Influencing Mechanism of Carbonyl and Thiophene on Cranial Nerve Based on Their Bridging and Steric Hindrance Effects on Titanium Coordination Compound

Zhiping Deng\textsuperscript{1,2+}, Yuan Li\textsuperscript{3}

ABSTRACT
This paper aims to disclose the damage or repair mechanism of carbonylation and thiophene on cranial nerves. To this end, the bonding pattern of binuclear titanium carbonyls with thiophene was investigated by two methods of density functional theory (DFT), namely, the B3LYP method and the BP86 method. Then, 8 stable isomer structures were found for binuclear titanium carbonyls with thiophene, including 5 doublet structures and 3 triplet structures. These structures were discussed in details and the energy needed to dissociate each of them into mononuclear fragments was calculated through the thermochemistry analysis. The results show that the Ti\textsubscript{2}(C\textsubscript{4}H\textsubscript{3}S)\textsubscript{m}(CO)\textsubscript{n} structures are linked by 2.8~3.6 Å-long Ti-Ti bonds. The bonds are relatively long and considered as formal single bonds. Every structure of the binuclear titanium carbonyls with thiophene is bridged by CO group or C\textsubscript{4}H\textsubscript{3}S group and sometimes dibridged by both the CO group and C\textsubscript{4}H\textsubscript{3}S group. The energy to dissociate Ti\textsubscript{2}(C\textsubscript{4}H\textsubscript{3}S)\textsubscript{2}(CO)\textsubscript{6} into Ti(C\textsubscript{4}H\textsubscript{3}S)(CO)\textsubscript{2} and Ti(CO)\textsubscript{4} fragments is 71.4kcal/mol (B3LYP)/89.6kcal/mol (BP86), higher than that to dissociate the other Ti\textsubscript{2}(C\textsubscript{4}H\textsubscript{3}S)\textsubscript{m}(CO)\textsubscript{n} structures into Ti(C\textsubscript{4}H\textsubscript{3}S)(CO)\textsubscript{2} fragments. The electron structure of the Ti atom in Ti\textsubscript{2}(C\textsubscript{4}H\textsubscript{3}S)\textsubscript{2}(CO)\textsubscript{6} is 17-electron structure, the nearest to the 18-electron structure. The research findings provide important insights into the influencing mechanism of carbonyl and thiophene on caranial nerve.

Key Words: Cranial Nerve, Binuclear Titanium Carbonyls, Thiophene, Bonding Pattern

DOI Number: 10.14704/nq.2018.16.5.1248

Introduction
Protein carbonylation is an irreversible process that induces the loss of protein function and variation in protein hydrolysis. During protein carbonylation lipid metabolism and oxidative stress to the covalent modification spectrum. Among them, the oxidative stress is a primary cause of secondary injuries after traumatic brain injury (TBI). The TBI, as a brain tissue lesion caused by trauma, many result in many pathological changes. One of the typical changes is axonal injury, a major factor in the prognosis and recovery of neurologic function after TBI.

In previous studies, protein carbonylation is often adopted as an indicator of the oxidative damage in proteins. However, it is still unclear if protein carbonylation is indeed related to the damage to the TBI axonal cord. Some scholars argued that the degree of brain injury and the oxidative stress is positively correlated with the post-TBI brain tissue and the carbonylation of cytoskeletal proteins (Di et al., 2009; Farias et al., 2009; Bizzozero et al., 2006; Feigin et al., 2010;...
The carbonylation of cytoskeletal proteins may cause the transport of neuraxons, which, in turn, induces neuroaxonal damages and worsens secondary brain injuries (Giza et al., 2009). In other words, the carbonylation of cytoskeletal proteins may cause the transport of neuraxons, which, in turn, induces neuroaxonal damages and worsens secondary brain injuries (Giza et al., 2009). In other words, the carbonylation of cytoskeletal proteins may cause the transport of neuraxons, which, in turn, induces neuroaxonal damages and worsens secondary brain injuries (Giza et al., 2009). In other words, the carbonylation of cytoskeletal proteins may cause the transport of neuraxons, which, in turn, induces neuroaxonal damages and worsens secondary brain injuries (Giza et al., 2009).

