



Low frequency vibrational spectra and the nature of metal-oxygen bond of alkaline earth metal acetylacetonates



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ABSTRACT

Theoretical quantum chemistry calculations were used to assign the observed vibrational band frequencies of Be, Mg, Ca, Sr, and Ba acetylacetonates complexes. Density functional theory (DFT) calculations have been carried out at the B3LYP level, using LanL2DZ, def2SVP, and mixed, GenECP, (def2SVP for metal ions and 6-311++G** for all other atoms) basis sets. The B3LYP level, with mixed basis sets, was utilized for calculations of vibrational frequencies, IR intensity, and Raman activity. Analysis of the vibrational spectra indicates that there are several bands which could almost be assigned mainly to the metal-oxygen vibrations. The strongest Raman band in this region could be used as a measure of the stability of the complex.

The effects of central metal on the bond orders and charge distributions in alkaline earth metal acetylacetonates were studied by the Natural Bond Orbital (NBO) method for fully optimized compounds. Optimization were performed at the B3LYP/6-311++G** level for the lighter alkaline earth metal complexes (Be, Mg, and Ca acetylacetonates) while the B3LYP level, using LanL2DZ (extrabasis, d and f on oxygen and metal atoms), def2SVP and mixed (def2SVP on metal ions and 6-311++G** for all other atoms) basis sets for all understudy complexes. Calculations indicate that the covalence nature of metal-oxygen bonds considerably decreases from Be to Ba complexes. The nature of metal-oxygen bond was further studied by using Atoms In Molecules (AIM) analysis. The topological parameters, Wiberg bond orders, natural charges of O and metal ions, and also some vibrational band frequencies were correlated with the stability constants of understudy complexes.

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1. Introduction

The infrared spectra of many acetylacetonates complexes have been assigned by a number of investigators [1–13], but the attention so far has mostly been confined to the middle infrared region (700–1600 cm^{-1}), and little is known about the low-frequency part of the spectra [5–8]. These studies indicate that several vibrations in the low-frequency region involve metal-oxygen, M–O, stretching character to a varying degree through the vibrational coupling. The M–O stretching bands are metal sensitive; they are shifted to higher or lower frequencies by changing the metal in a series of compounds having the same structure. Previous attempts to find a band or bands related to the stability of the chelates have met with only partial success. Measurements of metal-ligand vibrations have an advantage that their frequencies are directly related to the

strength of the metal-ligand bond and stability constants of complexes [1,3,5,8].

The investigation of the structure of beryllium acetylacetonate, $\text{Be}(\text{acac})_2$, have been performed by means of X-ray diffraction [14,15] and gas phase electron diffraction (GED) [16]. GED of magnesium acetylacetonate, $\text{Mg}(\text{acac})_2$, has been studied by Zakharov et al. [17]. The Be, Mg, and Ca complexes of malonaldehyde have been investigated by quantum mechanical calculation [18]. These studies indicated that all of these compounds belong to the D_{2d} symmetry point group.

The vibrational spectroscopy studies of $\text{Be}(\text{acac})_2$ were carried out by Nakamoto et al. [3], Junge and Musso [4], Dismukes et al. [5], and Tayyari et al. [9]. Junge and Musso [4] in an extensive work studied the IR spectra of $\text{Be}(\text{acac})_2$ and $\text{Mg}(\text{acac})_2$ and some other metal acetylacetonates in the 1600–400 cm^{-1} region by considering the ^{18}O , ^{13}C and ^2H labeling of the ligand atoms. Nakamoto [3] and Junge and Musso [4] did not assign any vibrational band below 600 cm^{-1} .

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The aim of the present work is the investigation of metal–oxygen bond nature by means of low frequency IR absorption and Raman scattering spectra, Natural Bond Orbital (NBO) method, and AIM analysis of Be, Mg, Ca, Sr, and Ba acetylacetonates. The effect of changing the metal on the frequency of metal–oxygen vibrational bands, the topological parameters, and bond orders are discussed in this work. To assign the vibrational band frequencies, a normal coordinate analysis (NCA) was performed on all complexes. An effort in this work is also carried out to find correlations between the metal–oxygen bond characters and vibrations with the stability constant.

2. Experimental

Alkaline earth metals acetylacetonates were prepared and purified according to the method described in the literature [19]. The anhydrous Be(acac)₂ and Mg(acac)₂ complexes have been obtained by vacuum sublimation (at 0.2 Torr; 80 and 220 °C, respectively) and identified by IR spectroscopy. Ca(acac)₂, Sr(acac)₂, and Ba(acac)₂ were dried over P₂O₅ in a vacuum desiccator.

The IR spectra were recorded on a Bomem B-154 Fourier transform spectrophotometer in the region 900–600 cm⁻¹ by averaging 20 scans with a resolution of 2 cm⁻¹. The spectra were measured as KBr pellets.

