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# A DFT analyses for molecular structure, electronic state and spectroscopic property of a dithiolene tungsten carbonyl complex



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## HIGHLIGHTS

- Molecular structure of two tungsten carbonyl complex isomers were constructed.
- Optimization geometry processes were done on three different GGA calculations.
- The IR spectrum of the complex matched the calculated vibrational frequency spectra.
- Orbital profiles for HOMO/LUMO of the *cis* and *trans* [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] are presented.

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## Introduction

# GRAPHICAL ABSTRACT



# ABSTRACT

Bis(dithiolene) tungsten carbonyl complex,  $W(S_2C_2Ph_2)_2(CO)_2$  was successfully synthesized and the structure, frontier molecular orbital and optical properties of the complex were investigated theoretically using density functional theory calculations. The investigation started with a molecular structure construction, followed by an optimization of the structural geometry using generalized-gradient approximation (GGA) in a double numeric plus polarization (DNP) basis set at three different functional calculation approaches. Vibrational frequency analysis was used to confirm the optimized geometry of two possible conformations of  $[W(S_2C_2Ph_2)_2(CO)_2]$ , which showed distorted octahedral geometry. Electronic structure and optical characterization were done on the ground states. Metal to ligand and ligand to metal charge transfer were dominant in this system.

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Transition metal carbonyl complexes have been extensively studied due to their attractiveness for luminescence and electron transfer reactions. Several of these complexes have been shown to be effective as catalysts in the catalytic process [1] and in medical application as coenzyme, antioxidant and anticancer [2–4]. Furthermore, metal carbonyl complexes are also frequently used as starting materials for other organometallic complexes since the CO ligands can easily be replaced partially or completely in chemical or photochemical reactions [5]. Carbonyl complexes [ $M(CO)_xL_{6-x}$ ] bearing dithiolene ligands are among the most widely investigated [6,7]. These complexes prepared from  $M(CO)_5$ (solvent) that react readily with any available donor atom of dithiolene ligands [5,8,9]. Molybdenum, tungsten and ruthenium are transition metals that are frequently used in dithiolene carbonyl complexes.

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Currently, computational explorations on carbonyl complexes have received much attention [2,10–13]. Although successful synthesis of carbonyl complexes have been reported previously, some of fundamental aspects such as molecular orbital configurations remain unsolved. With the aid of modern computational simulation method, the orbital, optical and structural properties can be accurately obtained and in most cases the results were comparable to the experimental values [14,15]. Therefore, the physical, chemical and optical data of various materials in various forms such as crystals, nano-materials and surface alloys can be predicted without experimental work [16].

In this paper we describe the synthesis, molecular structure and density functional study (DFT) analysis of a dithiolenes complex  $[W(S_2C_2Ph_2)_2(CO)_2]$ . The complex has been prepared from a reaction of thioester and  $[W(CO)_5]$  fragment, where  $[W(CO)_5(solvent)]$  was photogeneratively prepared from  $W(CO)_6$  in THF or CH<sub>3</sub>OH solvents [17]. In this class of complexes, the tungsten metal centre assumed an octahedral geometry and since  $W(L)_4(CO)_2$  molecule has two thio bidentat ligands, there are two isomers of the complex namely, *cis*- $[W(L)_4(CO)_2]$  and *trans*- $[W(L)_4(CO)_2]$  as shown in Fig. 1. The molecular structures reported in this paper were developed computationally based on the elemental and spectroscopy (IR and UV–visible) results. The complex structure, which was constructed as described in the experimental section.

## Experimental

## Materials and instrumentations

Benzoin, tungsten hexacarbonyl, phosphorus pentasulfide and solvents were purchased from Sigma–Aldrich and were used as received. IR spectra were determined using a Thermo Nicolet 6700 FTIR spectrometer, <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using an Avans Bruker 400 MHz spectrometer and the absorption spectra were recorded using a Varian Cary 5000 UV–Vis spectrophotometer. Elemental analyses were performed using an Elemental Micro CHNS analyser.

