



Theoretical investigation on the vibrational and electronic spectra of three isomeric forms of dicobalt octacarbonyl



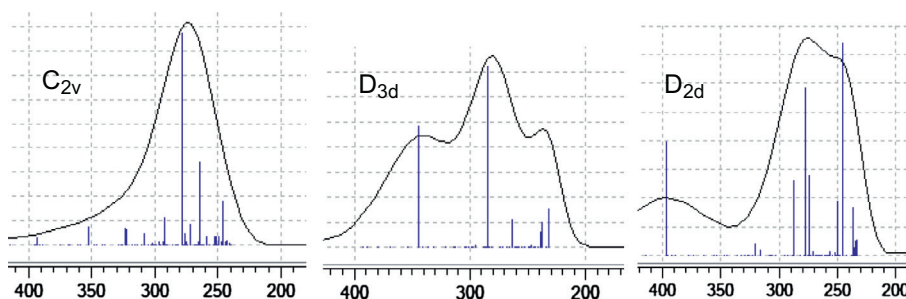
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HIGHLIGHTS

- $\text{Co}_2(\text{CO})_8$ isomers were optimized at B3LYP method with mix basis set.
- Electronic structures, carbonyl stretching frequencies and MPA were determined.
- Electronic spectra of isomers were obtained by using TD-B3LYP method.
- The calculated bands were assigned to metal-ligand charge transfer transitions.

GRAPHICAL ABSTRACT



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ABSTRACT

Three isomeric forms of dicobalt octacarbonyl, $[\text{Co}_2(\text{CO})_8]$, with C_{2v} , D_{3d} and D_{2d} point group were optimized by using density functional theory (DFT/B3LYP) method with LANL2DZ basis set for the cobalt atoms and 6-31G(d) basis set for the other atoms in the gas phase. Electronic structures, carbonyl stretching frequencies and Mulliken population analysis were determined from the optimized structures. Electronic structures indicate that each of the dicobalt octacarbonyl isomers have been constituted from two trigonal bipyramidal geometry. While the isomer C_{2v} has two bridged carbonyl groups, in the isomers D_{3d} and D_{2d} all carbonyl groups are coordinating as terminal. The calculated C–O stretching frequencies are in a good agreement with experimental frequencies. Experimental C–O stretching frequencies were assigned to isomers according to the calculated frequencies. Mulliken population analysis show that free carbonyl ligands transfer their electron to the cobalt atoms during formation of the complexes. The electronic spectra of isomers were obtained by using time dependent density functional theory (TD-DFT/B3LYP) method with LANL2DZ basis set for the cobalt atoms and 6-31G(d) basis set for the other atoms in the gas phase. The theoretical electronic spectra of isomers are in a good agreement with experimental spectra. The calculated bands at 277.9, 278.1 and 284.1 nm for isomers C_{2v} , D_{2d} and D_{3d} were assigned to metal–ligand charge transfer transitions and the shoulder at 344.6 nm was assigned to pure metal center transitions for isomer D_{3d} .

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1. Introduction

Dicobalt octacarbonyl is a catalyst precursor for industrially important carbonylation and hydroformylation reactions [1–6]. Extended Hückel theory calculations [7], the application of the ligand polyhedral model [8] and a detailed examination of infrared

spectra of $\text{Co}_2(\text{CO})_8$ in a range of different solvents and at different temperatures have shown the existence of at least three isomeric forms with symmetry C_{2v} , D_{3d} and D_{2d} [9–13]. Dicobalt octacarbonyl with C_{2v} symmetry contains two bridged CO groups, whereas isomers D_{3d} and D_{2d} correspond to nonbridged forms. Sweany and Brown proposed that the ranking of the free energy of isomers is in the form of $C_{2v} < D_{3d} < D_{2d}$ at temperatures below 77 K and the conversion of D_{2d} to D_{3d} is extremely facile and the conversion of D_{3d} to C_{2v} occurs in hexane matrices at 84 K [14]. To investigate

