Structure and vibrational assignment of bis(benzoylacetonato)copper(II)

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HIGHLIGHTS

- Vibrational band assignments for bis(benzoylacetonato)copper are performed.
- Experimentally shown that the trans isomer is predominant in the sample.
- The metal–O bond strength increases by substituting of CH_3 by C_6H_5 group.
- Metal–O stretching frequency is related to the metal–O bond length.

ARTICLE INFO

ABSTRACT

Fourier transform Raman (3200–150 cm^{-1}) and infrared (4000–100 cm^{-1}) spectral measurements have been made for the solid copper (II) benzoylacetonate, Cu(bzac)$_2$ and, for comparison, copper (II) acetylacetonate, Cu(acac)$_2$. The molecular electronic energies, equilibrium geometries, IR and Raman spectra, and the internal coordinates for the vibrational modes have been computed for the cis and trans structures of Cu(bzac)$_2$ at the B3LYP/6-311G* level of theory. Potential energy distribution (PED) and normal mode analysis have also been performed. A complete assignment of the observed band frequencies has been proposed. Comparing of observed and calculated vibrational spectra suggests that the predominant isomer in the sample is the trans isomer.

To realize the effect of CH$_3$ substitution by phenyl group on the structure, metal–O bond strength, and vibrational spectra, the geometrical parameters and vibrational wavenumbers of Cu(acac)$_2$ were also calculated at the same level of theory. The calculated vibrational frequencies were compared with the experimental results. All of the measured IR and Raman bands were interpreted in terms of the calculated vibrational modes. The metal–O bond strength was investigated by geometry calculations and spectroscopic results. All theoretical and vibrational spectroscopic studies confirm stronger metal–ligand bond in Cu(bzac)$_2$ than that in Cu(acac)$_2$.

1. Introduction

The metal complexes of β-diketones and especially those of acetylacetone are well known and have been extensively studied [1–7]. The investigation of the structures and properties of metal complexes of β-diketones is of significant importance because of a variety of potential applications. These compounds can be used in preparation of supported catalysts and as precursors of heterogeneous catalysts [8–11]. These complexes have various applications in industry, such as organic electroluminescent technology, luminescent materials, sensors for bioinorganic applications, and

luminescent labels in bioaffinity assays [12,13]. Because of their high formation constant, β-diketonate complexes can be used in determination of trace metals. Many 1,3-diketones have found increasing use as metal extractants [14–16] and some of their metal (lanthanon) chelates have found applications either as NMR shift reagents [17–21] or in laser technology [12,13].

The assignments of vibrational wavenumbers of copper (II) acetylacetonate, Cu(acac)$_2$, have been reported by several workers. Nakamoto [22] assigned the IR band frequencies based on a normal coordinate analysis, whereas Junge and Musso [6] assigned the IR band frequencies of several metal acetylacetonate complexes, including Cu(acac)$_2$ based on the ^{13}C, ^{18}O, and ^{2}H substitution frequency shifts. Raissi et al. [23] used density functional theory (DFT) calculations to assign the vibrational band frequencies. However, there are many discrepancies between the assignments reported

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by these workers. In the case of copper (II) benzoylacetonate, $Cu(bzac)_2$, a few IR bands have been considered by Nakamoto et al. [24] and David et al. [25]. To the best of our knowledge, there is no report in the literature discussing the full assignments of vibrational frequencies (except some tentative assignments for the IR spectrum by Nakamoto et al [24]), the theoretical structure, and the Raman spectrum for the $Cu(bzac)_2$ complex. In the present work, by the aid of DFT computations the observed vibrational band frequencies of $Cu(bzac)_2$ are assigned and the results are compared with those of the $Cu(acac)_2$ and copper(II) dibenzoylmethane, $Cu(dbm)_2$ [26], complexes to give a clear understanding of substitution effect of phenyl groups (in β-position) on the structure, stability, and Cu—O bond strength of the complex. Moreover, since there are many discrepancies between the observed vibrational wavenumbers and assignments for $Cu(acac)_2$ in the previously published papers [6,22,23], we also attempted to obtain a complete assignment based on quantum mechanical calculations for this complex in addition to that for $Cu(bzac)_2$. In addition, due to coupling of different vibrations in the normal modes, potential energy distribution (PED) and normal mode analysis have also been carried out to determine the contributions of bond oscillators in each normal mode.

The aim of the present work is to predict the structure and vibrational spectra (harmonic wavenumbers, potential energy distribution (PED), and relative intensities for Raman and IR spectra) of cis and trans isomers of $Cu(bzac)_2$ and $Cu(acac)_2$ by means of density functional theory (DFT) calculations, to estimate the strength of metal–oxygen bond. Comparing the geometrical parameters and vibrational spectra of $Cu(bzac)_2$ with those of $Cu(acac)_2$ and $Cu(dbm)_2$ gives a clear understanding of substitution effect of phenyl groups (in β-position) on the structure of this system. Also, the experimental vibrational spectroscopies have been employed as evidences for the quantum mechanical computed results. Finally, the obtained assignments and band frequencies will be compared with the previous results.