The neuroaxonal damages, especially synaptic plasticity, can be treated by Thienorphine, an opioid analgesic with mixed agonist-antagonist properties. The Thienorphine is created by a thiophene substitution. The bridging effect or steric hindrance of the carbonyls and thiophene in molecule is a mirror of how proteins are carbonylated and how neuroaxonal damages are treated by Thienorphine. To identify the damage or repair mechanism of carbonylation and thiophene on cranial nerves, it is necessary to explore the structures and energetics of the coordination compound of carbonyls with thiophene.

Much theoretical research has been done on the structure and features of the said coordination compound (Zhou et al., 2001; Zhang et al., 2010; Wang et al., 2006). Based on the density functional theory (DFT), Ou Z. et al., (2015) investigated the structures and energetics of binuclear titanium carbonyls with different number of carbonyls. The relevant research has been focused on the magnetic materials. These transition metal carbonyls are either mononuclear or binuclear/multinuclear. For mononuclear ones, the typical examples include Cu(II), Ni(II), Co(II) and Mn(II) with heterocyclic compounds (Martua et al., 1999; Romero et al., 2000); for binuclear/multinuclear ones, the typical examples include [CuCl₃(NITP-Py)₂]**, [Cu(hfac)₂]**(NITPhOme)**; trinuclear compound with bridge μ-1,3 for free radical (jiang et al., 1995), Ni(II), Co(II) and Mn(II) with heterocyclic compounds (Caneschi et al., 1996; Fish et al., 1988). As a heterocyclic compound, thiophene (thiophene-2, 5-d2) has a domain π bond formed through the conjugation of two pairs of lone electrons in atom S with two double bonds. Currently, there is no report on the theoretical or experimental analysis of the transition metal carbonyls with thiophene. To make up for the gap, this paper attempts to explore the stable isomer structures of binuclear titanium carbonyls with thiophene based on the previous research findings, and probes deep into the bonding pattern inside the binuclear and between transition metal Ti and free radical of thiophene. Below is a brief review of the methods adopted in this paper.

Two DFT methods (Ndambuki and Ziegler, 2013; Davis et al., 2012) were employed to calculate the structures of the stable isomers: the B3LYP method (Becke, 1993; Lee et al., 1998) and the BP86 method (Becke, 1998; Perdew, 1986). The double-zeta polarized (DZP) basis set of C and O atoms, denoted as (9s5p1d/4s2p1d), begins with Dunning's standard double-σ contraction (Dunning, 1970) of Huzinaga's primitive sets (Huzinaga, 1965), and adds a set of pure spherical harmonic d polarization functions with orbital exponents α₅(C) = 0.75 and α₅(O) = 0.85. The loosely contracted DZP basis set for Ti, denoted as (14s11p6d/10s8p3d), is the Wachters primitive set (Wachters, 1970) augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer and Schaefer (Hood et al., 1979). All structures were subject to the geometric optimization using the two DFT methods separately, and the configuration of electron (Pyykkö, 2006) was discussed in details.

**Calculation Results**

**Structures**

In total, 8 stable isomer structures were found for binuclear titanium carbonyls with thiophene.
Lung epithelial cells, including 5 doublet structures and 3 triplet structures. Each structure contains 8 thiophene groups and carbonyls. The upper and lower Ti-Ti distances were determined by B3LYP and BP86, respectively. The optimized structures are illustrated in Figure 1, while the total Hartree energy (E) and Ti-Ti distance (Å) of each structure are listed in Table 1.
Depending on the number of CO groups (the first number of each structure name), the structures are either singlet or doublet. If the number is an odd number, the structure has a doublet spin state; if the number of an even number, the structure has a singlet spin state. The eight structures are ranked as $E(1D-1) < E(2S-1) < E(3D-1) < E(4S-1) < E(5D-2) < E(5D-1) < E(6S-1) < E(7D-1)$ in ascending order of the total energy. The energetic relationships among them were determined by both B3LYP and BP86.

