A new insight of structures, bonding and electronic properties for 6-mercaptopurine and Ag₈ clusters configurations: a theoretical perspective

Hongjiang Ren*, Fan Chen, Xiaojun Li and Yaping He

Abstract

Background: Many reports have also shown that the silver nanoparticles can effectively increase the anticancer drug activity and intensely enhance the drug curative effect. The adsorption of 6MP on nanomaterials has received a lot of attentions because of the drug coordination to its chemotherapeutic activity. The geometrical structures, chemical bonds, molecular orbital properties as well as density of states for the configurations were analyzed to deeply understand the interactions between the 6MP and Ag₈ clusters for high effect anticancer drug production.

Results: In this work, the density functional theory B3LYP has been used to investigate the structures and properties of the configurations between 6-mercaptopurine (6MP) and Ag₈ clusters using 6-311+G** level as well as an effective pseudo potential LANL2DZ. The geometries of ten configurations were optimized with full freedom. The geometrical structures, chemical bonds, molecular orbital properties as well as density of states for partial configurations were analyzed based on the density functional calculations. Polarizable continuum solvent model (PCM) in self-consistent reaction field (SCRF) were used for the aqueous calculations. The influences of temperature and pressure on the stability of the predominant configurations in the gas phase were further considered using standard statistical thermodynamic methods from 50 to 500 K and at 1 bar or 100 bar.

Conclusion: The result shows that there are ten stable configurations in the gas phase and there is a strong chemical bond between a Ag and S atom in the most stable configuration. The analysis of density of states also shows that the Ag–S chemical bond in the most stable configuration has been formed. Moreover, the results show that the temperature and the pressure will significantly influence the stability of the configurations in the gas phase. Additionally, when the solvent effect was considered, we found that there are only seven stable configurations and the solvent have different effect on various configurations.

Keywords: 6-Mercaptopurine, Ag₈ cluster, Density functional theory, Density of states

Introduction

Nanotechnology is swiftly distensible in many fields including synthesis, catalysts, separation, chemiluminescence and sensing [1, 2]. Because of their unique physical and chemical properties such as large surface area, sensitivity and activity, the nanomaterials and products were required for many chemical reactions including the enhancers, catalysts, absorbing materials, energy acceptors and so on [3, 4]. Silver nanoparticles (AgNPs) are easy to be composed from inexpensive forerunners, which have displayed many optical characteristics and possessed good chemical stability, dramatic catalytic property and electrocatalytic property. It has also been found that the silver nanoparticles can effectively increase the anticancer drug activity and intensely enhance the...
drug curative effect [5–9]. At present, many first-principle reports have been limited to the Ag\textsubscript{n} clusters with n ≤ 13 and many candidate structures were considered [10, 11]. Huda and co-workers [10] have investigated the electronic and geometric structures of neutral, cationic, and anionic Ag\textsubscript{n} (n=5–9) clusters using second-order many-body perturbation theory (MP2), which shows that the Ag\textsubscript{8} cluster is a magic-number cluster with the highest binding energy, a relative higher adiabatic and vertical ionization potential, and a lower electron affinity among all the considered clusters. Fernandez and co-workers [11] systematically studied the geometrical structure and electronic properties of neutral, cationic and anionic metal clusters \(M_n\) (M=Cu, Ag or Au, n=2–13). Recently it is shown that Ag\textsubscript{8} neutral clusters embedded in an argon matrix have a strong fluorescence signal [12].

6-Mercaptopurine (6MP) has been utilized as the chemotherapy drug for many years. It is widely used as an effect medicine in treating a variety of diseases, such as rheumatologic disorder, lymphoblastic leukaemia, inflammatory bowel disease and prevention of rejection following organ transplantation [13–22]. The adsorption of 6MP on nanomaterials has received a lot of attentions because of the drug coordination to its chemotherapeutic activity [23–25]. Vivoni and co-workers [24] have experimentally reported the interaction between 6MP and a silver electrode using surface-enhanced Raman spectroscopy (SERS) and Urey-Bradley force field combined with semiempirical PM3 calculation. It was concluded that when the 6MP molecule is adsorbed onto a silver electrode surface, it can attach via the N(1) atom. Chu and co-workers [25] have carried out self-assembled monolayers (SAMs) research of 6-mercaptopurine (6MP) on a silver electrode in acid and alkaline medias via the SERS technique combined with Raman mapping. It was found that the adsorption mode of 6MP would change with the pH data of the environment. The coordination of 6MP onto nanomaterials has been investigated, which can lead to slow releasing drugs of 6MP [26] and exploiting the reaction for heavy-metal determination [27]. Although there are many investigations about the coordination of 6MP to Ag nanoparticles forming AgNPs [10, 11, 23–27], they are only limited to investigate the experimental Raman spectroscopy and the scales and so on. What are the adsorption structures? What are the bonding properties? How can the temperature and pressure affect the adsorption of 6MP onto the Ag clusters? These problems have been not been answered till today.