2. Experimental

$Cu(acac)_2$ was prepared according to the literature [27] and similar procedure was used for preparation of $Cu(bzac)_2$ complex. The precipitated $Cu(bzac)_2$ was recrystallized from CH_2Cl_2 solution. Calc. for $C_{20}H_{18}CuO_4$: C,62.17; H,4.66. Anal. Found: C,62.91; H,4.91.

The infrared spectra in the region 4000–500 cm^{-1} were recorded on a Bomem MB-154 Fourier transform spectrophotometer using KBr pellets and CCl_4 solution. The spectra were collected with a resolution of 2 cm^{-1} by signal averaging the results of 15 scans.

The Far-IR spectra in the region 600–100 cm^{-1} were obtained using a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter with use of polyethylene disks. The spectrum was collected with a resolution of 2 cm^{-1} by signal averaging the results of 32 scans.

The FT-Raman spectra in the region 3200–100 cm^{-1} were recorded employing a 180° backscattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer. The instrument was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Excitation wavelength at 1064 nm was obtained from a Nd/YAG laser. Rayleigh filtration was afforded by a set of two holographic technology filters. The spectra were accumulated for 1500 scans with a resolution of 2 cm^{-1}. The laser power at the sample was 500 mW.

3. Method of analysis

All the computations are performed using Gaussian 09W [28] software. The geometry optimization, vibrational frequencies, the internal coordinates of $Cu(acac)_2$, and the cis and trans isomers of $Cu(bzac)_2$ are obtained at the B3LYP [29,30] level, using 6-311G* basis set. Raman activities were computed at the same level of calculation, using standard procedures (Freq = Raman).

A normal coordinate analysis was carried out to provide a complete description of the fundamental vibrational wavenumbers for the molecules. For this purpose, the full set of 138 standard internal coordinates containing 51 redundancies for the $Cu(acac)_2$ complex is defined as given in Table S1 (Supplementary material). From these a non-redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal coordinates following the recommendation of Pulay et al. [31]. The combination coordinates and symmetry coordinates are given in Table S2 (Supplementary material). The potential energy distributions (PEDs) were obtained using the calculated symmetry coordinates.

By combining the results of the GaussView 4.1.2 program [32] with symmetry considerations and potential energy distribution (PED) the vibration descriptions were made with a high degree of accuracy. Vibrational assignments are based on comparison of calculated and observed Raman and IR frequencies and intensities.

Acetonitrile was selected for studying the isomerisation in solution following the SCRF/PCM method [33]. In this method the solute is embedded in the dielectric medium surrounded by a cavity shaped in the form of the solute [34,35]. The van der Waals radii suggested by Bondi [36] were adopted for atoms. In this level of calculation the specific solute–solvent effects are not taken into account and the obtained solvation energies correspond to the electrostatic contributions, which, still, play a dominant role in tautomerization reactions [37].

4. Results and discussion

4.1. Molecular geometry

To explore the effects of phenyl group on the metal–ligand strength, the optimized geometrical parameters of $Cu(bzac)_2$ and $Cu(acac)_2$ are calculated at the B3LYP/6-311G* level of theory.

Theoretically, two configurations are possible for $Cu(bzac)_2$. These are recognized as trans and cis configurations (Fig. 1), which, according to the calculations, have C_i and C_2 symmetries, respectively. Theoretical calculations in the gas phase indicate that the energy difference between cis and trans isomers is negligible (0.32 kcal mol^{-1}), which reduces to 0.11 kcal mol^{-1} in the CH_3CN solution. Zero point energy (ZPE) corrections in the gas phase not much change this energy difference (0.34 kcal mol^{-1}). Therefore, from the theoretical point of view, the coexistence of both cis and trans isomers of $Cu(bzac)_2$ in the sample is suggested. However, the vibrational frequency investigations suggest that the trans isomer in the sample is predominant and rule out the presence of the cis isomer, which will be discussed in Section 4.2.3.

Since, excellent results have been obtained for similar compounds by using the B3LYP/6-311G* level [38–40], this level of calculation is used in this work. The selected calculated geometrical parameters for $Cu(bzac)_2$, $Cu(acac)_2$, and $Cu(dbm)_2$ for comparison, are listed in Table 1. Some important geometrical parameters and vibrational band frequencies related to the M—O bond strength for these complexes are also collected in Table 2.

The comparison between geometry of cis and trans isomers shows that the steric hindrance between two phenyl groups in the cis isomer causes the dihedral angle between the phenyl groups and chelated ring in the cis isomer to be larger than that in the trans isomer. Therefore, it is expected that the conjugation between the phenyl group and chelated ring in the cis isomer is less than that in the trans isomer. According to Table 1, in both cis and trans isomers of $Cu(bzac)_2$, substitution of one of the methyl groups in each ligand and all methyl groups in $Cu(dbm)_2$