Preparation of  $[W(S_2C_2Ph_2)_2(CO)_2]$  complex

#### Preparation of $(S_2C_2Ph_2)$ (II) ligand

Benzoin (30 g) and phosphorus pentasulfide  $P_4S_{10}$  (45 g) were dissolved in dry dioxane (250 ml). The mixture was refluxed for 3–4 h in inert atmosphere. Hydrogen sulfide produced from the reaction was trapped using lead acetate. The mixture was then cooled to room temperature, filtered and the filtrate was concentrated *in vacuo* to give dark-red oil with a 37.5% yield. IR-spectra (cm<sup>-1</sup>):1254 (P=O); 1081 and 958 (P–O and P–O–P); 870 (P=S). UV/Vis spectrum  $\lambda_{max}/nm$  ( $\varepsilon \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) in acetone solution: 300 nm (35,000) and 400 nm (23,000).



## Fig. 1. Molecular conformations for octahedral of $W(L)_4(CO)_2$ complexes.

#### Preparation of $[W(S_2C_2Ph_2)_2(CO)_2]$ complex

A solution of W(CO)<sub>6</sub> (1 g) in tetrahydrofuran (THF) (40 ml) was irradiated under UV light in N<sub>2</sub> atmosphere at room temperature for 2 h to generate the W(CO)<sub>5</sub>THF intermediate. Thioester (II) (0.5 g) was added to this solution and the mixture was stirred for about 1 h at room temperature. The solvent was then removed under reduced pressure. An orange–red solid was isolated upon the addition of 30 ml of Et<sub>2</sub>O/hexane mixture (1:2 v:v) at approximately –15 °C. Yield: 39%. IR-spectra (cm<sup>-1</sup>): 3026 (C–H); 2071 and 1980 (C=O); 1677 cm<sup>-1</sup> (C=C); 1155 cm<sup>-1</sup> (C–S) and 697 (W=S). Elemental CHNS Analysis (%): C 50.28 (49.73); H 3.01 (2.78), S 15.92 (17.70).

#### Computational details

The molecular geometry and density functional theory (DFT) calculations were performed using the Dmol<sup>3</sup> module in Materials Studio 5.5, Accelrys Inc. DMol<sup>3</sup> is a unique, accurate, and reliable DFT quantum–mechanical code that can be used to predict the properties of materials and can be applied to simulations of processes in a gas phase, solvent, on a surface and solid state [18].

The molecular structure of the tungsten carbonyl complex was constructed based on octahedral geometry system. Self-consistent field (SCF) method was used for calculating the electronic structure with the treatment to DFT Semi-core Pseudopots (DSPP)[19] for being polarizable and spin-unrestricted. Generalized-gradient approximation (GGA) in a double numeric plus polarization (DNP) basis set was used in the simulation. The structure was optimized via the use of the following functions: the Becke exchange functional (B88) [20] in conjunction with the Perdew–Wang correlation (BP)[21], Lee–Yang–Parr correlation (BLYP) and Perdew–Burke–Enzerhof (PBE) functions [22]. Furthermore, TDDFT calculation was conducted on ground state in restricted Hatree-Folk (RHF) at vacuum and some of salvation schemes.

## **Results and discussion**

## Synthesis and spectroscopic characterization

Bis(dithiolene) tungsten carbonyl complex,  $W(S_2C_2Ph_2)_2(CO)_2$ , originally was prepared via the reaction of photogenerated intermediate of W(CO)<sub>5</sub>THF with a thioester that was prepared previously from the reaction of benzoin and  $P_4S_{10}$  [23] (Fig. 2). The complex was collected as a purple-red solid, soluble in CH<sub>3</sub>CN, THF, and dichloromethane (DCM) but was insoluble in non-polar solvents. The physical characteristics of the  $[W(S_2C_2Ph_2)_2(CO)_2]$ were similar to those previously reported in the literature [24]. The complex was stable as a solid under refrigeration but became unstable in solution. The FTIR spectrum exhibited two CO bands at 2071 (w) and 1980  $\text{cm}^{-1}$  (s) indicating the presence two of CO [25]. The W–S vibration frequency is indicated by the peak at 670 cm<sup>-1</sup> (vs) [23]. Other features of the IR-spectrum included various signals at 2953 cm<sup>-1</sup> (C–H aromatic), 1677 cm<sup>-1</sup> (C=C aromatic) and 1155 cm<sup>-1</sup> (C–S) as shown in Fig. 3A. The CHNS elemental analysis confirmed the empirical formula of the product as  $C_{30}H_{20}O_2S_4W$  that corresponded to the desired bis(dithiolene) tungsten carbonyl complex (III) in Fig. 2.