In this work, we will provide the answers to the former problems throughout carrying out the detailed density functional theory calculations using B3LYP/6-311++G** level. The stabilities of ten configurations between two 6MP tautomers and Ag\textsubscript{8} clusters will be explored. The geometrical structures, chemical bonds, molecular orbital properties as well as density of states for partial configurations were analyzed to understand the interactions between the 6MP and Ag\textsubscript{8} clusters.

**Methods**

In this work, the theoretical calculations were performed using the Gaussian 09 program package [28]. Density-functional theory (DFT) has also been employed in conjunction with pseudopotentials to study silver clusters. The geometries of all the configurations were optimized with DFT-B3LYP method combined with 6-311++G** basis set for non-metal atoms (C, H, N, S) and an effective pseudo potential basis set LANL2DZ only for Ag atoms. In this core potential, the inner 28 electrons (1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)3d\(^10\)) are replaced by RECP and the outer 19 electrons (4s\(^4\)4p\(^4\)5s\(^1\)) are taken as valence electrons. The optimizations were performed in all degrees of freedom. Harmonic vibrational frequencies were analyzed to verify the stationary points at the same theoretical level. Zero-point vibrational energies (ZPVE) and thermal corrections were evaluated under standard state conditions (298.15 K and 100 kPa) via frequency analysis. The thermochemistry energy parameters were calculated at the B3LYP functional level of theory. The binding energies between the Ag\textsubscript{8} clusters and 6MP molecule were denoted by \(\Delta E_b\), which were given for per configuration:

\[
\Delta E_b = - [E(C_n) - E(Ag_8) - E(6MP-7)]
\]  

(1)

Here is an example for 6MP-7, in which n represents the labeled number. For the configurations, it is named as C\textsubscript{n} (n=1–10). For the 6MP-9, it is the same method with 6MP-7, in which, 6MP-7 and 6MP-9 are the two isolated tautomers. In the aqueous calculations, the solvent effect (water) has been considered using continuum models: polarizable continuum model (PCM) in self-consistent reaction field (SCRF). As usual, the solvent is viewed as a continuous dielectric medium characterized by a uniform dielectric constant (\(\varepsilon\)) in this model (\(\varepsilon = 78.39\) for water).

The bonding properties and bond strength variations were analyzed based on the NBO calculations using the NBO package version 3.1, which were conducted at the DFT-B3LYP/6-311++G**/LANL2DZ theoretical level, implemented in the Gaussian 09 program. The analysis can provide a comprehensive insight for the configurations of 6-mercaptopurine (6MP) on Ag\textsubscript{8} clusters.

Heat capacity, entropy, enthalpy and Gibbs free energy of the corresponding four configurations at 298.15 K were evaluated with the standard statistical thermodynamics procedures by using the B3LYP/6-311++G** geometries and frequencies. The heat capacities as a function of temperature in 50–500 K were also developed with the same
method and fitted into an analytical equation (Eq. 2). By using the heat capacities, the energy at any temperature (e.g., 500 K) were derived classically.

\[
C_{p,m}^0 = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^{-2}
\]  

(2)

