

Calculation Research of the Titanium Carbonyls with Thiophene on Structures and Thermochemistry

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The structures and energetics of the mononuclear titanium carbonyls $Ti(C_4H_3S)_i(CO)_j$, ($i+j=4$, $i=1,2,3,4$, $j=1,2,3,4$) and binuclear titanium carbonyls with thiophene $Ti_2(C_4H_3S)_m(CO)_n$ ($m=1, 2, 3, 4$; $n=1, 2, 3, 4$; $m+n=8$) have been investigated using density functional theory. Every structure of the binuclear titanium carbonyls with thiophene is bridged by CO group or C_4H_3S group and sometimes dibridged by both CO group and C_4H_3S group. The energy required for the dissociation of $Ti_2(C_4H_3S)_2(CO)_6$ into $Ti(C_4H_3S)_2(CO)_2$ and $Ti(CO)_4$ fragments is 71.4 kcal/mol by the B3LYP method and 89.6 kcal/mol by the BP86 method respectively, which is higher than the energy for the dissociation of other $Ti_2(C_4H_3S)_m(CO)_n$ structure into $Ti(C_4H_3S)_i(CO)_j$ fragments. All the binuclear titanium carbonyls with thiophene are unsaturated system and the electron configuration of the titanium atom of $Ti_2(C_4H_3S)_2(CO)_6$ is 17-electron configuration, which is nearest to the 18-electron configuration.

1. Introduction

Transition metal carbonyls, especially with transition metal atom Ti, are very important organic metal compound. Plenty of studies have been established on their structures and characters with theoretical method (Zhou et al., 2001; Zhang et al., 2010; Wang et al., 2006). Ou et al. (2015) have studied the structures and energetics of binuclear titanium carbonyls with different number of carbonyls, symmetries and different electronic state of isomer using density functional theory, and especially discussed the bonds between two Ti atoms through structure optimization, frequency calculation and spectrum analysis. Theoretical and experimental studies on transition metal carbonyls with heterocyclic compounds have been mainly focused on magnetic materials areas for present time. Since the first nitrogen oxygen free radicals-transition metal complexes $[Mn(hfac)_2-NITR]$ has been reported in mid-Eighties of twentieth century, either theoretical model or structure and property of the transition metal carbonyls with heterocyclic compounds have developed rapidly. As for the mononuclear transition metal carbonyls with heterocyclic compounds, Cu(\square), Ni(\square), Co(\square) and Mn(\square) with heterocyclic compounds have been mostly reported (Martua et al., 1999; Romero et al., 2000). For binuclear or multinuclear transition metal carbonyls with heterocyclic compounds, Caneschi et al., (1990) have reported $[CuCl_2(NITP-Py)_2]_2$ binuclear compound in 1990. Jiang et al., reported $[Cu(hfac)_2]_3(NITPhOMe)_2$ trinuclear compound with bridge $\mu-1,3$ for free radical in 1995, and after that similar transition metal carbonyls have been widely reported (Caneschi et al., 1996; Fish et al., 1988) such as multinuclear transition metal carbonyls with heterocyclic compounds Ni(\square), Co(\square) and Mn(\square). have conducted the design and synthesis of six new kind of transition metal carbonyls with heterocyclic compounds $[Mn(hfac)_2(IMHBithph)]_2$ (NIT2-bithph)(C_6H_{14}), $[Cu(hfac)_2]_3(NIT2-thph)_2$, $[Co(hfac)_2(NIT2-thph)_2]$, $[Ni(hfac)_2(NIT2-thph)_2]$, $[Mn(hfac)_2(NIT2-thph)_2]$ and $[Ni(hfac)_2(EtOH)_2] \cdot NIT2-thph$ with thiophene radical and nitrogen oxygen free radicals in 2007, and crystal structures of these compounds have been analyzed.

