

## TDDFT-DFT Theoretical Method and Topological Analysis to the Behavior Understanding of Two Tungsten Carbonyl Complexes

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**Abstract:** We present here a study based on Density Functional Theory (DFT) calculations, to contribute to the understanding of the complexes behavior based on tungsten carbonyls ( $[W(C_7H_7NS)(CO)_5]$ ,  $[W(C_3H_6N_2S)(CO)_5]$ ), which consider as targets molecules of biological interest and easily detectable probes by IR spectroscopy. The results showed good agreements between the calculated and experimental values of the geometric parameters for the two complexes. A peak in the IR spectrum at 2030  $cm^{-1}$  is due to the stretching of the C-O triple bond, according to the AIM analysis ( $0.07 < \rho < 0.15$ ), the existence of an intermediate interaction between the tungsten and the CO ligand. Moreover, these complexes are stable, the spectra of TD-DFT analysis showed these complexes absorb in the same domain of wavelengths, through absorption features at about 110-160 nm, characterized by natural transitions of HOMO/LUMO; of type MLCT for both complexes

**Keywords:** TDDFT, AIM, DFT, Tungsten, Carbonyl complexes.

### Introduction

Metal-carbonyl complexes have been widely studied and mainly used not only due to their catalytic activity or as an antioxidant but also as a coenzyme, anticancer and due to their application in sensors and molecular recognition [1-6]. Since organic molecules do not absorb in the mid-infrared region (1800-2200  $cm^{-1}$ ) [7, 8], carbonyl (CO) ligands in this region exhibit unique, characteristic and intense spectral properties. As well as the metal carbonyl compounds their photochemical characterization requires an understanding of the molecular or bitals properties. The electronic structures, as well as their spectra, and usually, Tungsten carbonyl complexes exhibit intense charge transfer between metal and ligand (MLCT) and the experimental techniques may not always be able to provide an adequate interpretation of molecular properties [9]. As a result, the support of the theoretical computational methods using DFT techniques can help fill the existing gaps and further corroborate the results in predicting the reactivity, structural properties and evaluating the physico-chemical properties of the studied molecules [10-14]. Merniz S and his collaborators synthesized by photochemical substitution two complexes based on tungsten carbonyl [14, 15] as target molecules of biological interest, and on the other hand the experimentation possibility of these compounds in the field of conductivity and these compounds have not been studied exhaustively.

In this paper, we report a quantum chemical investigation of both compounds reported in Literature [15, 16].

The geometric calculation based on the DFT/TDDFT (density and Time-Dependent density functional theory) were accomplished to understand better the different physicochemical, structural, spectral properties of both compounds and topological analysis that are performed to elucidate information regarding charge transfer within the molecule, and supporting efforts to explain the significance of diverse theoretical properties [17-20].

### Computational Methods

All theoretical calculations and geometry optimizations in this study, were fully optimized in the gas phase without symmetry constraints using the density functional theory (DFT), by the Perdew, Burke, and Ernzerhof's exchange functional along, with generalizing the gradient approximations, exchange, and correlation functional GGA (PBE) [21, 22] employing the TZP (TripleZeta Polarized) basis set through the Amsterdam Density function (ADF) software [23].

The first singlet-excited state was optimized using the Time-Dependent Density Functional Theory calculations (TDDFT) [24-27] with the same functional and basis set.

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The calculation of the global electrophilicity index  $\omega$ , the electronic chemical potential ( $\mu$ ), and the chemical hardness ( $\eta$ ) of C1 and C2 is to understand the chemical selectivity and reactivity in studied molecules [28], they have been made using the following equations:

$$\omega = \mu^2/2\eta \quad (1)$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2 \quad (2)$$

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2 \quad (3)$$

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2 \quad (3)$$

The Atoms in Molecules (AIM) approach is a quantum chemical model characterizing the chemical bond of a system based on a topological approach to the electron density  $\rho$ , it allows giving a topological description of a molecule and more particularly of its chemical bonds. AIM's theory has become a valuable tool, especially in defining what a bond in a quantum calculation is, and recently characterized the interactions between metal-ligand bonds. The atoms in molecules theory (AIM) [29], according to the properties of the electron density  $\rho$ , the Laplacian  $\nabla^2$ , and the energy density  $H$ , Espinosa et al [30] have divided the atomic interaction into three categories: closed-shell interactions, intermediary interactions, and a pure covalent interaction.