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the dynamic equilibrium between different isomers of dicobalt octacarbonyl, Anna et al. [15] have used 2DIR chemical exchange spectroscopy. They suggested that the value of ΔG^\ddagger at 298 K for the conversion of D_{3d} to C_{2v} is 2.72 kcal/mol, and for the conversion of C_{2v} to D_{3d} is 2.76 kcal/mol. This data indicated that the isomer C_{2v} is more stable than isomer D_{3d} at 298 K. Onaka and Shriver [16] concluded from solid and solution phase Raman spectroscopy that the three distinct structures of $\text{Co}_2(\text{CO})_8$ have Co–Co stretching frequencies of 235, 185, and 159 cm^{-1} , respectively [17].

Hieber and Hofmann [18] and Cable et al. [19] reported that the electronic spectra of dicobalt octacarbonyl shows two absorption bands at 350 and 280 nm in cyclohexane solvent and the spectra of gaseous state are similar to the spectra in cyclohexane solvent except shorter wavelength shift of the band maxima. The band at 280 nm has been assigned to $n \rightarrow \pi^*$ transition for bridged carbonyls by Hieber and Cable. van Schooneveld et al. [20] have reported that the band at 350 nm is derived from Co–Co bond electrons. Therefore this band has assigned to $\sigma \rightarrow \sigma^*$ transitions. But these bands belong to which isomer have not been investigated theoretically. The theoretical studies have indicated that the calculations based on DFT have an important role for the interpretation of experimental, spectroscopic and electrochemical results. In this study we investigated the electronic structures for three isomeric forms of dicobalt octacarbonyl and assigned the experimental C–O stretching frequencies to isomers by comparing the calculated frequencies with DFT/B3LYP method. Additionally we obtained electronic spectra for three isomer by using TD-DFT/B3LYP method and performed the labeling of bands at electronic spectra in the gas phase.

2. Computational method

In the first step, the geometries of the $\text{Co}_2(\text{CO})_8$ isomers were prepared with GaussView 5.0.8 [21]. All calculations were made in the gas phase by using Gaussian 09 Revision-A.02 [22]. In the second step, the geometries were fully optimized at DFT/B3LYP method by considering symmetry restriction [23,24]. It was taken into account that each of the isomers have singlet spin multiplicity. All the geometry optimizations were followed by frequency calculations and no imaginary frequency were found [25].

DFT/B3LYP is a hybrid method, including the electron correlation effects into Hartree–Fock determinant via general functionals of the electron density. We used LANL2DZ basis set for the cobalt atoms and 6-31G(d) basis set for the C and O atoms. LANL2DZ basis set is widely used for atoms beyond the third row of periodic table. In this basis set, electrons close to the nucleus in the atoms with very large nuclei are represented by an effective core potentials. 6-31G(d) basis set adds d functions to heavy atoms and is widely used for medium-sized systems.

Electronic absorption spectra of complexes were calculated by using TD-DFT/B3LYP method with LANL2DZ basis set for the cobalt atoms and 6-31G(d) basis set for the other atoms in the gas phase [26]. Recently, the TD-DFT approach has been suggested as an accurate method for the calculation of vertical excitation energies in organic and inorganic compounds [27]. The TD-DFT methodology provides a good compromise between accuracy and computational efficiency as compared to the computationally more expensive CASSCF and MRCI approaches. In TD-DFT, the entire spectrum is calculated in a single run, and the computational costs are lower than those of the high-level ab initio methods [27].

3. Results and discussion

3.1. Geometry optimization

Three isomeric forms of dicobalt octacarbonyl were optimized at DFT/B3LYP method in the gas phase. Fig. 1 shows the optimized

molecular structures, atomic numbering scheme and point groups for each of the isomers. As can be seen from Fig. 1, each of the isomers has been constituted from two trigonal bipyramidal (TBP) geometry. The isomer with C_{2v} symmetry is obtained by connecting axial carbonyl (C6) of Co1 to axial position of Co2 and equatorial carbonyl (C7) of Co2 to equatorial position of Co1. The isomer with D_{3d} point group constitutes by connecting on axial position of two TBP and by rotating one 180° around the other. D_{2d} structure is formed by connecting on equatorial position of two TBP and by rotating one 180° around the other. These predictions can be verified with the calculated structural parameters. The calculated and experimental [17,28,29] structural parameters of isomers were given in Table 1.