## Molecular structure and geometry optimization

The molecular structure of  $W(S_2C_2Ph_2)_2(CO)_2$  complex was constructed by computations based on the results from the elemental and spectral analyses. The bond lengths and angles were adjusted according to references [26,27]. Construction of the complex started with fixing an octahedral geometries of tungsten metal



Fig. 2. The reaction scheme for preparation of W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub> complex.



**Fig. 3.** Comparison of FTIR experiment (A) and harmonic vibrational frequencies spectrum of: *cis*  $[W(S_2C_2Ph_2)_2(CO)_2]$  (B) and *trans*- $[W(S_2C_2Ph_2)_2(CO)_2]$ (C).

centre before adding the ligand at the appropriate positions using the Materials Studio suite of programmes. The calculation began with a geometry optimization of the complex structure using the Dmol<sup>3</sup> module. The geometrical optimization was an iterative procedure in which the coordinates of the atoms were adjusted until the energy of the structure was brought to a stationary value. The stationary value of the minimum energy was determined by analysis of the vibrational frequencies at the ground state geometry of the complex. The absence of imaginary eigenvalues confirmed the geometry's validity, from which further properties can be calculated [28]. Fig. 3 was shown a comparison of FTIR experiment and harmonic vibrational frequencies spectra of *cis* and *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$ . Although the spectra are not exactly the same, however, the important peaks appear in both spectra. A comparison between the calculated frequencies and the experimental values from the infrared spectra was used as an additional measure to confirm the molecular structure of  $[W(S_2C_2Ph_2)_2(CO)_2.$ 

The optimized structure and energy of the cis and trans  $[W(S_2C_2Ph_2)_2(CO)_2]$  calculated using BLYP, BP and PBE functions are shown in Table 1. The optimized functional energies in ascending order were BLYP, BP, and PBE, respectively. In the functional calculation, energy of optimized *cis* was larger than that of transgeometry with only slight differences in bond length and angle of similar moeities. The bond lengths (Å) and angles (°) were collected in Table 2 and a comparison to similar structure reported in the literature was also presented. All calculated bond lengths were found to be longer than the experimental data. However, the magnitudes of bond length and angle of PBE were the closest to the standard values reported by Allen et al. and Chandrasekaran et al. [24,29]. PBE functional results also depicted the greatest kinetic energy which, resulted in the shortest bond length that was in agreement with experimental data. Since geometry optimization process of  $W(S_2C_2Ph_2)_2(CO)_2$  using PBE functional was more accurate compared to BLYP and BP calculations, the structure was applied in DFT investigations and calculations.

In the optimized geometry, cis [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] has four S-atom from the chelating dithiolene bonded to tungsten metal centre and two C-atom of the CO ligands, in a distorted octahedral geometry. PBE calculations showed that S-W-S angles in two five-member (WS<sub>2</sub>C<sub>2</sub>) rings denoted by  $\angle$ S1WS2 and  $\angle$ S3WS4 were 78.847° and 78.602°, respectively. Whereas the angles of the S-W-S between two five-member (WS<sub>2</sub>C<sub>2</sub>) rings denoted by ∠S1WS3 and ∠S2WS4 were 77.070° and 138.613°, respectively, while the angle of the C–W–C was 97.797°. The calculated angles were smaller than that was reported for the X-ray single crystal structure of  $[W(S_2C_2Me_2)_2(CO)_2]$  complex denoted by  $\angle$ S1WS2,  $\angle$ S3WS4,  $\angle$ S1WS3, and  $\angle$ S2WS4 with values of 81.05°, 80.96°, 88.80° and 148.03°, respectively [24]. The differences indicated that the octahedral distortion suggested by the theoretical modeling was greater than experimental values, in which the bidentate dithiolene ligand was supposed to affect the geometry. In addition, the calculated W–S bond lengths were between 2.456 Å and 2.471 Å, which were longer by between 0.04 and 0.09 Å, respectively, compared to the X-ray structural data reported for sulfidobridged dinuclear tungsten (V) complex of dithiolene reported by Umakoshi et al. [30]. However, the calculated results were