Thiophene (thiophene-2, 5-d2) is a kind of heterocyclic compound from the perspective of structural style, in which the two pair lone electrons of atom S conjugate with two double bonds and form the domain π bond. So far, there is no relevant experimental and theoretical report on the transition metal carbonyls with thiophene. This paper mainly studies the stable structures of the isomers of binuclear titanium carbonyls with thiophene

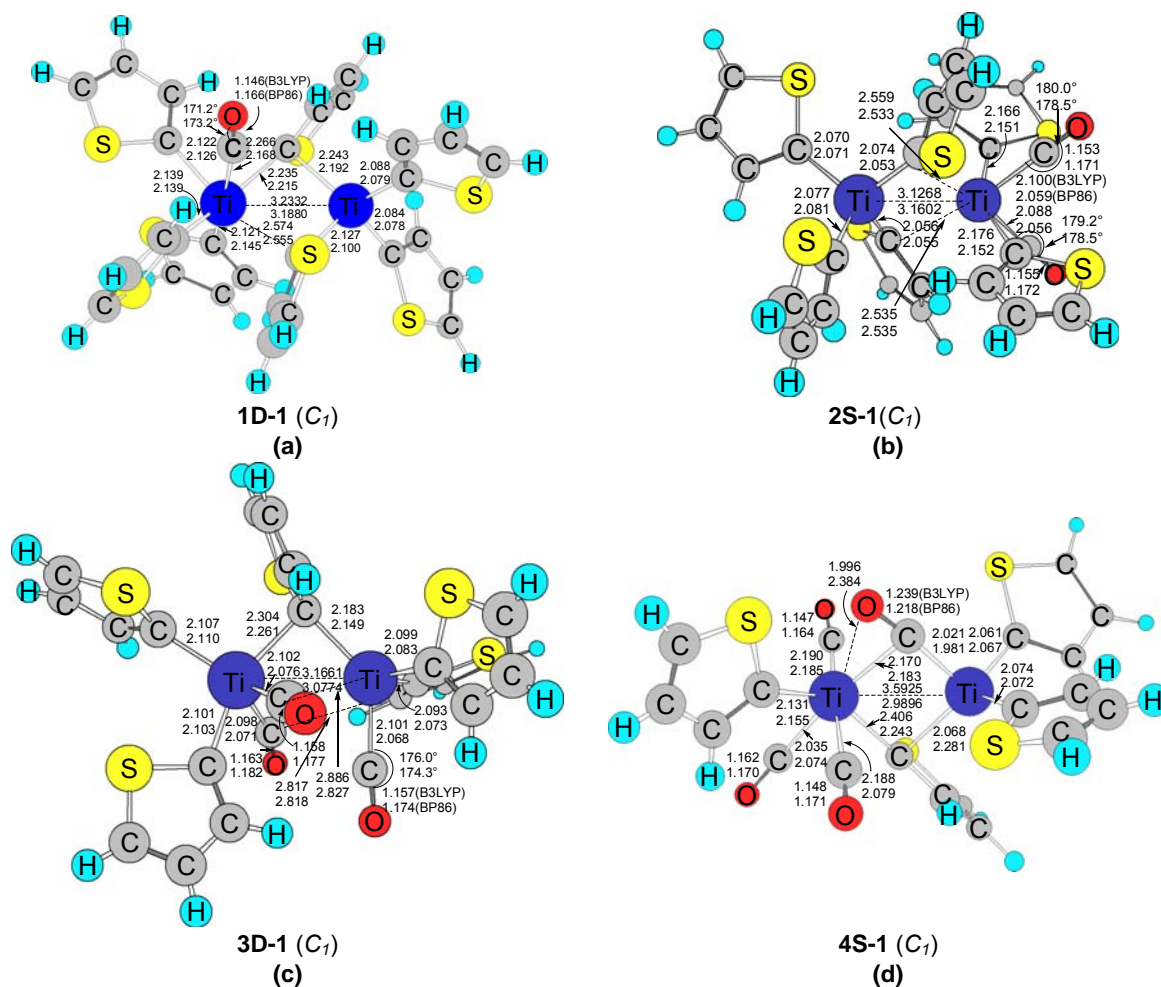
based on the previous research on binuclear titanium carbonyls. The bonding regularity inner the binuclear and between transition metal Ti and free radical of thiophene are especially studied.

To conduct this research, the density functional theory (DFT) (Ndambuki and Ziegler, 2013; Davis et al., 2012) was used to calculate the structures of these isomers of binuclear titanium carbonyls with thiophene. Two different density functional theory (DFT) methods were used in this paper. One of them is the B3LYP method (Becke, 1993; Lee et al., 1998), and another one is the BP86 method (Becke, 1998; Perdew, 1986). The DZP basis set for C and O atoms begins with Dunning's standard double-contraction (Dunning, 1970) of Huzinaga's primitive sets (Huzinaga, 1965) and adds a set of pure spherical harmonic d polarization functions with orbital exponents $\alpha_d(\text{C})=0.75$ and $\alpha_d(\text{O})=0.85$, designated as (9s5p1d/4s2p1d). The loosely contracted DZP basis set for titanium 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) designated as (14s11p6d/10s8p3d). The geometries of all structures were fully optimized using the two DFT methods independently and the electron configuration (Pyykkö, 2006) was discussed.