## Results and Discussion

*Structural analysis:* All important bond distances and bond angles calculated along with the corresponding experimental data are listed in Table-1. Calculated structural parameters reveal a better agreement with experimental data obtained from X-ray analyses, which indicates significant stability of both compounds.

Table-1: Experimental and theoretical bond lengths (Å) and bond angles (°) for tow tungsten complex.

Bond lengths(Å)	C 1		C 2	
	GGA(PBE)	X-ray	GGA(PBE)	X-ray
W-C <sub>1</sub>	2.03	1.97	2.04	1.98
W-C <sub>2</sub>	2.10	2.05	2.09	2.05
W-C <sub>3</sub>	2.08	2.04	2.09	2.06
W-C <sub>4</sub>	2.10	2.04	2.10	2.03
W-C <sub>5</sub>	2.09	2.05	2.10	2.05
W-S	2.65	2.60	2.65	2.55
S-C <sub>6</sub>	1.69	1.71	1.69	1.68
N-C <sub>6</sub>			1.34	1.30
<b>Bond angles (°)</b>				
W- $\hat{S}$ -C <sub>6</sub>	110	110	113	113
S- $\hat{C}_6$ -C <sub>7</sub>			121	119
S- $\hat{C}_6$ -N			122	123

### AIM topological analysis

The analysis by the AIM theory indeed makes it possible to determine the exact number of Metal-Carbon bonds.

The results of this analysis clearly indicate the existence of a critical point (BCP) between each pair of bound atoms (Fig 3 and Table 2). Also characterizes the metal-ligand bond (see Table 2), with an electron density of  $0.07 < \rho < 0.15$  which means that it is an intermediate interaction between tungsten and the CO ligand, which facilitates the release of this ligand. From Table-2, W-S ( $\rho(r) < 0.07, \nabla^2\rho(r) > 0$ ) we notice aclosed-shell interactions between the tungsten and the sulfur (W-S), and about sulfur-carbon bonds (S-C) the negative value of laplacian( $\nabla^2$ ) and electron density ( $\rho$ ) in order  $> 10^{-1}$  indicates that there is a concentration of electronic charge at the BCP, which indicates a pure covalent interaction.

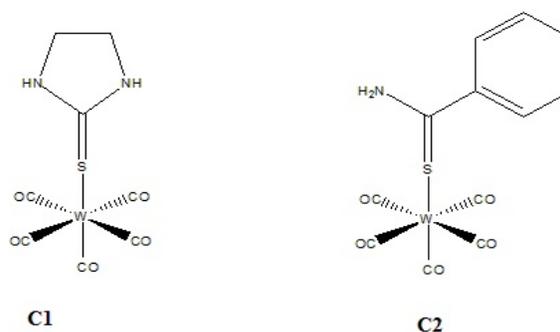


Fig. 1: Molecular structure of the tow tungsten complexes.

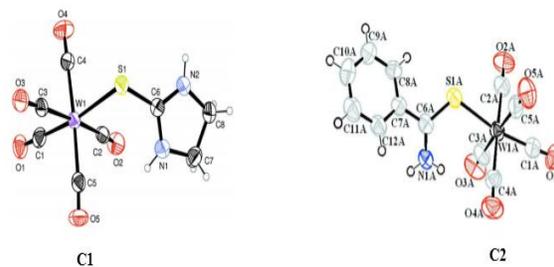
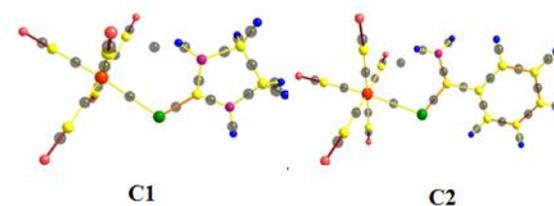


Fig. 2: Optimized structure of C1 and C2.



The black spheres are BCPs

Fig. 3: The critical point founded between every pair of nuclei of Complex C1 and C2

*The electronic properties:* The relative energy levels of molecular orbitals for C1 and C2 are

typically shown in Fig.4. It shows that the band gap is large between the highest occupied and lowest unoccupied molecular orbital (HOMO/LUMO) for C1 (8.17 eV) and C2 (7.62 eV), predict the strength and stability of these complexes.