The Far-IR spectra in the region 600–50 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. The spectrum of the polyethylene pellet was collected with a resolution of 2 cm⁻¹ by averaging the results of 64 scans.

The FT-Raman spectra were recorded employing the 180° back-scattering 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. Rayleigh filtration was afforded by two sets of two holographic technology filters. The spectra were accumulated for 500 scans with a resolution of 2 cm⁻¹. The laser power at the sample was 300 mW.

3. Method of analysis

In this study, the molecular equilibrium geometry, harmonic force field, and vibrational transitions of alkaline earth acetylacetonates were computed with the GAUSSIAN 09 software system [20] by using density functional theory. The B3LYP level [21–23], using 6-311++G** basis set, have been used for Be, Mg, Ca acetylacetonates. The 6-311++G** basis set is undefined for Sr and Ba atoms, thus the B3LYP level, using LANL2DZ [24,25] (extrabasis, 6d and 7f orbitals on metal and oxygen atoms) and def2SVP [26] basis sets were used for all complexes. Furthermore, the B3LYP/GENECP (def2SVP for metal ions and 6-311++G** for all other atoms) was used to perform the geometry optimization and calculating the vibrational frequencies and IR and Raman intensities of all compounds. However, the wave functions created at the B3LYP/GENECP level were not convenient for NBO analysis [27], therefore, an extra “f” function was also added on the metal ions.

Normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational wavenumbers for understudy compounds. By combining displacement Cartesian coordinates of the atoms for each vibrational frequency and the Cartesian coordinates of atoms at the equilibrium position, obtained from Gaussian output, the displacement internal coordinates were calculated [28–30]. The full sets of 126 standard internal coordinates containing 45 redundancies are defined as given in Table 1S (supplementary materials). From these internal coordinates, a non-redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal

coordinates as shown in Table 2S (supplementary material). Then all symmetry coordinates were normalized through all 81 normal coordinates. The normalized symmetry coordinates were used to calculate the potential energy distributions (PEDs) for each normal mode. The “HPModes” keyword was applied in Gaussian, using the B3LYP/GENECP level, to obtain the high-precision format (to five decimal places) for vibrational frequency eigenvectors (Cartesian displacement coordinates) in the frequency output of the Gaussian program. All geometrical parameters, displacement (internal) coordinates (changes in bond lengths, bond angles, and dihedral angles), symmetry coordinates, and normalization of symmetry coordinates were carried out using the mathematics build in Microsoft Office Excel 2016. By combining the results of the GaussView program [31] with symmetry considerations and potential energy distributions (PED), the vibration descriptions were made with a high degree of accuracy. Vibrational assignments are based on comparison of calculated and observed infrared and Raman wavenumbers and intensities.

Orbital population and Wiberg bond orders [32] were calculated with NBO 3.0 program implemented in Gaussian 09.

For better elucidation of nature and strength of the M–O bonding interactions of the titled complexes, a topological analysis, using Bader’s theory of Atoms in Molecules (AIM) [33–35], was performed.

Upon formation of chemical bond between two neighboring atoms a bond critical point, BCP, appears between them. The nature of the chemical bonds and reactivity of molecules could be described by the electron density, $\rho(r)$, and the corresponding Laplacian, $\nabla^2\rho(r)$, at the BCPs [36]. The Laplacian of electronic density at BCPs is related to the kinetic, $G(r)$ and potential, $V(r)$, electronic energy densities at BCPs by the following equation of the virial theorem [36]:

$$\frac{1}{4} \nabla^2 \rho(r) = 2G(r) + V(r) \quad (1)$$

The sign of $\nabla^2\rho(r)$ at BCP is an important indicator for description of chemical bonds. Positive values of Laplacian at the BCPs shows that the kinetics energy, $G(r)$, is greater than potential energy, $V(r)$, therefore, implies depletion of electronic charge along the bond path, which is specification of a closed-shell interaction, such as ionic or hydrogen bond. Negative values of Laplacian indicate excess potential energy at the BCP which indicate existing of shared interactions and concentration of electronic charge in the internuclear region, such as covalent bonds [37]. Another useful parameter is the potential energy at the BCPs, which is related to the strength of the bonds by the following equation [38].

$$EB = 1/2V(r) \quad (2)$$

Although, according to our knowledge, Equation (2) has been applied only to hydrogen bonds, we applied this equation to M–O bonds in the titled complexes to follow the effect of metal on the nature of this bond.

4. Results and discussion

4.1. Geometrical parameters

Two different structures are theoretically expected for the enol forms of bivalent metal acetylacetonate complexes, D_{2h} and D_{2d} symmetry point groups. The geometry calculations are performed at the B3LYP/GENECP level for both structures. For all understudied complexes, the D_{2d} structure is considerably more stable than D_{2h} geometry. The energy difference between D_{2h} and D_{2d} structures is given in Table 1. Furthermore, calculations of vibrational

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