2. Calculation results

2.1 Structures

A total of 8 stable structures of the binuclear titanium carbonyls with thiophene were found, and these stable structures are baptized five doublet structures and three triplet structures. For each of the structure, the total number of thiophene groups and carbonyls is eight. The optimized structures are displayed in Figure 1, while the corresponding total energies (E in hartrees) and Ti-Ti distances (in Å) are showed in Table 1.



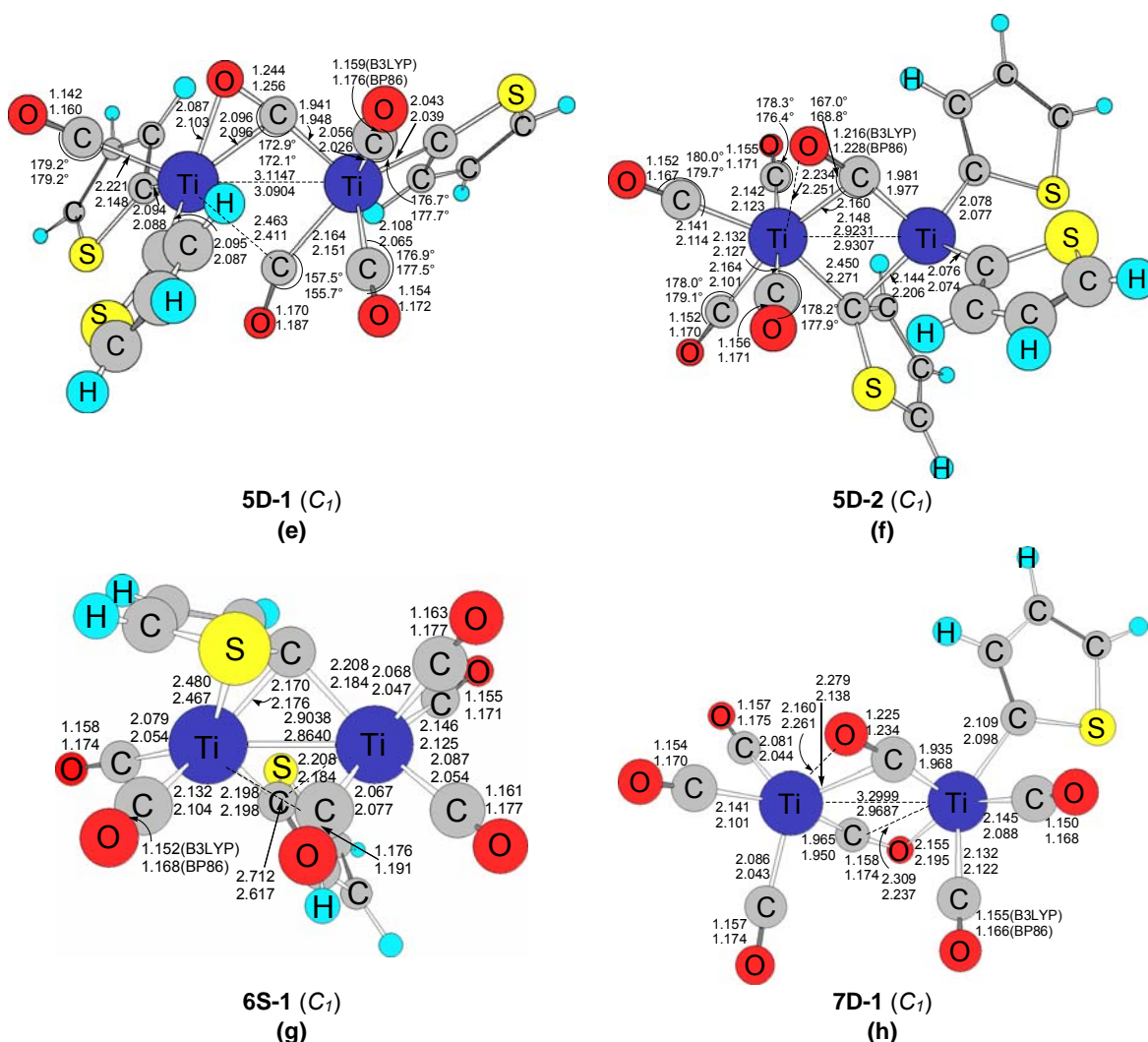


Figure 1: Eight optimized $Ti_2(C_4H_3S)_m(CO)_n$ structures. The distances are given in Å. The upper distances were determined by the B3LYP method and the lower distances by the BP86 method.

Table 1: Total energies (E in hartrees) and Ti-Ti distances (in Å) for the eight structures in Figure 1.

	1D-1 (C_1)	2S-1 (C_1)	3D-1 (C_1)	4S-1 (C_1)
B3LYP				
E	-5679.26401	-5240.22385	-4801.13798	-4362.07657
Ti-Ti	3.2332	3.1268	3.1661	3.1294
BP86				
E	-5679.71252	-5240.64872	-4801.53853	-4362.46659
Ti-Ti	3.1880	3.1602	3.0774	2.9896
	5D-1(C_1)	5D-2(C_1)	6S-1(C_1)	7D-1(C_1)
B3LYP				
E	-3923.01605	-3923.04375	-3483.96955	-3044.89686
Ti-Ti	3.1147	2.9231	2.9038	3.2999
BP86				
E	-3923.37504	-3923.39814	-3484.31484	-3045.20931
Ti-Ti	3.0904	2.9307	2.8641	2.9687

In Figure 1, the result of bond lengths is displayed, of which the upper one is the result calculated by B3LYP method while the lower one is the bond length by BP86 method. For different number of CO groups, the structure is either singlet or doublet. If the number of CO groups (the first number of the name for each

structure in Figure 1) is odd number the doublet spin state structure is obtained, while if the number of CO groups is even number the singlet spin state structure is obtained. The energetic relationships of the eight structures is $E(1D-1) < E(2S-1) < E(3D-1) < E(4S-1) < E(5D-2) < E(5D-1) < E(6S-1) < E(7D-1)$ by both the B3LYP and the BP86 methods.