(a) 1D-1(Ci)

As shown in Figure 1(a), the minimum structure for doublet Ti$_2$(C$_4$H$_6$S)$_n$(CO)$_n$ is an asymmetric C1 structure with a real mono-bridging C$_4$H$_6$S group and a similar di-bridging C$_4$H$_6$S group: (C$_4$H$_6$S)$_n$(CO)$_2$Ti(μ-C$_4$H$_6$S) (μ-C$_4$H$_6$S)Ti(C$_4$H$_6$S)$_n$. The structure, denoted as 1D-1, is predicted to have all real harmonic vibrational frequencies by both B3LYP and BP86. The Ti-Ti distance is 3.2332 Å (B3LYP)/3.1880 Å (BP86), indicating a relatively weak bond, possibly a Ti-Ti single bond. The real mono-bridging C$_4$H$_6$S group can donate an electron pair to the other Ti atom through a π-interaction from the thiophene ring. If the di-bridging C$_4$H$_6$S group is a four electrons pair donor, the Ti atom with carbonyl can form a 17-electron structure while the other Ti atom can form a 13-electron structure. If the di-bridging C$_4$H$_6$S group is a two electrons pair donor, the Ti atom with carbonyl can form a 16-electron structure while the other Ti atom can form a 12-electron structure.

In the real mono-bridging C$_4$H$_6$S group, the shorter bridging Ti-C distance is 2.235 Å (B3LYP)/2.192 Å (BP86), while the longer one is 2.243 Å (B3LYP)/2.215 Å (BP86). In the di-bridging C$_4$H$_6$S group, the shorter distance is 2.127 Å (B3LYP)/2.100 Å (BP86), while the longer one is 2.574 Å (B3LYP)/2.555 Å (BP86).

For the terminal carbonyl in the 1D-1 structure, the Ti-C distance is 2.266 Å (B3LYP)/2.168 Å (BP86), and the C-O distance is 1.146 Å (B3LYP)/1.166 Å (BP86). For the terminal C$_4$H$_6$S groups, the Ti-C distance falls in the range of 2.084~2.139 Å.
(B3LYP)/2.078~2.145 Å (BP86). This distance is shorter for the Ti atom with a 13- or 12-electron structure (2.084~2.139 Å (B3LYP)/2.078~2.145 Å (BP86)) than for the other Ti atom (2.122~2.139 Å (B3LYP)/2.126~2.145 Å (BP86)).

For the terminal carbonyl group in the 1D-1 structure, the Ti-C-O angles are below 172° (B3LYP)/174° (BP86), a signal of insignificant linearity. This is attributable to the interaction of the bridging C\(^4\)H\(^3\)S group interaction and steric effect of the terminal C\(^4\)H\(^3\)S groups.

(b) 2S-1(C\(_4\))

The second isomer structure of binuclear titanium carbonyls with thiophene contains six C\(^4\)H\(^3\)S groups and two CO groups. As shown in Figure 1(b), the minimum structure for Ti\(_2\)(C\(^4\)H\(^3\)S)\(^4\)(CO)\(_2\) with similar di-bridging C\(^4\)H\(^3\)S groups: (C\(^4\)H\(^3\)S)\(_2\)Ti (q-C\(^4\)H\(^3\)S)\(_2\)Ti(C\(^4\)H\(^3\)S)\(_4\)(CO)\(_2\). The structure, denoted as 2S-1, is predicted to have all real harmonic vibrational frequencies by both B3LYP and BP86. The Ti-Ti distance is 3.1268 Å (B3LYP)/3.1602 Å (BP86), slightly shorter than that of ID-1. The distance also indicates a relatively weak bond, possibly a Ti-Ti single bond.

If each similar di-bridging C\(^4\)H\(^3\)S group is a four electrons pair donor, the Ti atom with carbonyl can form a 17-electron structure while the other Ti atom can form a 13-electron structure. If each similar di-bridging C\(^4\)H\(^3\)S group is a two electrons pair donor, the Ti atom with two carbonyls can form a 15-electron structure while the other Ti atom can form a 13-electron structure.

In each of the two groups, the shorter bridging Ti-C distance is 2.056 Å (B3LYP)/2.053 Å (BP86), while the longer one is 2.559 Å (B3LYP)/2.535 Å (BP86). For the terminal carbonyl group in the 2S-1 structure, the Ti-C distance is 2.088~2.100 Å (B3LYP)/2.056~2.059 Å (BP86), and the C-O distance is 1.153~1.155 Å (B3LYP)/1.171~1.172 Å (BP86).

