ complex belongs to a very important class of coordination compounds, no conclusive structural, vibrational, and electronic study have been carried out. Due to this lack of information, we propose for this complex a synthesis route analysis, based on graphical method and complete spectroscopy study. The structural studies of the solid powder were carried out by means of FT-IR and FT-Raman vibrational spectra as well as quantum mechanical theoretical calculations.

Experimental

General

Copper(II) nitrate, sodium diethyldithiocarbamate trihydrate salt and HNO_3 were purchased from Vetec Co. All solvents and reagents were used as received without further purification. Elemental analysis (CHN) was carried out in a Sinc EA 1110 analyzer. The infrared spectra between 4000 and 370 cm^{-1} were measured as a KBr pellet and polyethylene pellet at room temperature, on a Perkin Elmer 2000 FT-IR spectrometer. Data was collected with a resolution of 4 cm^{-1}. Scanning speed 0.2 cm^{-1} s^{-1} and 120 scans were used. The Raman spectra between 4000 and 100 cm^{-1} were measured of a solid sample at room temperature, on a FT-Raman Bruker model RFS 100/S spectrometer. Data was collected with a resolution of 4 cm^{-1} and 120 scans were used. Source setting: laser of 9394.75 cm^{-1}; 500 mW. Aperture setting: 7.0 mm. The percentage of copper was determined by atomic absorption spectrometry using a Perkin Elmer AAnalyst 100 spectrophotometer. The pH_3O^+ control during the synthesis of the complex was carried out with the potentiometer Micronal B 375.

Synthesis of bis(diethyldithiocarbamate)Cu(II)

A solution of diethyldithiocarbamate (5 mmol) in 50 mL of deionized water was stirred by 20 min obtaining a $pH_3O^+ = 10$. The pH_3O^+ was adjusted to 6.5 with HNO_3 6 mol L^{-1}. Then copper(II) nitrate (0.914 g, 5 mmol) was added to this solution and the pH_3O^+ was maintained around 6.5. This control was done using a potentiometer and all the synthesis was carried out while stirring at room temperature. The agitation was maintained for 10 min until the formation of a green solid precipitate, which was then filtered under reduced pressure and washed for three times with deionized water. $[Cu(DDTC)_2]$ solid was kept under vacuum in a desiccator with sulfuric acid. Elemental analysis (CHN) and atomic absorption, for $C_{10}H_{20}N_2S_4Cu$: found C, 33.25%; N, 7.56%; H, 5.57%; and Cu, 17.42%. Calculated: C, 33.35%; N, 7.78%; H, 5.60%; and Cu, 17.65%.

Calculations

The calculations were carried out for the neutral complex, $[Cu(DDTC)_2]$, considered it as no interacting independent units. For geometry optimization, the density functional theory method B3LYP was used in the Gaussian 03 program [13]. For all calculations, we used the 6-311G(d, p) basis set for all atoms. All calculations have been optimized from several initial geometries, in order to guarantee the global minima energy structures in two symmetry groups, C_{2v} and C_1, with the complex with C_1 symmetry being more stable by 2.6×10^{-3} kcal/mol.

After this procedure, the vibrational calculations were performed. No imaginary mode was observed. Characteristic normal stretching and bending modes from the —C_2H_5 groups were visualized using the graphical Chemcraft program [14]. The skeletal or framework normal modes were determined using the percentage deviation of the geometrical parameters (PDPG), from its equilibrium position.

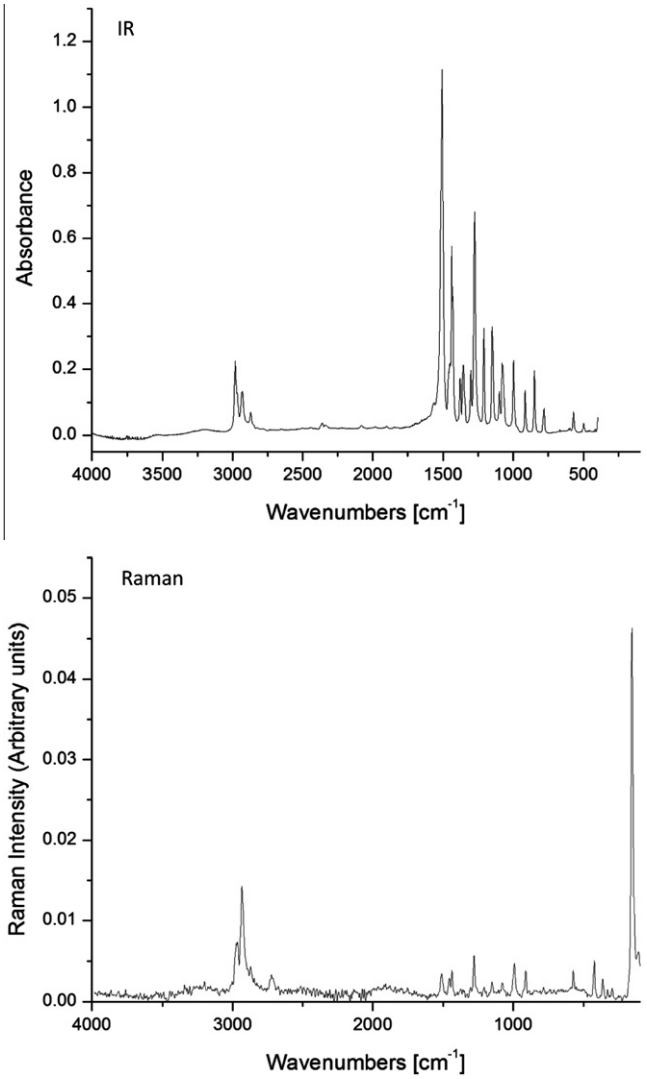

Fig. 1. FT-IR and FT-Raman spectra of $[Cu(DDTC)_2]$ complex.