The minimum found for doublet $Ti_2(C_4H_3S)_7(CO)_1$ is an unsymmetrical C1 structure 1D-1 (Figure 1. (a)) with a real mono-bridged C_4H_3S group and a similar dibridged C_4H_3S group structure $(C_4H_3S)_3(CO)_1Ti(\mu-C_4H_3S)(\eta^2-C_4H_3S)Ti(C_4H_3S)_2$. The minimum found for $Ti_2(C_4H_3S)_6(CO)_2$ is singlet result and unsymmetrical C1 structure 2S-1 (Figure 1. (b)) with two similar dibridged C_4H_3S groups structure $(C_4H_3S)_2Ti(\eta^2-C_4H_3S)_2Ti(C_4H_3S)_2(CO)_2$. The structure of 3D-1 (Figure 1. (c)) for $Ti_2(C_4H_3S)_5(CO)_3$ was found to be a genuine minimum with all real vibrational frequencies. The fourth structure for the minimum found of binuclear titanium carbonyls with thiophene (4S-1, Figure 1. (d)) is singlet result and is also unsymmetrical C1 structure. The structure 4S-1 has a real mono-bridged C_4H_3S group and a dibridged carbonyls structure $(C_4H_3S)_1(CO)_3Ti(\eta^2-\mu-C_4H_3S)(\eta^2-\mu-CO)_1Ti(C_4H_3S)_2$, and is predicted to have all real harmonic vibrational frequencies by both the B3LYP and BP86 methods. The minimum found for doublet $Ti_2(C_4H_3S)_3(CO)_5$ is an unsymmetrical C1 structure 5D-1 (Figure 1. (e)) with a real mono-bridged CO group and a dibridging CO group structure $(C_4H_3S)_2(CO)_1Ti(\eta^2-\mu-CO)_2Ti(C_4H_3S)_1(CO)_2$, and is predicted to have all real harmonic vibrational frequencies by both the B3LYP and BP86 methods. The second stationary point of $Ti_2(C_4H_3S)_3(CO)_5$ is 5D-2, which is a C_1 symmetry dibridged structure having all real harmonic vibrational frequencies by both the B3LYP and BP86 methods, and the energy lies slightly below 5D-1 by both the B3LYP and BP86 methods. The C1 structure 6S-1 (Figure 1. (g)) is triply bridged structure with a real mono-bridged C_4H_3S group, a similar dibridged carbonyl and a dibridged C_4H_3S group structure. The last minimum structure is unsymmetrical 7D-1 (Figure 1. (h)) for $Ti_2(C_4H_3S)_1(CO)_7$ with two dibridged carbonyls structure, and is predicted to have all real harmonic vibrational frequencies by both the B3LYP and BP86 methods.