For the terminal C\(^4\)H\(^3\)S groups, the Ti-C distance falls in the range of 2.070~2.176 Å (B3LYP)/2.071~2.152 Å (BP86). This distance is shorter for the Ti atom with a 13- or 11-electron structure (2.070~2.077 Å (B3LYP)/2.071~2.081 Å (BP86)) than for the other Ti atom (2.166~2.176 Å (B3LYP)/2.151~2.152 Å (BP86)).

For the terminal carbonyl group in the 2S-1 structure, the Ti-C-O angles are greater than 179° (B3LYP)/178° (BP86), an evidence of significant linearity.

(c) 3D-1(C\(_4\))

As shown in Figure 1(c), the minimum structure for Ti\(_2\)(C\(^4\)H\(^3\)S)\(_4\)(CO)\(_2\) is also an asymmetric C\(_1\) structure 3D-1 with a real mono-bridging C\(^4\)H\(^3\)S group and two similar di-bridging C\(^4\)H\(^3\)S groups. The structure is predicted to have all real harmonic vibrational frequencies by both B3LYP and BP86. The Ti-Ti distance is 3.1661 Å (B3LYP)/3.0774 Å (BP86), indicating a relatively weak bond, possibly a Ti-Ti single bond.

The real mono-bridging C\(^4\)H\(^3\)S group can donate an electron pair to the other Ti atom through a π-interaction from the thiophene ring. If each di-bridging C\(^4\)H\(^3\)S group is a four electrons pair donor, the Ti atom with two carbonyls can form a 15-electron structure while the other Ti atom can form a 17-electron structure. If each di-bridging C\(^4\)H\(^3\)S group is a two electrons pair donor, the Ti atom with two carbonyls can form a 13-electron structure while the other Ti atom can form a 15-electron structure.

In the real mono-bridging C\(^4\)H\(^3\)S group, the shorter bridging Ti-C distance is 2.183 Å (B3LYP)/2.149 Å (BP86), while the longer one is 2.304 Å (B3LYP)/2.261 Å (BP86). In the di-bridging C\(^4\)H\(^3\)S groups, the shorter distance is 2.817 Å (B3LYP)/2.818 Å (BP86), while the longer one is 2.886 Å (B3LYP)/2.827 Å (BP86).

For the terminal carbonyl group in the 3D-1 structure, the Ti-C distance is 2.101 Å (B3LYP)/2.068 Å (BP86), and the C-O distance is 1.157 Å (B3LYP)/1.174 Å (BP86). For the terminal C\(^4\)H\(^3\)S groups, the Ti - C distance falls in the range of 2.093~2.107 Å (B3LYP)/2.073~2.110 Å (BP86). This distance is shorter for the Ti atom with one carbonyl (2.093~2.099 Å (B3LYP)/2.073~2.083 Å (BP86)) than for the other Ti atom (2.101-2.107 Å (B3LYP)/2.103-2.110 Å (BP86)).

For the terminal carbonyl group in the 3D-1 structure, the Ti-C-O angles are over 176° (B3LYP)/174° (BP86), an indicator of significant linearity. For the bridging carbonyl groups, these angles are below 166° (B3LYP/BP86). The significant deviation from linearity is consistent with the proposed electron donation from a C-O π-bond to the more remote Ti atom.
(d) 4S-1(C₁)
As shown in Figure 1(d), the minimum structure for singlet bimetallic titanium carbonyls with thiophene is still an asymmetric C1 structure with a real mono-bridging C₄H₅S group and a di-bridging C₄H₅S₂ group: (C₄H₅S)₂(CO)₂Ti(η²-µ-C₄H₅S)₃(η²-µ-CO)₂Ti(C₄H₅S)₂. The structure, denoted as 4S-1, is predicted to have all real harmonic vibrational frequencies by both B3LYP and BP86. Its energy is 2.064 Å (B3LYP)/2.148 Å (BP86), indicating a relatively weak bond, possibly a Ti-Ti single bond.

Both the real mono-bridging C₄H₅S group and the di-bridging C₄H₅S₂ group can donate an electron pair to the other Ti atom through a π-interaction. The difference is the electron pair is from the thiophene ring in the real mono-bridging C₄H₅S group and from the C=O multiple bond in the di-bridging C₄H₅S₂ group. Since the two bridging groups come from same Ti atom, the Ti atom with three carbonyls can form a 17-electron structure while the other Ti atom can form a 13-electron structure.

