

Synthesis, thermogravimetric, spectroscopic and theoretical characterization of copper(II) complex with 4-chloro-2-nitrobenzenesulfonamide

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ABSTRACT

4-Chloro-2-nitrobenzenesulfonamide (CINbsa) was purified and characterized. A new copper(II) complex, $[\text{Cu}(\text{CINbsa})_2(\text{NH}_3)_2]$, has been prepared using the sulfonamide as ligand. The thermal behavior of both, the ligand and the Cu(II) complex, was investigated by thermogravimetric analyses (TG) and differential thermal analysis (DT), and the electronic characteristics analyzed by UV–VIS, FTIR, Raman and ^1H NMR spectroscopies. The experimental IR, Raman and UV–VIS spectra have been assigned on the basis of DFT calculations at the B3LYP level of theory using the standard (6-31 + G**) basis set. The geometries have been fully optimized in vacuum and in modeled dimethylsulfoxide (DMSO) solvent, using for the latter a continuum solvation model that reproduced the experimental conditions of the UV–VIS spectroscopy. The theoretical results converged to stable conformations for the free sulfonamide and for the complex, suggesting for the latter a distorted square planar geometry in both environments.

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1. Introduction

Sulfonamides, which have been clinically used for many years, have been found to possess a large number of different biological activities, including antibacterial, antiviral, antidiabetic, diuretic, and anti thyroid activities [1]. They exert their diverse pharmacological effects by interacting with a wide range of different cellular targets. The coordination chemistry of sulfonamides has undergone noticeable development in recent years due to the interesting properties of these substances, such as those related to superoxide dismutase (SOD) mimetic activity [2] and chemical nucleases. In 1941 Braun and Towel obtained the silver salt of sulfanilamide [3]. Nevertheless, it was not until the early 1980 that, after the work by Bult [4] and Malecki, [5] the sulfonamide anion started to be broadly used as s-donor ligand for cations. Later on Supuran et al. investigated the metal complexes as a new class of carbonic anhydrase inhibitors [6]. Carbonic anhydrases (CAs) are ubiquitous zinc enzymes that catalyze the interconversion between carbon dioxide and the bicarbonate ion [7]. Complexes based on sulfonamides as ligands are also artificial chemical nucleases that degrade DNA in the presence of sodium ascorbate. Thus, copper complexes

are known to be promising reagents for the cleavage of nucleic acids [8].

In the light of the interest on coordination chemistry of sulfonamides, we describe here the synthesis and characterization of the sulfonamide 4-chlorine-2-nitro benzenesulfonamide as well as its copper complex. Due to their poor solubility in water and in most organic solvents, it was not possible to obtain crystals of the metallic complex to analyze their structure by single-crystal X-ray diffraction (XRD) technique. Thus, the theoretical optimized geometry is reported, together with the spectroscopic (FTIR, Raman, ^1H NMR and UV–VIS) and thermogravimetric properties of the copper(II) complex, as an alternative way to infer details of the molecular structure. The assignment of experimental electronic, infrared and Raman bands was accomplished with the aid of the theoretical results based in density functional theory.

2. Experimental

2.1. Physical and chemical measurements

4-Chloro-2-nitrobenzenesulfonamide (CINbsa) and copper chloride were purchased from Fluka AG and all reagents used were of analytical grade. Chemical analyses for carbon, hydrogen, and nitrogen were performed on 1108 elemental analyzer from Carlo

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Erba EA and copper content was determined by iodimetry. The FTIR (KBr pellets) and Raman spectra were recorded with a Bruker IFS 66v FTIR spectrophotometer with a NIR Raman attachment. UV–VIS spectra were recorded with a Hewlett–Packard 8453 diode-array using 10 mm quartz cells. The electronic spectra of the ligand and the complex were recorded at room temperature using dimethylsulfoxide as solvent. DT and TG analyses were performed with Shimadzu TGA-50 and DTA-50H units at a heating rate of 5 °C/min. and oxygen flow of 50 ml/min. ¹H NMR spectrum of CINbsa in CDCl₃ purchased from Sigma solution was recorded on a Varian Mercury Plus, 200 MHz instrument at room temperature with TMS as an internal standard.

2.2. Synthesis of complex

4-Chloro-2-nitrobenzenesulfonamide was purified by several crystallizations from ethyl acetate (AcOEt)/hexane.

The copper complex was prepared by direct reaction of ethanolic solutions of sulfonamide and copper(II) chloride in the 2:1 M ratio, followed by dropwise addition of 2 ml of NH₃ 2 M. The resulting mixture was stirred for ca. 12 h. and the light blue solid was filtered. Yield was in the 70–75% range. The elemental analysis of the complex suggests the general formula, [Cu(CINbsa)₂(NH₃)₂]: Analytical Calculation for C₁₂H₁₀Cl₂N₄O₄S₂Cu–N₂H₆ C, 25.5%; H, 2.6%; N, 14.7%; S, 11.2% Found: C, 25.6%; H, 2.4%; N, 14.3%; S, 11.1%.