2.2 Thermochemistry

Chapter 2 Table 2 lists the energies of mononuclear fragments after dissociation of $Ti_2(C_4H_3S)_m(CO)_n$. Table 3 lists the predicted dissociation energies for the reactions $Ti_2(C_4H_3S)_m(CO)_n \rightarrow Ti(C_4H_3S)_i(CO)_j + Ti(C_4H_3S)_k(CO)_l$, ($m+n=8$, $i+j=4$, $k+l=4$). All results reported refer to the lowest energy singlet and doublet structures, respectively, of $Ti(C_4H_3S)_i(CO)_j$, ($i+j=4$, $i=1,2,3,4$, $j=1,2,3,4$), and in order to obtain these data, the minima for $Ti(C_4H_3S)_i(CO)_j$ were optimized by the same DFT methods.

Table 2: Total energies (E in hartrees) for the mononuclear structures with four ligands of CO or C_4H_3S group.

	$Ti(C_4H_3S)_4$	$Ti(C_4H_3S)_3(CO)_1$	$Ti(C_4H_3S)_2(CO)_2$	$Ti(C_4H_3S)_1(CO)_3$	$Ti(CO)_4$
B3LYP					
E	-3059.18307	-2620.09343	-2180.99308	-1741.93813	-1302.86265
BP86					
E	-3059.41088	-2620.29547	-2181.17348	-1742.09694	-1302.99861

Table 3: Predicted energies (kcal/mol) for CO loss and dissociation into mononuclear fragments for the $Ti_2(C_4H_3S)_m(CO)_n$ structures.

	B3LYP	BP86
$Ti_2(C_4H_3S)_7(CO)_1(1D-1) \rightarrow Ti(C_4H_3S)_4 + Ti(C_4H_3S)_3(CO)_1$	-7.8	3.9
$Ti_2(C_4H_3S)_6(CO)_2(2S-1) \rightarrow Ti(C_4H_3S)_4 + Ti(C_4H_3S)_2(CO)_2$	29.9	40.4
$Ti_2(C_4H_3S)_5(CO)_3(3D-1) \rightarrow Ti(C_4H_3S)_3(CO)_1 + Ti(C_4H_3S)_2(CO)_2$	32.3	43.7
$Ti_2(C_4H_3S)_4(CO)_4(4S-1) \rightarrow Ti(C_4H_3S)_3(CO)_1 + Ti(C_4H_3S)_1(CO)_3$	28.2	46.5
$Ti_2(C_4H_3S)_3(CO)_5(5D-1) \rightarrow Ti(C_4H_3S)_2(CO)_2 + Ti(C_4H_3S)_1(CO)_3$	53.2	65.6
$Ti_2(C_4H_3S)_3(CO)_5(5D-2) \rightarrow Ti(C_4H_3S)_3(CO)_1 + Ti(CO)_4$	55.0	65.3
$Ti_2(C_4H_3S)_2(CO)_6(6S-1) \rightarrow Ti(C_4H_3S)_2(CO)_2 + Ti(CO)_4$	71.4	89.6
$Ti_2(C_4H_3S)_1(CO)_7(7D-1) \rightarrow Ti(C_4H_3S)_1(CO)_3 + Ti(CO)_4$	60.3	71.4