#### Table 1

Fnergy	calculation for structural	optimization of two	isomers of W(Sat	$(CO)_{2}$ at three	different DFT f	unctional calculations
LIICI gy	calculation for structura.	optimization of two	130111013 01 00(320		unicicilit Di I I	anctional calculations.



considered to be in the normal range [26]. The two five-member  $(WS_2C_2)$  rings in the model were neither symmetrical nor planar.

In addition, the two dithiolenes bidentat ligands were twisted relative to each other and the phenyl rings attached to each C—C olefin were position away from each other. The average calculated values of C—S and C—C bond lengths in the dithiolene moieties were 1.734 Å and 1.385 Å, respectively. The considerably shorter and longer values for both C—S and C—C olefin bond lengths, respectively, are significant in the determination of the oxidation state of the complex (Fig. 4). Dithiolene ligands are known potentially to be redox active non-innocent ligands, meaning that they can exhibit a variety of redox states and that frequently show interesting optical properties [31,32]. Similarly, the calculated bond length for C—S and C—C could also be influenced by the involvement of a thienyl radical monoanion from both dithiolene ligands resulting in the tungsten centre to exhibit a W(II) oxidation state in the *cis*-[W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] molecule.

Distortion of tungsten octahedral geometry in the *trans* [W(S<sub>2</sub>-C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] was smaller than that of the *cis*geometry. Angles of  $\angle$ SWS bonds were between 92.058° and 97.056°, while the W–S bond lengths were between 2.481 and 2.524 Å. The two five-membered (WS<sub>2</sub>C<sub>2</sub>) rings conformation was planar and the two dithiolenes bidentat ligands were twisted relative to each other.

# Molecular orbital configuration

The orbital profiles for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of *cis*and *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  complexes are presented in Figs. 5 and 6, respectively. The HOMO–LUMO band gaps in both

conformations are different. The band gap is an important measure of stability [16,33] which influences the light absorption ability of a molecule. The HOMO and LUMO band gap of *cis*  $[W(S_2C_2Ph_2)_2$  (CO)<sub>2</sub>] is 0.05906 Ha (1.607 eV), while that of *trans*  $[W(S_2C_2Ph_2)_2$  (CO)<sub>2</sub>] is 0.03563 Ha (0.970 eV). These energy gaps were reflected in the light absorption characteristics of the molecules which showed the *trans* molecule absorbs light radiation in a wider range compared to the *cis* molecule (Fig. 7).

The HOMO of *cis*  $[W(S_2C_2Ph_2)_2(CO)_2]$  is located on the tungsten and sulfur atoms with some electron density in the aromatic ring, and surprisingly, no involvement was found from the CO ligands. While the LUMO was concentrated on the W, S and C—C olefin of the  $W(S_2C_2)$  ring and the carboxyl ligands. On the other hand, the *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  molecular orbital configuration was slightly different to the *cis*  $[W(S_2C_2Ph_2)_2(CO)_2]$  isomer. The HOMO of *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  is located along the  $W(S_2C_2)$  rings and W—CO bonds. The LUMO configuration of *trans* was similar to the HOMO, the electron density populates the same atoms and bonds, but the electron density population in both HOMO and LUMO were slightly different.

The molecular orbital of the HOMO - 1 in the *cis* [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub> (CO)<sub>2</sub>] complex was found to be concentrated on the W—S bonds and the CO ligands with some density in the C—C olefin and aromatic rings. In the HOMO - 2, the distribution of molecular orbital was similar to HOMO - 1, however the electron density was found to be more concentrated on W—CO bonding. In the LUMO + 1 and LUMO + 2, the electronic distributions were similar to the LUMO, which were concentrated on the W and C—O ligands with some electron density found at the S and C-olefin atoms. The HOMO - 1 and HOMO - 2 energies were -5.606 and -5.940 eV, respectively.