Table-2: Results of atom in molecule approach (AIM) for compounds tungsten complex.

	$\rho$		$A$		$ v /G$		$H$	
	C1	C2	C1	C2	C1	C2	C1	C2
W-S	0.05	0.05	0.14	0.15	1.15	1.17	-0.01	-0.01
S-C6	0.20	0.21	-0.21	-0.31	2.67	2.80	-0.18	-0.18
W-C1	0.12	0.10	0.41	0.39	1.26	1.21	-0.03	-0.03
W-C2	0.10	0.10	0.39	0.39	1.20	1.20	-0.03	-0.02
W-C3	0.10	0.11	0.39	0.40	1.20	1.25	-0.02	-0.03
W-C4	0.10	0.10	0.38	0.38	1.20	1.20	-0.02	-0.02
W-C5	0.10	0.10	0.38	0.38	1.20	1.20	-0.02	-0.02

Table-3: Frontier orbital energy, electronic chemical potential, chemical hardness and global electrophilicity index of Complex C1 and C2

Compound	$E_{HOMO}$	$E_{LUMO}$	gap	$\eta$	$\mu$	$\omega$	$\rho$
C1	-5.14	3.03	8.17	4.08	-1.05	0.27	9.30
C2	-5.40	2.22	7.62	3.81	-1.59	0.66	7.68

Table-4: Hirshfeld charge analysis of Complex C1 and C2.

Compound	W	S	Nc6	C6	Ow	Cw
C1	0.20	0.12	0.10	0.10	0.10	0.10
C2	0.21	0.10	0.10	0.11	0.10	0.10

In general, the HOMO for C1 and C2 shows that composition has a strong metallic character with 43 and 45% for C1 and C2 respectively, while the LUMO is a nonmetallic character for the two complexes. Table-3 ( $\omega = 0.27, 0.66$  for C1 and C2) shows that the two compounds are weakly electrophilic.

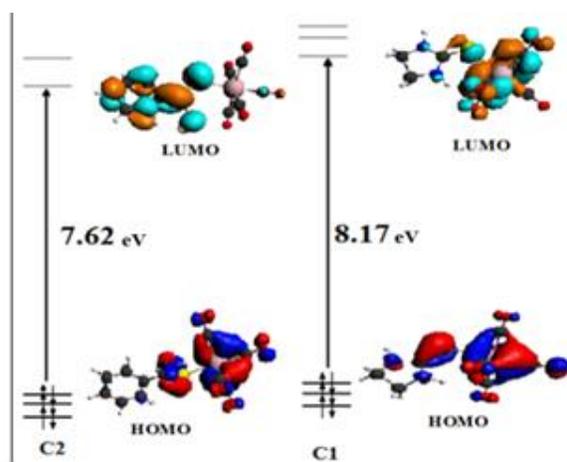


Fig. 4: Frontier molecular orbital diagram of Complex C1 and C2.

The dipole moment ( $p$ ) is important; this means that the molecule can have a strong asymmetry in the electronic charge distribution, so it can be more reactive. From Table-3, we see that the dipole moment ( $p$ ), of the complex C1, is greater than C2; so we conclude that the C1 is more reactive than C2. In addition, by comparing, the HOMO and LUMO energies for the studied compounds, we find that the C1 compound has the high energy ( $E_{HOMO} = -5.14\text{eV}$ ), which allows it to be a good electron donor. On the other hand, the compound that has the lowest LUMO energy is that of C2 compound ( $E_{LUMO} = -2.22\text{eV}$ ). Which means that it is an electron attractor.

**Population analysis:** The atomic net charge study was performed by Hirshfeld charges [31], the evolution of the net atomic charges obtained by Hirshfeld analysis for C1 and C2 which shows that the biggest positive charges ((0.20, 0.21 respectively)) (Table-4), are found on the tungsten atom. We conclude that the interactions are electrostatic.

**Vibrational frequencies:** The vibration frequencies were calculated using the DFT method. The vibration frequency calculation allowed the determination and knowledge of the nature of each stationary point; the results (Fig.5) proved that for the two tungsten complexes: the absence of an imaginary spectrum confirms that their geometries are stable and real. A strong absorption band was detected at about  $1900\text{-}2100\text{ cm}^{-1}$  of C1 and C2 shown in Fig.5. The peaks at  $2030\text{ cm}^{-1}$  and is due to the stretching of the C-O Triple bond.