The disproportionation reaction $Ti_2(C_4H_3S)_7(CO)_1 \rightarrow Ti(C_4H_3S)_4 + Ti(C_4H_3S)_3(CO)_1$ is exothermic by the B3LYP method with -7.8 kcal/mol and endothermic by BP86 method with 3.9 kcal/mol (BP86). The dissociation energy for structure $Ti_2(C_4H_3S)_7(CO)_1$ is near zero, which indicates that the structure $Ti_2(C_4H_3S)_7(CO)_1$ is not stable and can easily dissociate autonomously. The disproportionation reaction for $Ti_2(C_4H_3S)_6(CO)_2$ is endothermic by both the B3LYP method and BP86 method with 29.9 kcal/mol (B3LYP) or 40.4 kcal/mol (BP86). And the disproportionation reaction for $Ti_2(C_4H_3S)_5(CO)_3$ is also endothermic by both the B3LYP method and BP86 method with 32.3 kcal/mol (B3LYP) or 43.7 kcal/mol (BP86). Except the disproportionation

reaction for $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_7(\text{CO})_1$, the reactions $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_m(\text{CO})_n \rightarrow \text{Ti}(\text{C}_4\text{H}_3\text{S})_j(\text{CO})_j + \text{Ti}(\text{C}_4\text{H}_3\text{S})_k(\text{CO})_i$, ($m+n=8$, $i+j=4$, $k+l=4$) is all endothermic by both the B3LYP method and BP86 method. The dissociation energy for $\text{Ti}(\text{C}_4\text{H}_3\text{S})_5(\text{CO})_3$ into $\text{Ti}(\text{C}_4\text{H}_3\text{S})_3(\text{CO})_1 + \text{Ti}(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_2$ is even larger at 32.3 kcal/mol (B3LYP) or 43.7 kcal/mol (BP86). The predicted energy for dissociation of $\text{Ti}(\text{C}_4\text{H}_3\text{S})_4(\text{CO})_4$ into two $\text{Ti}(\text{C}_4\text{H}_3\text{S})_3(\text{CO})_1$ and $\text{Ti}(\text{C}_4\text{H}_3\text{S})_1(\text{CO})_3$ fragments is higher than $\text{Ti}(\text{C}_4\text{H}_3\text{S})_5(\text{CO})_3$ at 46.5 kcal/mol by BP86. For $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_6$ into $\text{Ti}(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_2$ and $\text{Ti}(\text{CO})_4$ is predicted to reach the max energy of 71.4 kcal/mol by the B3LYP method and 89.6 kcal/mol by the BP86 method respectively. Thus, except for the $\text{Ti}(\text{C}_4\text{H}_3\text{S})_7(\text{CO})_1$, binuclear $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_m(\text{CO})_n$ complex is energy favorable compared with the mononuclear fragments. And generally, the structure $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_6$ is more stable with respect to dissociation into mononuclear fragments.

3. Conclusions

The eight structures discussed in this paper of these isomers of binuclear titanium carbonyls with thiophene do not obey the 18-electron rule. For the binuclear titanium carbonyls without thiophene, it requires number of CO groups to fulfill the 18-electron configuration for both titanium atoms. However, for the binuclear titanium carbonyls with thiophene, the configuration of the titanium atom can not fulfill the 18-electron rule because of the existence of $\text{C}_4\text{H}_3\text{S}$ group. The large volume of $\text{C}_4\text{H}_3\text{S}$ group can as limit the number of CO groups around the central titanium atom as for the space location-obstruct effect, to impede the enough electron donation of the ligand consisted by CO group or $\text{C}_4\text{H}_3\text{S}$ group. Moreover, the $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_m(\text{CO})_n$ structures are linked by Ti-Ti bonds of lengths 2.8 to 3.6 Å, which is relatively long and considered to be formal single bonds. Every structure of the binuclear titanium carbonyls with thiophene is bridged by CO group or $\text{C}_4\text{H}_3\text{S}$ group and sometimes dibridged by both the CO group and $\text{C}_4\text{H}_3\text{S}$ group.

The energy required for the dissociation of $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_6$ into $\text{Ti}(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_2$ and $\text{Ti}(\text{CO})_4$ fragments is 71.4 kcal/mol by the B3LYP method and 89.6 kcal/mol by the BP86 method respectively, which is higher than the energy for the dissociation of other $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_m(\text{CO})_n$ structure into $\text{Ti}(\text{C}_4\text{H}_3\text{S})_j(\text{CO})_j$ fragments. The electron configuration of the titanium atom of $\text{Ti}_2(\text{C}_4\text{H}_3\text{S})_2(\text{CO})_6$ is 17-electron configuration, which is nearest to the 18-electron configuration.

Acknowledgments

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