In the real mono-bridging C₄H₅S group, the shorter bridging Ti-C distance is 2.026 Å (B3LYP)/2.148 Å (BP86), while the longer one is 2.406 Å (B3LYP)/2.281 Å (BP86). In the di-bridging C₄H₅S₂ group, the shorter distance is 2.021 Å (B3LYP)/1.981 Å (BP86), while the longer one is 2.170 Å (B3LYP)/2.183 Å (BP86).

For the terminal carbonyl groups in the 4S-1 structure, the Ti-C distance falls in the range of 2.131~2.190 Å (B3LYP)/2.074~2.185 Å (BP86), and the C-O distance falls in the range of 1.147~1.162 Å (B3LYP)/1.164~1.171 Å (BP86).

For the terminal C₄H₅S₂ groups, the Ti-C distance falls in the range of 2.061~2.131 Å (B3LYP)/2.067~2.155 Å (BP86). This distance is shorter for the Ti atom with one carbonyl (2.061~2.074 Å (B3LYP)/2.067~2.072 Å (BP86)) than for the other Ti atom (2.131 Å (B3LYP)/2.155 Å (BP86)).

For the terminal carbonyl group in the 4S-1 structure, the Ti-C-O angles are above 174° (B3LYP)/176° (BP86), a symbol of significant linearity. By contrast, the Ti-C-O angles of the bridging carbonyl group are below 174° (B3LYP/BP86), which also shows an obvious linearity.

(e) 5D-1(C₁)
As shown in Figure 1(e), the minimum structure for doublet Ti₂(C₄H₅S)₃(CO)₃ is an asymmetric C1 structure with a real mono-bridging CO group and a di-bridging CO group: [(C₄H₅S)₃(CO)]₂(Ti(η²-µ-CO)₂Ti(C₄H₅S)₃(CO)). The structure, denoted as 5D-1, is predicted to have all real harmonic vibrational frequencies by both B3LYP and BP86. The Ti-Ti distance is 3.1294 Å (B3LYP)/3.0904 Å (BP86), indicating a relatively weak bond, possibly a Ti-Ti single bond.

Each of the bridging CO group can donate an electron pair to the terminal Ti atom through a π-interaction from the C=O multiple bond. Thus, each group acts as a donor of 4 electrons. In this case, each Ti atom can form a 15-electron structure.

In the two groups, the shorter bridging Ti-C distance is 2.056 Å (B3LYP)/2.026 Å (BP86) and 2.164 Å (B3LYP)/2.151 Å (BP86), respectively, and the longer one is 2.096 Å (B3LYP)/2.098 Å (BP86) and 2.463 Å (B3LYP)/2.411 Å (BP86), respectively: the C-O distance is 1.244 Å (B3LYP)/1.256 Å (BP86) and 1.170 Å (B3LYP)/1.187 Å (BP86), respectively.

For the terminal carbonyls, the Ti-C distance falls in the range of 2.056~2.221 Å (B3LYP)/2.026~2.148 Å (BP86), and the C-O distance falls in the range of 1.142~1.159 Å (B3LYP)/1.160~1.176 Å (BP86).

The Ti-C-O angles for the two bridging carbonyl groups are below 173°(B3LYP/BP86), while that for the other 8 terminal carbonyls are all above 176° (B3LYP/BP86). The significant linearity is resulted from the interaction of the bridging carbonyls.

(f) 5D-2(C₁)
As shown in Figure 1(f), the second stationary point of Ti₂(C₄H₅S)₃(CO)₃ is an asymmetric C1 bridging structure. The structure, denoted as 5D-2, is predicted to have all real harmonic vibrational frequencies by both B3LYP and BP86. Its energy is slightly lower than that of 5D-1 (B3LYP/BP86). The Ti-Ti distance is 2.9231 Å (B3LYP)/2.9307 Å (BP86). The relatively short distance suggests a relatively weak bond, possibly a Ti-Ti single bond.