Results and discussion
Structures and energies
From Refs. [29, 30], it can be seen that 6MP molecule can exist in the eight potential configurations, and the two tautomers 6MP-7 and 6MP-9 can be predominant with the large quantity in the gas and aqueous phases. Other six tautomers can exist in a little quantity. Hence, in this work, the two tautomers 6MP-7 and 6MP-9 are considered for the next discussions and the geometries as well as atomic number of two tautomers 6MP-7 and 6MP-9 were shown in Fig. 1. It can be seen from Fig. 1 that when considering possible coordination atoms, three potential positions N(3), N(7) and S(10) for 6MP-7 or N(3), N(9) and S(10) for the molecule 6MP-9 can be attacked by the metal Ag atom, mainly because of the lone pair electrons for the N and S atoms being extremely important for promoter action. Therefore when considering the adsorption reaction, the orientation of adsorbed 6MP is critical in its action as a mediator of electron transfer. According to the reports by Huda et al. [10], the Ag₈ cluster is a magic-number cluster among the investigated clusters and it has two representative superiority structures. And two potential configurations were considered in this work based on the reported structures [10]. Six stable configurations of 6MP-7 adsorbed onto the Ag₈ clusters surface were shown in Fig. 2, which are named as C1, C2, C3, C4, C5 and C6. Four stable ones of the 6MP-9 with the Ag₈ clusters were also given in Fig. 3, which are named as C7, C8, C9 and C10. Additional file 1: Table S1 gives out the zero point energy, total energy, standard Gibbs free energy and enthalpy of all the configurations at the temperature 298.15 K with B3LYP/6-311++G**/LANL2DZ dual level. The relative energy data is shown in Table 1.

It is seen from Figs. 2, 3 that the structure of Ag₈ cluster in the configurations C1, C2, C3, C7 and C8 is dramatically different from that of C4, C5, C6, C9 and C10. In the configurations C1, C2, C3, C7 and C8, the Ag₈ cluster owned a trigonal pyramid over an approximate square and however, in C4, C5, C6, C9 and C10 the Ag₈ cluster owned a square pyramid over a triangle. In the two clusters configurations, the purine ligand attached to the top vertex of the corresponding pyramid. In the C4 configuration, there is forming a two center coordination of the ligand to the two Ag atoms of the metal cluster. In the C8 and C10 configurations, there are forming a bidentate coordination of the ligand to only one Ag atom of the metal cluster. Other configurations formed a single coordination between the ligand molecule and Ag₈ clusters. From Table 1, the lowest energy configuration is C5 and the energy was taken as a zero. And the relative energies of other nine configurations are based on this. And the second one is C2 with a relative energy of 1.77 kJ/mol. The third and fourth ones are C3 and C8 with a relative energy of 7.17 and 9.46 kJ/mol, respectively. The relative Gibbs free energies of other six configurations C1, C4, C10, C6, C9 and C7 are 10.41, 11.73, 12.11, 15.08, 26.09 and 27.69, respectively. These results show that the configuration C5 is the most stable one of all the configurations and C2 is also possibly predominant one.
The configurations $C_3$ and $C_8$ can exist in large quantity because of lower relatively energies. Other configurations have slightly higher energies and the stabilities are slightly lower than that of the former four configurations. When these configurations were put into the water solvent, we found that the $C_2$, $C_3$ and $C_{10}$ configurations can not been obtained. Even now, in the gas phase discussion, we still consider $C_2$ and $C_3$ for comparisons with other configuration.

In the configuration $C_5$, the Ag11–S10 bond is formed with a distance of 2.692 Å and is slightly longer than the experimental data of 2.48 Å [18], implying that there is existing the classical chemical bonding between the Ag(11) atom and S(10) atom. The chemical bond $S(10)–C(6)$ has been lengthened to 1.694 Å from the 1.670 Å by 0.024 Å and the N(1)–H has also been lengthened to 1.025 Å from the 1.013 Å by 0.012 Å. In $C_2$, the chemical bond $S(10)–C(6)$ is 1.688 Å and in the configurations $C_1$, $C_3$, $C_4$ and $C_6$, the N(3)(or N(9))–Ag(10) chemical bonds are 2.449, 2.407, 2.645 and 2.419 Å, respectively, suggesting that the Ag–S or Ag–N chemical bonds are formed in the end. In these six configurations, the different positions can be attacked by Ag atom of the Ag$_8$ clusters. In $6MP-9$ configurations, we try to find all the configurations and but only four possible configurations were found. All the structures are shown in Fig. 2. In these four configurations, the Ag atom also formed the chemical bond with the N or S atoms, and it can seen

**Fig. 2** Six geometries of the formed configurations on $6MP-7$ with the Ag$_8$ clusters (Bond lengths are given in Å and the data in the parentheses is in the aqueous phase)
that in C2 and C4, the N and S atoms simultaneously formed the chemical bonds with one Ag atom. In C2, the N(7)–Ag(11) and S(10)–Ag(11) bond lengths are 2.578 and 2.936 Å, respectively. And in C4, the N(7)–Ag(11) and S(10)–Ag(11) bond lengths are 2.570 and 3.017 Å, respectively. However, in C1 and C3, only the single N(3)–Ag(11) bond is formed with the distances of 2.438 and 2.460 Å, respectively. These data show that there are existing strong chemical bonds between the 6MP and Ag8 clusters.