The calculated bond lengths in Table 1 are in a good agreement with experimental data. Maximum deviation is around 0.01 \AA , and this deviation is an acceptable value. The calculation method suggests that two Co–C bond in the environment of each cobalt atoms are equal for isomer C_{2v} . The changes in Co–C lengths also support that each of the isomers constitute from two TBP geometry. There are three different Co–C bond lengths (Co–C_{ax}, Co–C_{eq} and Co–C_{brid}) for isomer C_{2v} and two different Co–C bond lengths (Co–C_{ax} and Co–C_{eq}) for isomer D_{3d} and D_{2d} . Generally axial bonds are shorter than the equatorial bonds in TBP complexes due to participate low energy d orbitals to hybridization [30]. For isomer D_{3d} axial Co1–C3 and equatorial Co1–C4 distances were calculated as 1.785 and 1.815 \AA , respectively. There are also similar situations in the other isomers.

The calculated bond angles are slightly different from the bond angles of ideal TBP geometry. Bond angles vary slightly due to the formation of the bridged carbonyl bonds and Co–Co bonds. For example C4–Co1–C6 angles were calculated as 157.6° (180°), 119.3° (120°) and 97.2° (90°) for isomers C_{2v} , D_{3d} and D_{2d} , respectively. The values in parentheses are the angles in ideal TBP geometry. For C_{2v} structure Co1–C6–Co2 angle was given as 80° [19]. As can be seen from Table 1, this angle was calculated as 81.5° . The calculated values are in a good agreement with experimental data.

3.2. C–O stretching frequencies

According to C–O factored force fields, symmetry species of C–O stretching bands for isomers C_{2v} , D_{3d} and D_{2d} symmetries are obtained as $3a_1 + a_2 + 2b_1 + 2b_2$, $2a_{1g} + 2a_{2u} + e_g + e_u$ and $2a_1 + 2b_2 + 2e$, respectively [31,32]. a_2 Symmetry for isomer C_{2v} , a_{2u} and e_u symmetries for isomer D_{3d} and a_1 symmetry for isomer D_{2d} are IR inactive [33]. Therefore seven bands for C_{2v} , three bands for D_{3d} and four bands for D_{2d} are expected in IR spectra of isomers. The assigned to symmetry species C–O stretching frequencies of isomers C_{2v} , D_{3d} and D_{2d} were obtained from optimized geometries in gas phase and given in Table 2. The calculated harmonic frequencies were scaled by 0.9611 [25].

The calculated frequencies in gas phase are consistent with experimental frequencies obtained in Ar matrix for isomers. Small differences between experimental and theoretical frequencies may be associated with different environments. 2035.3 cm^{-1} frequency has been assigned to isomer D_{2d} by Sweany and Brown [14]. But a_1 symmetry species for D_{2d} structure are IR inactive. Therefore 2035.3 cm^{-1} was labeled to isomer C_{2v} in this study. 1867.9 and 1857.4 cm^{-1} frequencies are specific to bridged carbonyls. These frequencies were calculated as 1889.7 and 1874.1 cm^{-1} for isomer C_{2v} .

Onaka and Shriver have obtained three distinct Co–Co stretching frequencies at 235, 185, and 159 cm^{-1} from solid and solution phase Raman spectroscopy. These frequencies were calculated as 213, 171 and 158 cm^{-1} for isomers with C_{2v} , D_{2d} and D_{3d} symmetry, respectively. In that case, the frequencies at 235, 185 and 159 cm^{-1} can be assigned to isomer C_{2v} , D_{2d} and D_{3d} , respectively.

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