Structural, stability and electronic properties of Os\textsubscript{m}C\textsubscript{n} (m+n\leq7) clusters

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The structures, relative stabilities and electronic properties of Os\textsubscript{m}C\textsubscript{n} clusters for m+n\leq7 have been investigated by the density functional theory. The planar geometries have been preferred for small carbon mixed clusters up to m-n=5, for those with size of m+n\geq6, the C-rich clusters are still planar structures, while Os-rich clusters are three-dimensional structures, and the most energetic favourable structures tend to be capped pyramid or irregular prism. The stability analysis indicates that the mixed clusters are more stable than those of the corresponding pure Os\textsubscript{n} clusters, among which OsC\textsubscript{2}, Os\textsubscript{2}C\textsubscript{2}, Os\textsubscript{4}C\textsubscript{2}, Os\textsubscript{2}C\textsubscript{4} exhibit higher stability than their neighbouring clusters. Os5d and C2p electrons play dominant roles in chemical reaction of mixed clusters.

Keywords: Os\textsubscript{m}C\textsubscript{n} (m+n\leq7) clusters, Structures, Stability, Density functional theory, Electronic properties

1 Introduction

The mixed clusters have rich diversities in composition, structure and properties which can greatly expand the properties of pure clusters and make them have more extensive and excellent performance\textsuperscript{[1-3]}. Transition metals (TM) play important roles in the field of metallurgy and catalysis due to their d electrons, which make them exhibit special electronic structures and physical-chemical properties. Therefore, TM clusters and TM-mixed clusters have been extensively studied\textsuperscript{[4-10]}. Os as one of the important TM especially Os-mixed clusters have been carried out in the past few years. Zheng et al\textsuperscript{[11]} calculated Os, OsC and OsN clusters by using first principle calculations, their results confirmed that Os, OsC, and OsN in the hexagonal structures are more stable than those under the structure of sodium chloride. Chen et al\textsuperscript{[12]} investigated the structures and electronic properties of OsB\textsubscript{2}. Young et al\textsuperscript{[13,14]} found that mixing C, N, B, O and other light elements into transition metals may form a directed covalent bond. By the first principles plane-wave pseudopotential calculations based on the density functional theory, Liang et al\textsuperscript{[15]} studied the equations of states and structural properties of transition metal compounds OsB\textsubscript{2} and OsO\textsubscript{2}, the possible high pressure phase transitions of OsO\textsubscript{2} and its rutile, pyrite and fluorite phases under high pressure, found that incorporating light elements (boron, oxygen, carbon or nitrogen) into osmium is possibly a new way to prepare super hard material. It would be a significant work to investigate lighter elements mixed osmium clusters.

Our research group\textsuperscript{[16-18]} has studied the pure osmium clusters, Os-N and Os-B cluster system. However, the structural information of the mixed Os\textsubscript{m}C\textsubscript{n} clusters with m+n\leq7 has not been investigated so far. Therefore, the geometries, stabilities and electronic properties of Os\textsubscript{m}C\textsubscript{n} (m+n\leq7) clusters have been investigated in the present work. The density functional theory has been taken to study the lowest-energy optimized structures. However, it is a difficult task to experimentally determine the ground-state structures of small atomic clusters, so the density functional theory has been taken to find the lowest-energy optimized structures. As for each size cluster, hundreds of initial configurations are designed and the lowest energy structures are chosen from them.

The lowest energy structures of Os\textsubscript{m}C\textsubscript{n} (m+n\leq7) are reported. The average binding energies, the second-order differences of total energies, the energy gaps and the density of state are presented in the present study. The main goal of the work is to lay foundations for further studying the properties of carbon-osmium clusters and developing new materials with special functions.
2 Computational Methods

All the calculations were carried out with spin-polarized DFT at the level of generalized gradient approximation (GGA) via the Perdew-Wang exchange-correlation functional. In the calculation of the electronic structure, a double-numerical polarized basis set that includes d-polarization functions (DND) was chosen by us to describe the electronic wave functions. All of the possible spin multiplicities include singlet, triplet, quintet and seven spin states were calculated for each configuration to ensure that the obtained spin states are the lowest in energy. In order to accelerate the convergence of self-consistent field (SCF), the Pulay’s direct inversion in an iterative subspace (DIIS) approach was designed with a convergence criterion of 10^{-5} Hartree. For the total energy, 0.0040 Hartree/Å for gradient of force and 0.005 Å for atomic displacement. All our spin-unrestricted calculations were performed with the Accelrys DMOL3 package.