When these configurations were put into the water solvent, we found that the most largest data of bond length changing is Ag–N bond in C4 and it is decreasing with 0.091 Å. The second is Ag–N bond in C9 and it is increasing with 0.089 Å. In C5, the Ag–S bond is also increasing with 0.084 Å and in C8, the Ag–S bond is also decreasing with 0.082 Å. Other bonds are changing slightly. Obviously, the solvent have different effect on various configurations.

**Binding energies**

Table 2 gives out the binding energies of ten configurations, in which, \( \Delta E_p \) is the uncorrected interaction energy without basis set superposition error (BSSE) and \( \Delta E_{p}^{\text{corr}} \) (BSSE) is the corrected interaction energies including BSSE corrections. In Table 2, it can be concluded that BSSE data are 5.27–6.95 kJ/mol, which are 10.46–17.06% of the uncorrected interaction energies, suggesting that

### Table 1 Relative standard Gibbs free energy (\( \Delta G^\theta \), kJ/mol) at 298.15 K obtained at the B3LYP/6-311++G**//LANL2DZ level for all the complexes both in the gas and aqueous phases

| Complexes | In the gas phase \( \Delta G^\theta \) | In the aqueous phase \( \Delta G^\theta \) |
|-----------|----------------------------------|----------------------------------|
| 6MP-7     |                                  |                                  |
| C1        | 10.41                            | 8.35                             |
| C2        | 1.77                             | –                                |
| C3        | 7.17                             | –                                |
| C4        | 11.73                            | 16.14                            |
| C5        | 0.00                             | 0.00                             |
| C6        | 15.08                            | 9.03                             |
| 6MP-9     |                                  |                                  |
| C7        | 27.69                            | 14.19                            |
| C8        | 9.46                             | 9.75                             |
| C9        | 26.09                            | 9.93                             |
| C10       | 12.11                            | –                                |
| Reactants |                                  |                                  |
| 6MP-7 + Ag8(1)\(^a\) | 3.59 | – 10.67 |
| 6MP-7 + Ag8(2)\(^b\) | 2.72 | – |
| 6MP-9 + Ag8(1)\(^a\) | 15.77 | – 7.68 |
| 6MP-9 + Ag8(2)\(^b\) | 14.90 | – |

\(^a\) Ag8(1) represent the a trigonal pyramid Ag8 cluster over an approximate square

\(^b\) Ag8(2) represent the a square pyramid Ag8 cluster over a triangle. But in the aqueous phase it is not found

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**Fig. 3** Four geometries of the formed configurations on 6-MP-9 with the Ag8 clusters (Bond lengths are given in Å and the data in the parentheses is in the aqueous phase)
the basis set effect should be included in this work. In the next discussion, the corrected energies are used for illustrating these problem. In Table 2, the obtained binding energy of C8 is 50.63 kJ/mol and that of C2 is 48.70 kJ/mol. And the binding energy difference between them is 1.93 kJ/mol. The obtained binding energies of C5 and C10 are 46.61 and 44.02 kJ/mol, respectively. The binding energies of C1, C3, C4, C6, C7 and C9 are 33.72, 39.12, 36.44, 35.61, 30.70 and 28.95 kJ/mol, respectively and the average binding energy of these six configurations are 34.09 kJ/mol. The result illustrates that the interaction effects between 6MP and Ag8 clusters in C8 and C2 are larger. From Table 2, it can be seen that the lower relative Gibbs free energies, the larger the binding energies of those configurations especially for the configurations C2, C5 and C8.

However, the binding energy of C3 is lower than C2, which can attribute to the various interaction between 6MP and Ag8 cluster. Seen from Fig. 3, in C8 there are forming two chemical bonds for N(7)–Ag(11) and S(10)–Ag(11), which results from the double coordination of 6MP and Ag8. And the interaction effect should be much stronger than that of single coordination of Ag8 and 6MP in C3 or C5, which can explain why the configuration C8 has the greatest binding energy. In order to further expose the bonding property between the 6-MP molecules and Ag8 clusters, the following orbital analysis are carried out for answering the problems.