#### Table 2

 $Comparison \ of \ selected \ bond \ lengths \ ({\rm \AA}) \ and \ angles \ (^{\circ}) \ of \ optimized \ W(S_2C_2Ph_2)_2(CO)_2 \ geometries \ using \ three \ DFT \ functional \ calculations.$ 

Parameter	cis-[W(S <sub>2</sub> C <sub>2</sub> Ph <sub>2</sub>	$_{2})_{2}(CO)_{2}]$		X-ray ( <sup>a</sup> )	trans-[W(S <sub>2</sub> C <sub>2</sub> Ph <sub>2</sub> ) <sub>2</sub> (CO) <sub>2</sub> ]				
	BLYP	BP	PBE		BLYP	BP	PBE		
Bond length (Å)									
W(1)-S(1)	2.504	2.469	2.471	2.372	2.512	2.450	2.449		
W(1)-S(2)	2.497	2.465	2.463	2.371	2.481	2.491	2.487		
W(1)-S(3)	2.508	2.471	2.469	2.369	2.524	2.452	2.445		
W(1)-S(4)	2.495	2.465	2.456	2.365	2.482	2.475	2.474		
W(1)-C(5)	2.077	2.054	2.048	2.019	2.146	2.131	2.128		
W(1)-C(6)	2.075	2.052	2.052	2.020	2.126	2.099	2.095		
S(1) - C(1)	1.753	1.737	1.735	1.722	1.744	1.731	1.731		
S(2)-C(2)	1.754	1.737	1.734	1.720	1.748	1.735	1.734		
S(3)-C(3)	1.753	1.737	1.740	1.726	1.751	1.734	1.733		
S(4) - C(4)	1.756	1.737	1.736	1.721	1.744	1.731	1.731		
C(1)-C(2)	1.386	1.385	1.385	1.365	1.409	1.404	1.402		
C(3)-C(4)	1.385	1.385	1.386	1.361	1.408	1.402	1.400		
C(5)-O(1)	1.160	1.160	1.160	1.141	1.158	1.157	1.156		
C(6)—O(2)	1.161	1.166	1.159	1.142	1.155	1.156	1.155		
Angles (°)									
S(1) - W(1) - S(2)	78.19	78.61	78.85	81.05	79.59	78.62	78.70		
S(1) - W(1) - S(3)	139.34	138.79	138.61	88.34	87.26	124.14	126.66		
S(1) - W(1) - S(4)	137.94	138.79	138.73	148.03	166.11	154.78	152.07		
S(1) - W(1) - C(5)	77.92	78.06	77.87	129.44	92.06	93.14	94.29		
S(1) - W(1) - C(6)	75.44	75.34	75.32	76.77	88.67	85.24	84.76		
S(2) - W(1) - S(3)	138.56	138.51	138.16	141.56	161.28	153.32	151.49		
S(2) - W(1) - S(4)	77.631	77.79	77.07	88.80	112.80	76.50	73.97		
S(2) - W(1) - C(5)	103.77	104.16	104.04	133.22	97.06	95.78	94.77		
S(2) - W(1) - C(6)	140.72	141.11	141.58	79.01	82.78	85.91	86.29		
S(3) - W(1) - S(4)	78.18	78.62	78.60	80.96	79.17	79.211	78.98		
S(3) - W(1) - C(5)	75.44	75.57	75.30	133.05	96.67	96.46	95.77		
S(3)-W(1)-C(6)	77.92	77.71	77.77	78.49	83.66	82.80	83.80		
S(4) - W(1) - C(5)	140.72	141.81	140.57	129.32	92.54	93.31	93.61		
S(4) - W(1) - C(6)	103.77	103.33	104.96	77.15	86.82	89.01	87.81		
C(6)—W(1)—C(5)	98.49	98.14	97.78	84.20	179.25	177.40	178.42		

X-ray single crystal structure data of complex dithiolene-carbonyl [W(S<sub>2</sub>C<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>].