The reliability of the proposed computational method was checked by calculating the bond length of C2 and Os2 dimers, the value obtained for C2 is 1.312 Å, which is in excellent agreement with the experimental value (1.312 Å) reported in the previous studies. As for Os2, the calculated bond length of 2.296 Å is consistent with the experimental data of 2.28 Å. The above results indicate that our calculation method is reasonable and will provide reliable results for the OsnCm (m+n≤7) clusters.

3 Results and Discussion

3.1 Geometrical structures of OsnCm (m+n≤7) clusters

We have searched for a series of possible initial configurations for each size of the clusters on the basis of taking into full account the spin multiplicity to ensure the high accuracy of our determination for the ground-states of OsnCm (m+n≤7) clusters. The lowest-energy optimized structures are shown in Fig. 1. The spin multiplicity (S), structure symmetries and average bond lengths are listed in Table 1.

As can be seen from Fig. 1, for pure Cn (n≤7) clusters the most stable structures are linear with Dvh symmetry except n=3 and 6. This is in good agreement with the results reported by Zhang et al. The C-C bond lengths in pure Cn (n≤7) clusters are in the range 1.288-1.326 Å, which correspond to C-C double bond. As for C3, the ‘V’ shaped configuration with an apex angle of 142.171° is the lowest-energy structure. While the lowest energy structure of C4 is a regular hexagon (D6h) with side length of 1.326 Å. This is in excellent agreement with the Binkley et al. result. For the pure Osn (n≤7) clusters, all the lowest energy structures obtained in our work are well consistent with the previous results except the symmetry of Os3 (C3v).

For the binary clusters, the smallest one-OsC is in triplet state with C3v symmetry. The Os-C distance (1.690 Å) is shorter than the (1.981 Å) previous theoretical result. In the isomers of OsC, equi-circular triangle geometry with C2v symmetry and singlet spin multiplicity has the lowest energy. The ground state of OsC is a linear structure (Os-C-Os) with Dvh symmetry in quintet state which can be viewed as an Os atom located at the C atom of the OsC cluster rather than a C atom located at Os2 cluster. This may be because the energy of C-C bond is higher than that of Os-Os bond. The OsnCm (m+n=4) clusters are the smallest ones that can display 3D structures, so we not only designed the linear and planar structures but also considered the tetrahedral structures. However, according to the optimized results, the planar configurations are found to be more stable than the tetrahedral structures in total energy. For the OsC3 linear geometry with triplet multiplicity is found to be the ground state, which is similar to the GaC3 cluster. The ground state of Os2C2 is a planar rhombus (D2h) with bond length of 1.837 Å. In the case of OsC, the planar quadrilateral with a C atom bridged over two Os atoms is the most preferred one, it can be seen to add a C atom to one side of Os3. All the optimized geometries of OsnCm (m+n=5) binary clusters are also planar structures. The OsC4 with C4 symmetry is an irregular pentagon, while the Os3C3 with C2v symmetry is a regular pentagon, in this isomer the C-C bond length is 1.381 Å, which is obviously shorter than Os-C. This may be caused by the interaction between the C atoms. The ground state of Os3C2 (C2v) is similar to OsC4, in which the Os-Os bond length is 2.350 Å and Os-C bond length is 1.801 Å. The OsC can be viewed as adding two Os atoms to opposite ends of Os2C.

For the hexamer, we attempted planar, octahedron, triple prisms and capped trigonal bipyramidal structures. As seen from Fig. 1, the structures of Os6Cm (m+n=6) clusters transform from planar into three-dimensional structures with increasing number
of Os atoms. The most stable structure of OsC₅ with $C_5$, symmetry is found to be obtained by using one Os atom substituting for the C atom at the apex of $C_6$ cluster, C-C bond lengths are shortened due to the influence of Os. A regular hexagonal structure with $D_{3h}$ symmetry is obtained to be the ground state of Os₂C₄, the two Os atoms are at the opposite position. The Os₃C₃ cluster shows analogical triangular prism ($C_5h$) as the ground-state geometry, in which there is no C-C bond. For Os₄C₂, the binary edge capped triangular pyramid geometry in singlet state with $D_{2d}$ symmetry is found to have the lowest energy. Influenced by the function of C atoms, the bond lengths of Os-Os that close to C atom are 2.927 Å, while the others away from C atom are 2.490 Å, all the bond lengths of Os-C are 1.837 Å. In the Os₅C, the C edge capped the square pyramid with $C_3$ symmetry is the most stable one.