**Orbital analysis**

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the four relative stable configurations C2, C3, C5 and C8 are depicted in Fig. 4. It is shown that the HOMO orbital electrons of C5 are mainly delocalized in the Ag8 clusters, which are far from the 6MP molecule. The contributions could not be found from the purine ring, suggesting that the HOMO contribution does not mainly result from the purine ring. However, the LUMO electrons are delocalized in the purine ring and S atom via delocalized π bond. These contributions mainly attributed to the covalent bond in the purine ring. The HOMO and LUMO distributions illustrate that C5 has the largest energy gap. The electronic clouds of the HOMO orbital in C2, C3 and C8 configurations are not much larger than that of C5 because of little overlapping field of Ag d electrons, but the LUMO electronic mainly attributed to anti-bonding orbital of purine ring, showing that these configurations have smaller gaps. At the same time, the energy gaps of four configurations C2, C3, C5 and C8 are 198.83, 159.50, 221.75 and 146.03 kJ/mol, showing that among these configurations, C5 has the highest one. And moreover, the stability for C5 is also the largest one of the four configurations, which is almost same with the predicted stability from energy

| Complexes | ΔE_b | ΔE_b (BSSE) | ΔBSSE | Complexes | ΔE_b | ΔE_b (BSSE) | ΔBSSE |
|-----------|------|-------------|-------|-----------|------|-------------|-------|
| C1        | 39.00| 33.72       | 5.28  | C7        | 36.65| 30.71       | 5.94  |
| C2        | 54.98| 48.70       | 6.28  | C8        | 56.53| 50.63       | 5.90  |
| C3        | 44.39| 39.12       | 5.27  | C9        | 34.90| 28.95       | 5.95  |
| C4        | 43.39| 36.44       | 6.95  | C10       | 50.08| 44.02       | 6.06  |
| C5        | 52.76| 46.61       | 6.15  |           |      |             |       |
| C6        | 41.00| 35.61       | 5.39  |           |      |             |       |
information. For further exposing the bonding properties, the NBO analysis obtained at B3LYP/6-311++G**//LANL2DZ level of theory are listed in Table 3. Seen from Table 3, the second order perturbation interaction energy \( \text{LP}[S(10)] \rightarrow \text{LP}^*[\text{Ag}(1)] \) of \( \text{C5} \) is 101.25 kJ/mol and the \( \text{LP}[S(10)] \rightarrow \text{LP}^*[\text{Ag}(1)] \) interaction of \( \text{C2} \) is 92.76 kJ/mol, implying that there are existing strong chemical bonds and the interaction energies of \( \text{C2} \) and \( \text{C8} \) are 57.66 and 50.38 kJ/mol, respectively. As we can know, the second order perturbation interaction energy can show the strength of formed chemical bonds.

| Complexes | Donor \( \rightarrow \) acceptor | \( E^{II} \) (kJ/mol) |
|-----------|---------------------------------|------------------|
| C5        | \( \text{LP}[S(10)] \rightarrow \text{LP}^*[\text{Ag}(11)] \) | 101.25 |
| C2        | \( \text{CR}[S(10)] \rightarrow \text{LP}^*[\text{Ag}(11)] \) | 25.98 |
|           | \( \text{LP}[S(10)] \rightarrow \text{LP}^*[\text{Ag}(11)] \) | 92.76 |
|           | \( \text{LP}[\text{Ag}(1)] \rightarrow \text{BD}^*[S(10)-\text{Ag}(11)] \) | 13.14 |
| C3        | \( \text{LP}[N(9)] \rightarrow \text{LP}^*[\text{Ag}(11)] \) | 57.66 |
| C8        | \( \text{LP}[S(10)] \rightarrow \text{LP}^*[\text{Ag}(11)] \) | 50.38 |