<sup>a</sup> Ref. [23].



Fig. 4. Various oxidation states of a dithiolene ligand [23].

While the LUMO + 1 and LUMO + 2 energies were -2.917 and -2.466 eV, respectively. The HOMO -1 to HOMO energy gap is about 0.201 eV, which is smaller than the energy gap between LUMO to LUMO + 1 (0.881 eV). This indicates that the *cis* [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] geometry is much easier to be oxidized rather than reduced.

The HOMO – 1 of *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  was distributed on the W—S bond, C—C olefin and aromatic rings but there was no contribution from the CO ligand. While The HOMO – 2 was distributed evenly throughout the molecule except for sulfur atoms. HOMO – 1 and HOMO – 2 energies were –5.004 and –5.409 eV, respectively. While the energy of LUMO + 1 and LUMO + 2 were –3.980 and –2.393 eV, respectively. The HOMO – 1 to HOMO energy gap was about 0.405 eV while the energy gap of LUMO to LUMO + 1 was much lower, 0.055 eV. The energy separation between HOMO – 1 to HOMO of *trans*geometry were larger compared that of LUMO to LUMO + 1. A comparison between the energy of the *cis* and the *trans*geometry suggested that the *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  molecule will be easier to be reduced than oxidized.

## Electronic spectra

## TDDFT excitation energies

Dithiolene carbonyl complexes of  $d^6$  metals are known as highly photoactive material [34]. By using the TD-DFT approach, the electronic transitions of these complexes can be evaluated. Table 3



Fig. 5. Energies and orbital structures of cis-[W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>].



Fig. 6. Energies and orbital structures of *trans*-[W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>].



Fig. 7. Calculated absorption spectra of cis-[W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] (A) and trans-[W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] (B) in vacuum.

Table 3 Summary of 12 lowest singlet TDDFT excitations energies for optical transitions of *cis*- and *trans*- [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] in vacuum.

cis	Overlap	Excitation			Oscilator	Charge	trans-	Overlap	Excitation			Oscilator	Charge
From To		eV	nm	Ha	strength	transfer	From To		eV	nm	Ha	strength	transfer
$147 \rightarrow 148$	0.75	1.97	631	0.07226	0.00773	LMCT	$147 \rightarrow 148$	0.66	1.06	1165	0.03912	0.00166	MMCT, MLCT
$146 \rightarrow 148$	0.68	2.03	610	0.07472	0.25851	LMCT, MLCT	$147 \rightarrow 149$	0.70	1.16	1071	0.04252	0.00018	MMCT, MLCT
$145 \rightarrow 148$	0.58	2.26	548	0.08317	0.01031	LMCT, MLCT	$146 \rightarrow 148$	0.70	1.57	790	0.05765	0.00599	LMCT, MLCT
$147 \rightarrow 149$	0.59	2.59	478	0.09532	0.00115	LMCT	$146 \rightarrow 149$	0.74	1.62	763	0.05971	0.00846	LMCT, MLCT
$144 \rightarrow 148$	0.43	2.63	472	0.09661	0.01239	LMCT	$145 \rightarrow 148$	0.58	1.88	659	0.06915	0.10799	LMCT, MLCT
$143 \rightarrow 149$	0.54	2.66	466	0.09771	0.00119	LMCT	$145 \rightarrow 149$	0.64	1.99	622	0.07331	0.14867	LMCT, MLCT
$142 \rightarrow 148$	0.37	2.70	458	0.09939	0.00265	LMCT	$144 \rightarrow 148$	0.58	2.26	549	0.08303	0.00384	LMCT, MLCT
$141 \rightarrow 148$	0.34	2.74	453	0.10054	0.00304	LMCT	$144 \rightarrow 149$	0.65	2.35	527	0.08644	0.00145	LMCT, MLCT
$146 \rightarrow 148$	0.70	2.82	440	0.10347	0.07225	LMCT	$143 \rightarrow 148$	0.53	2.38	520	0.08758	0.00345	LMCT, MLCT
$140 \rightarrow 148$	0.43	2.88	431	0.10581	0.09563	LMCT	$143 \rightarrow 149$	0.46	2.41	515	0.08848	0.00055	LMCT
$139 \rightarrow 148$	0.38	2.89	430	0.10602	0.00415	LMCT	$142 \rightarrow 148$	0.41	2.43	510	0.08932	0.00520	LMCT
$138 \rightarrow 148$	0.48	3.01	412	0.11072	0.02195	LMCT	$142 \rightarrow 149$	0.40	2.48	499	0.09127	0.00208	LMCT