3. Computational methods

The computational study of the ligand and the copper complex were performed using the density functional theory (DFT) methods implemented in Gaussian 09 [9]. The systems studied herein were subjected to unrestrained energy minimizations using the B3LYP functional [10] with the 6-31+G** basis set [11] for nonmetal atoms and the Los Alamos effective core potentials LANL2DZ [12] for the metal. DFT methods have been shown to reproduce the structural properties of several biologically interesting transition metal centers, and their validity to model ground-state properties is widely accepted [13]. The basis sets were chosen as those that better reproduces the experimental UV–VIS data.

The geometries of both ligand and Cu-complex have been optimized in gas phase and in DMSO modeled solvent, and their calculated spectral features compared with experimental IR, Raman and UV–VIS data respectively. The geometry optimized in gas phase has been used to calculate the IR frequencies, as they were determined in solid phase. IR frequencies have been corrected using 0.96 as scaling factor. In order to model the UV–VIS spectra experimentally determined in DMSO, the geometries were optimized modeling the solvent within a continuous approach (Polarizable Continuous Model, PCM) [14] and used to calculate the UV–VIS spectra in the same conditions. Time dependent DFT models were used for the latter, allowing us to assign the nature of the observed electronic transitions.

4. Results and discussion

4.1. Spectroscopic properties

4.1.1. Infrared and Raman spectra

The FTIR spectra of the sulfonamide (CINbsa) and its Cu(II) complex are given in Fig. 1a and b, respectively. The Raman spectra of both samples are also included (Fig. 1c for complex and Fig. 1d for ligand). For a proper understanding of FTIR and Raman spectra, reliable assignment of all vibrational bands is essential. However no reliable crystal structure has been yet determined for the Cu

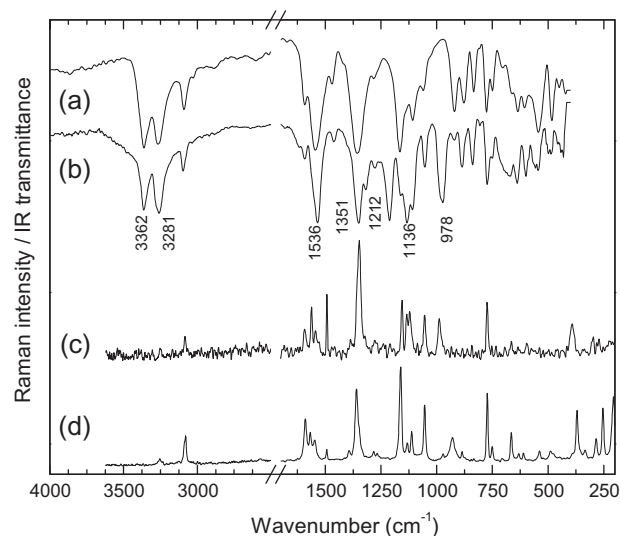


Fig. 1. FTIR and Raman spectra at room temperature. (a) IR spectrum of the free sulfonamide. (b) IR spectrum of the copper complex. (c) Raman spectrum of the copper complex. (d) Raman spectrum of the free sulfonamide.

complex and the assignments of the bands become more complicated. Nevertheless, on the basis of group frequencies, tentative assignments of the most prominent spectral features can be done, and further confirmed by theoretical calculations [15–17]. The spectrum of the complex was compared with those of the free sulfonamide in order to determine the coordination atoms that may be involved in chelation. It was also compared with similar complexes reported in the literature [18–20]. Table 1 summarizes the main observed and calculated bands, their approximate intensities and their proposed assignments.

The FTIR spectrum of the ligand shows bands at 3400–3250 cm⁻¹ and at 1550–1500 cm⁻¹ associated with the presence of the sulfonamide NH₂ groups, which are assigned to stretching and bending vibrations, respectively. As Table 1 shows, these bands are shifted in the complex. These results and the disappearance of one νNH band in the spectrum of the complex indicate that the NH₂ group is involved in the coordination with the copper atom. The broad band at ~3400 cm⁻¹, together with a new band at ~700 cm⁻¹ are also indicative of the presence of coordinating NH₃.

Among the IR bands originated in the ligands, those associated with the SO₂ group are most informative. Bands due to the anti-symmetric and symmetric vibration modes of the SO bonds in the complex are recorded close to 1300 and 1000 cm⁻¹, i.e. at lower frequencies than those corresponding to the free ligand. This spectral feature is associated with the binding of the sulfonamides through the deprotonated sulfonamide moiety [18–20]. This mode is observed at 1348 cm⁻¹ as a strong band (calc. 1283) in the IR spectrum of the ligand and as a shoulder in Raman spectrum. It is shifted to 1212 cm⁻¹ (calc. 1212) in the IR spectrum of the copper complex and is not visible in Raman. The symmetric SO₂ mode is poorly affected in both infrared and Raman spectra, displaying at 1060 (calc. 1064) in the ligand and at 1055 cm⁻¹ (calc. 1042) in the complex [20–22].

As a general behavior, the deprotonation and metal coordination of sulfonamide nitrogen increases the S–N bond order [20–23], leading to a shift of the ν(S–N) band to higher frequency. The changes of the ν(S–N) vibrations from 920 cm⁻¹ in the complex to 978 cm⁻¹ in the ligand, are expected from the shortening of the S–N bond length. The coordination of the NH₃ molecules is indicated by the broad band centered at 688 cm⁻¹ (calc. 655 cm⁻¹) assigned to a torsion mode. This band is absent in the

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