**DFT/TDDFT Analysis:** The calculated optical transition energies and their corresponding oscillator strengths ( $f$ ) for C1 and C2 are shown in Table-5, and Fig.6.

Table-5. The calculated optical transitions energies and their corresponding oscillator strengths ( $f$ ) for Complex C1 and C2

$\lambda$ (nm)	$f$	E (ev)	Transition	Character
<b>C1</b>				
111	0.70	11.21	HOMO→LUMO+16	MLTC/ ICT
121	0.11	10.21	HOMO-2→LUMO+6	MLTC
151	0.02	8.20	HOMO→LUMO	MLTC
<b>C2</b>				
112	0.12	11.07	HOMO→LUMO+15	ICT
127	0.28	9.78	HOMO-3→LUMO	LLTC
158	0.63	7.84	HOMO→LUMO	MLTC

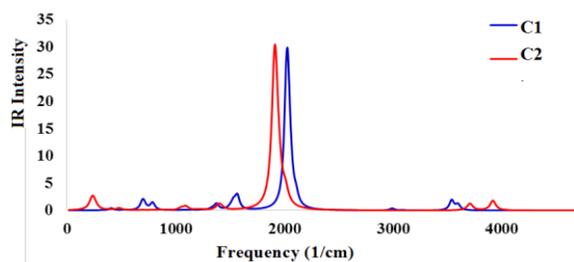


Fig. 5: Theoretical vibrational spectra of Complex C1 and C2.

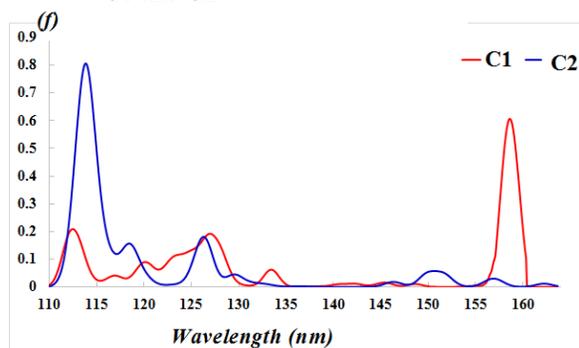


Fig. 6: Theoretical UV-vis absorption spectra of Complex C1 and C2

From Fig.6, the spectra of TD-DFT analysis shows these complexes absorb in the same domain of wavelengths, by absorption features at about 110-160 nm, and demonstrate a different profile for the two compounds. According to the HOMO / LUMO energy, leads to a bathochromic shift of the corresponding spectrum. The absorption bands correspond to the HOMO  $\rightarrow$  LUMO transitions of the complexes are metal to ligand transfer charge MLCT. Finally, the metal's contribution to electronic transitions is great.

### Conclusion

In this article, we applied a theoretical approach based on the DFT method, where we tried to analyze the structural and electronic parameters in order to contribute to the behavior understanding of TUNGSTEN CARBONYL COMPLEXES. Rational analysis based on the results of quantum calculations in DFT and TD-DFT allowed us to determine the electronic structure of the two complexes. The UV-visible spectrum domain of the complexes extends over wavelengths of 110- 160 nm, which belong to the region electromagnetic between UV and X-rays. Metal largely contributes to the transitions; these transitions are of MLCT character for the HOMO-LUMO transition nature and are bath-chromically shift.

Quantum descriptors from conceptual DFT define these complexes as very weak electrophiles. Compound C1 was found to have the highest energy ( $E_{\text{HOMO}} = -5.14\text{eV}$ ), that makes it a good electron donor and C1 has the lowest LUMO energy ( $E_{\text{LUMO}} = -2.22\text{eV}$ ). Which allows it to be an electron attractor. The most intense band in the IR spectrum of C1 and C2 is at  $2030\text{ cm}^{-1}$ , in the mid-infrared region it is due to the stretching of the C-O triple bond. AIM analysis showed that there is an intermediate interaction between tungsten and the ligand CO, which facilitates the release of this ligand and a closed checkmark interaction between tungsten and sulfur (WS) these results led us to study these compounds biologically if not we move towards the field of semiconductors or both in parallel

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