Each bridging CO group can donate 4 electrons: an electron pair to one Ti atom through a Ti-C σ-bond, and another pair to the other Ti atom through a π-interaction from the C=O multiple bond. Thus, these groups are similar to the unique bridging CO group in [μ-CH₂(PPh₂)]₂Mn₄(CO)₄(η-µ-CO). The real monobridging C₄H₅S group can donate an electron pair to the other Ti atom through a π-interaction from
the thiophene ring. Thus, the Ti atom with four terminal CO groups can form a 17-electron structure and the other Ti atom can form a 13-electron structure.

In the mono-bridging C₄H₃S group, the shorter bridging Ti-C distance is 2.144 Å (B3LYP)/2.206 Å (BP86), while the longer one is 2.450 Å (B3LYP)/2.271 Å (BP86). In the di-bridging carbonyl group, the shorter distance is 1.981 Å (B3LYP)/1.977 Å (BP86), while the longer one is 2.234 Å (B3LYP)/2.251 Å (BP86).

For the terminal carbonyls in the 5D-2 structure, the Ti-C distance falls in the range of 2.067~2.146 Å (B3LYP)/2.043~2.122 Å (BP86), and the C-O distance falls in the range of 2.208 Å (B3LYP)/2.184 Å (BP86). In the di-bridging carbonyl group, the shorter distance is 2.067 Å (B3LYP)/2.077 Å (BP86), while the longer one is 2.712 Å (B3LYP)/2.617 Å (BP86).

In the di-bridging carbonyls, the shorter bridging Ti-C distance is 2.170 Å (B3LYP)/2.174 Å (BP86), while the longer one is 2.208 Å (B3LYP)/2.184 Å (BP86). In the similar di-bridging carbonyl group, the shorter distance is 2.067 Å (B3LYP)/2.077 Å (BP86), while the longer one is 2.712 Å (B3LYP)/2.617 Å (BP86).

For the terminal carbonyl group in the 6S-1 structure, the Ti-C distance falls in the range of 2.068~2.146 Å (B3LYP)/2.047~2.125 Å (BP86), and the C-O distance falls in the range of 1.152~1.161 Å (B3LYP)/1.168~1.177 Å (BP86).

For the terminal carbonyl group in the 6D-2 structure, the Ti-C-O angles are above 175° (B3LYP)/174° (BP86), exhibiting a significant linearity. The Ti-C-O angles for the bridging carbonyl group are below 168° (B3LYP)/BP86).

(g) 6S-1(C₄)
As shown in Figure 1(g), the C1 structure, denoted as 6S-1, is a tri-bridging structure, involving a real mono-bridging C₄H₃S group, a similar di-bridging carbonyl and a di-bridging C₄H₃S group. The Ti-Ti distance is 2.9038 Å (B3LYP)/2.8640 Å (BP86). The distance is similar to the distance of 5D-2, and reflects the possibility of a Ti-Ti single bond.

The real mono-bridging C₄H₃S group and the di-bridging C₄H₃S group can donate an electron pair to the other Ti atom through a π-interaction from the thiophene ring. If the di-bridging carbonyl group is a four electrons pair donor, each Ti atom can form a 17-electron structure; if it is a two electrons pair donor, the Ti atom with two carbonyls can form a 15-electron structure while the other Ti atom can form a 13-electron structure.

In the mono-bridging C₄H₃S group, the shorter bridging Ti-C distance is 2.198 Å (B3LYP)/2.198 Å (BP86), while the longer one is 2.208 Å (B3LYP)/2.184 Å (BP86). In the di-bridging C₄H₃S group, the shorter distance is 2.170 Å (B3LYP)/2.174 Å (BP86), while the longer one is 2.208 Å (B3LYP)/2.184 Å (BP86). In the similar di-bridging carbonyl group, the shorter distance is 2.067 Å (B3LYP)/2.077 Å (BP86), while the longer one is 2.712 Å (B3LYP)/2.617 Å (BP86).

Thermochemistry
Table 2 lists the energies of mononuclear fragments after the dissociation of Ti₂(C₄H₃S)₉(CO)₉. Table 3 presents the predicted dissociation energies for the reactions: Ti₂(C₄H₃S)ₙ(CO)ₙ→Ti(C₄H₃S)(CO)₉+Ti(C₄H₃S)ₙ(CO)ₙ (m+n=8, i+j=4, k+l=4). The results were analysed to find singlet and doublet structures of the lowest energy of Ti(C₄H₃S)(CO)₉ (i+j=4,
i=1,2,3,4, j=1,2,3,4). For this purpose, the minimum values of Ti(C₄H₃S)[(CO)] were optimized by the two DFT methods.