Fig. 8. TDDFT excitations energies for optical transitions spectra of cis- [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] in benzene (A), ethanol (B), dimethylsulfoxide (C) and water (D).

collects the electronic transitions of TDDFT for 12 lowest singlet state excitation energies of the *cis* and *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  complexes in vacuum, while the spectra are shown in Fig. 7. The calculated optical transitions for the *cis* isomer showed the lowest

absorption band at 631 nm was attributed to the d-d transition from HOMO to LUMO which was allowed due to the distorted nature of the structure. Since it is symmetrically forbidden for octahedral complexes, the corresponding extinction coefficient was small. The highest oscillator strength at 610 nm corresponded to the transition of the HOMO – 1 to LUMO. There are some possibilities that other electronic transitions can occur such as a metal-to-ligand-charge transfer (MLCT) from the W to dithiol and ligand-to-metal charge transfer (LMCT). MLCT and LMCT also possible occurred at 548 nm, which is transition of HOMO – 2 to LUMO. In addition there were other intense transitions in the region of 412–478 nm, which were attributed to LMCT form the lower HOMO orbitals.

The electronic transitions of the *trans*  $[W(S_2C_2Ph_2)_2(CO)_2]$  showed HOMO to LUMO transition at 1165 nm, which is most likely due to *d*-*d* transition or MLCT. The highest oscillator strength at 622 nm was most likely originated from the HOMO – 2 to LUMO + 1 transition for the LMCT and MLCT. The lowest absorption band at 499 nm was contributed by LMCT transition from the HOMO – 4 to LUMO + 1 orbitals.

#### Solvatochromism

The calculated optical absorption spectra and solvatochromism effects study of cis [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] are shown in Fig. 8. The calculations were done in different dielectric solvents, namely: benzene (A), ethanol (B), dimethysulfoxide (C) and water (D). All optical calculations were carried out using an energy function on an optimized geometry structure of PBE. The spectrum in benzene with dielectric constant K = 2.284, was similar to the spectrum in vacuum (Fig. 7A). There were two major absorption bands in the visible region with the highest oscillator strength maximizes at around 440 and 620 nm, which were more likely belong to charge transfer bands. The spectrum in benzene was red-shifted about 10 nm compared the spectrum in vacuum. The similar spectrum pattern was also observed in ethanol (K = 24.3) and other similar solvents. The spectra for these solvents were slightly red-shifted in solvents with increasing of dielectric constants. A slightly different spectrum pattern was found for dimethysulfoxide (K = 46.7), in which a new peak appeared at around 420 nm, while others peaks will remain the same with a shift to a much lower energy (redshifted). The spectrum pattern in DMSO and water with dielectric constant *K* = 78.54 were very similar and the whole spectra were slightly red-shifted ( $\Delta = 10 \text{ nm}$ ).

The pattern of the simulated spectra in all solvent calculation were relative similar with some changes in the peaks position and appearance of new peak for high dielectric constant solvents. However, the oscillator strength of each peak in all solvents was not much different. This study has shown that the solvent affects the optical properties of the  $[W(S_2C_2Ph_2)_2(CO)_2]$  complex.

#### Conclusion

The investigation of dithiolene tungsten carbonyl complex by density functional theory study has successfully developed the molecular structure and probe the electronic energy states for both *cis* and *trans* [W(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] complex isomers. The HOMO and LUMO and the electronic transitions in both isomers have been determined. The CO ligand contribute more to the electronic properties of *trans*isomer compared to the *cis*isomer. The study

showed that the *trans* molecule absorbs light radiation in a wider range compared to the *cis* molecule. In addition the electronic absorption spectra of the complexes were affected the choice of the solvents.

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