Density of states analysis

In order to well understand the electronic properties of the titled clusters and the interaction between Ag\(_8\) clusters and 6MP molecule, the density of states of two more stable adsorption configurations C5 and C8 were calculated, as shown in Fig. 5, because the energies of C5 and C8 in the solvent are relatively lower than others. In Fig. 5a, b represent the electron density of molecule after adsorption (c, d) represent electron density of Ag surface after adsorption (e, f) represent total DOS most stable adsorption configuration. In the present work, the density of states near fermi levels were focused because those density of states near the Fermi levels are significant. As seen from the Fig. 5, it is shown that for the density of states near the Fermi levels, the contributions of p electrons are the maximum and the contributions of s electrons are the minimum for the 6MP molecule after adsorption shown in (a, b), and that of d electrons are in between p electrons and s electrons for C8 from (d) and that of d electrons are the maximum for C5 from (c). Also seen from Fig. 5, in the negative field, there are strong interaction between the p electrons of molecules and d electrons of Ag clusters. Hence, the p electrons have the largest contributions to the Fermi levels, which may be originated from that the Ag elements are the evident p-block elements, which have resulted from the 6MP molecules adsorption on Ag\(_8\) clusters. For the density of states in the range of \(-0.5 \text{ to } -0.3 \text{ Ha}\), the p electrons almost have the same contributions from (a, b), whereas s electrons have the smallest contributions. In comparison with (c, d), it also shows that d contribution from Ag\(_8\) in C5 are more than that in C8, which is in agreement with the most stable order of the configuration C5.

Temperature and pressure effect

For exploring the temperature and pressure influence on the configurations, the different temperatures and pressure are considered in this work. The temperature was from 50 to 500 K and the pressure was given at two conditions 1 bar and 100 bar. The Gibbs free energies obtained using the standard statistical thermodynamic method ranged from 50 to 500 K are employed in the next discussion. The relations between the Gibbs free energies and temperature for the configurations C2, C3, C5 and C8 at 1 bar and 100 bar are illustrated in Fig. 6a, b, respectively. As can be seen from Fig. 6a, b, the Gibbs free energies of the four configurations dramatically decrease with the increasing of the temperature from 50 to 500 K, implying that the temperature can affect the stability of the four configurations. In Fig. 6, the Gibbs free energies differences of the four configurations are very slight regardless of at 1 bar or 100 bar, implying that the temperature can almost have same effect on the stabilities of the four configurations. Seen from Fig. 6 the Gibbs free energy of C8 is the most highest among four configurations between 50 and 300 K either at 1 bar or 100 bar. The stabilities of C2 and C5 are also same within the investigated pressure and temperature range. The results also show that in different temperatures these configurations have different stabilities, which can be attributed to formed different chemical bonds. The stabilities of C2 and C5 are obviously lower than other two configurations.

Conclusions

Theoretical investigations have been carried out for the configurations between 6-mercaptopurine and Ag\(_8\) cluster using the density functional method B3LYP with 6-311++G**//LANL2DZ basis set. The configurations geometrical structures were optimized with no constraints. The energies, bonding properties and density of states of the corresponding configurations were analyzed in detail. Additionally, the influences of temperature and pressure on the stability of the four configurations were also explored using standard statistical thermodynamic methods. The result shows that the configuration C5 can be the most stable among the investigated configurations, in which the Ag(11) atom interacts with the S(10) atom forming the strong chemical bond. The density of states
Fig. 5  Densities of states of C5 (a, c, e) and C8 (b, d, f) for the most stable two adsorption configuration. a, b Represent the electron density of molecule after adsorption; c, d Represent electron density of Ag surface after adsorption; e, f represent total DOS most stable adsorption configuration.
also show that the Ag–S chemical bond is formed and the d contribution from Ag in C5 are more than that in C8, which support the most stable order of the configuration C5. The temperatures and the pressure can significantly influence the stability of the four stable configurations.

**Additional file**

*Additional file 1: Table S1.* Zero point energy (ZPE, a.u.), total energy ($E_T$, a.u.), standard Gibbs free energy ($G_\theta$, a.u.) and enthalpy ($H_\theta$, a.u.) at 298.15 K obtained at the B3LYP/6-311++G**//LanL2DZ level for ten complexes.

**Authors’ contributions**

HJR designed the research, performed the research, and analyzed the data. FC carried out the calculations. HJR wrote the paper. XJL and YPH carried out some relevant works for analyzing the data. All authors read and approved the final manuscript.

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**Competing interests**

The authors declare that they have no competing interests.

**Availability of data and materials**

Provided as Additional file 1.

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**Fig. 6** The Gibbs free energies of the considered configurations C5, C2, C3 and C8 with the temperature increasing from 50 to 500 K and pressures of 1 bar for (a) and 100 bar for (b)
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