The disproportionation reaction Ti₂(C₄H₃S)[(CO)] → Ti(C₄H₃S)₄ + Ti(C₄H₃S)₃(CO) is exothermic by B3LYP (-7.8 kcal/mol) and endothermic by BP86 (3.9 kcal/mol). The dissociation energy for structure Ti₂(C₄H₃S)[(CO)] is near zero, indicating that the structure Ti₂(C₄H₃S)[(CO)] is too unstable to withstand automatic dissociation.

**Table 2.** Total hartree energies (E) for the mononuclear structures with four CO groups or C₄H₃S groups

<table>
<thead>
<tr>
<th>Structure</th>
<th>E  (B3LYP)</th>
<th>E  (BP86)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(C₄H₃S)₄</td>
<td>-3059.18307</td>
<td>-2620.09343</td>
</tr>
<tr>
<td>Ti(C₄H₃S)₃(CO)</td>
<td>-2180.99308</td>
<td>-1741.93813</td>
</tr>
<tr>
<td>Ti(C₄H₃S)₂(CO)</td>
<td>-1302.99861</td>
<td>-1302.86265</td>
</tr>
</tbody>
</table>

**Table 3.** Predicted energies (kcal/mol) that the dissociation of CO group releases into mononuclear fragments of the Ti₂(C₄H₃S)₄[(CO)]₃ structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>B3LYP</th>
<th>BP86</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (1D-1) → Ti(C₄H₃S)₄ + Ti(C₄H₃S)₃(CO)</td>
<td>-7.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (2S-1) → Ti(C₄H₃S)₄ + Ti(C₄H₃S)₃(CO)</td>
<td>29.9</td>
<td>40.4</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (3D-1) → Ti(C₄H₃S)₃[(CO)] + Ti(C₄H₃S)₂(CO)₂</td>
<td>32.3</td>
<td>43.7</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (4S-1) → Ti(C₄H₃S)₃[(CO)] + Ti(C₄H₃S)₂(CO)₃</td>
<td>28.2</td>
<td>46.5</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (5D-1) → Ti(C₄H₃S)₃[(CO)] + Ti(C₄H₃S)₂(CO)₃</td>
<td>53.2</td>
<td>65.6</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (5D-2) → Ti(C₄H₃S)₃[(CO)] + Ti(C₄CO)₄</td>
<td>55.0</td>
<td>65.3</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (6S-1) → Ti(C₄H₃S)₃[(CO)] + Ti(CO)₄</td>
<td>71.4</td>
<td>89.6</td>
</tr>
<tr>
<td>Ti₂(C₄H₃S)₄[(CO)] (7D-1) → Ti(C₄H₃S)₂[(CO)] + Ti(CO)₄</td>
<td>60.3</td>
<td>71.4</td>
</tr>
</tbody>
</table>
The disproportionation reaction of $\text{Ti}_2(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_2$ is endothermic by both B3LYP and BP86. The amount of absorbed heat stands at 29.9 kcal/mol (B3LYP) and 40.4 kcal/mol (BP86). The disproportionation reaction of $\text{Ti}_2(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_3$ is also endothermic by both B3LYP and BP86. The amount of absorbed heat stands at 29.9 kcal/mol (B3LYP) and 40.4 kcal/mol (BP86). Except that of $\text{Ti}_2(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_3$, the disproportionation reactions of $\text{Ti}_2(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_m(\text{CO})_n(\text{CO})_k$ (where $m+n=8$, $i+j=4$, $k+l=4$) are all endothermic by both B3LYP and BP86. The energy to dissociate $\text{Ti}_2(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_3$ into $\text{Ti}(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_i+\text{Ti}(\text{C}_3\text{H}_5\text{S})_3(\text{CO})_j$ is 17-electron structure, the nearest to the 18-electron structure.

### Acknowledgements

This research is funded by the Chinese Natural Science Foundation Project of CQ CSTC (cstc2014jcyjA50026) and the Graduate Student Innovation Fund of Chongqing (CYB16127) for support of this research.

### References


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