While for Os₆Cₙ ($m+n=7$), all the optimized geometries are three-dimensional structures except OsC₆, which is an irregular seven-membered ring with $C_5$ symmetry. For Os₇C₅, the ground-state geometry likes a basket with long handle ($C_{2v}$). In Os₈C₄, the most stable isomer in triplet state with $C_3$ symmetry can be viewed as adding a C atom to the bottom of Os₃C₃. Similarly, Os₉C₃ can be viewed as bridging the third C atom over the existed two C atoms in Os₈C₂, the average Os-Os bond length in it lies in the range
ground state Os

For the purpose of analyzing the stabilities of the

3.2 Stabilities of Os

2.437-3.325 Å. Os₃C₂ and Os₆C can be obtained by
dобавление атома C к Os₃C и Os₆C, соответственно.

3.2 Stabilities of OsₘₙCₙ (m+n≤7) clusters

For the purpose of analyzing the stabilities of the
ground state OsₘₙCₙ clusters, the average binding
energies per atom (Eₐ/atom), the second-order
differences of total energies (Δ₂E) and the energy gaps
between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been calculated.

The average binding energies reflect the stability of
the clusters. For the same size clusters, the higher the
average binding energy is, the more stable the cluster will be.

The average binding energies of the mixed clusters
can be described by the following formula:

\[
E_a = \left[ mE(\text{Os}) + nE(C) - E(O_{m\text{-}n}C_n) \right] / (m+n) \quad \text{(1)}
\]

where \(E(\text{Os})\), \(E(C)\) represent the energy of isolated
Os and C, respectively. \(E(O_{m\text{-}n}C_n)\) represents the total
energy of the OsₘₙCₙ clusters, and \(E_a\) represents the
average binding energy of system. These quantities of
average binding energies are shown in Fig. 2 as a function of the number of C atoms. Both the average
binding energies of pure Osₙ and Cₙ clusters increase
as the cluster sizes fill out, and all the average binding
energies of pure Cₙ clusters are larger than those of
Osₙ clusters, this indicates that the stability of carbon
clusters is better than that of osmium (Fig. 2). Whereas for mixed clusters, all the average binding
energies increase with the number of carbon atoms
and are between pure osmium clusters and pure
carbon clusters except for C₂. Thus, from the above
analysis, we conclude that the energy of C-C bond
is stronger than that of Os-Os bond and the C-rich
clusters are more stable than Os-rich clusters with
the same number of total atoms. Though there is no
obvious odd-even oscillation, five slight lifts
appearing to OsC₂, Os₂C₂, Os₂C₄, Os₃C₂, Os₃C₄,
respectively. The emergence of these local magnitude
maxima means that these clusters have stronger
stabilities relative to their neighbours.

As the second-order differences of total energies
(Δ₂E) can be used to measure the relative stability of
clusters, so we calculated the Δ₂E of OsₘₙCₙ (m+n≤7).
In order to investigate, the effect of the increasing
number of C and Os atoms to the stabilities clearly,
both \( \Delta_2E_n \) and \( \Delta_2E_m \) have been calculated and the relationship between \( \Delta_2E \) and \( n \) are shown in Figs 3 and 4, respectively. The \( \Delta_2E \) is estimated in the following way:

\[
\Delta_2E(n) = E(n+1) + E(n-1) - 2E(n)
\]

(2)

From Fig. 3, it is evident that the values of the second-order differences of total energies for \( C_3, C_5, OsC, OsC_2, Os_2C_2, Os_3C, Os_2C_2 \) and \( Os_4C_2 \) clusters are positive numbers, this shows that the stabilities of these clusters are relatively better. There exist clear even-odd oscillations in the curves of \( C_n \) and \( Os_3C_n \) clusters, \( C_3, C_5, Os_2C_2, Os_3C_2 \) and \( Os_4C_2 \) are more stable than their neighbouring ones. As well, we can easily find that the values of the second-order differences of total energies for \( Os_2, Os_4, OsC, Os_3C, Os_3C_2, Os_3C_3, Os_2C_2, Os_3C_4 \) and \( Os_4C_2 \) clusters are positive numbers from Fig. 4, indicating that these clusters possess stronger stabilities relative to their neighbours. The curves of \( Os_3n \) and \( Os_4C_n \) clusters show the odd-even oscillation behaviour and two peaks can be found corresponding to \( Os_4 \) and \( Os_3C \).

Combining the above analysis of both \( \Delta_2E_n \) and \( \Delta_2E_m \), we can draw a conclusion that \( OsC, OsC_2, Os_2C_2, Os_3C_2, Os_3C_3 \) and \( Os_4C_2 \) are much more stable than other clusters in \( Os_mC_n \). The energy gaps \( E_g \) between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are able to used to reflect the stabilities of clusters from the chemical stability point of view, they are defined as:

\[
E_g = E_{\text{LUMO}} - E_{\text{HOMO}}
\]

(3)

where \( E_{\text{LUMO}} \) is the energy of the lowest unoccupied molecular orbital, \( E_{\text{HOMO}} \) is the energy of the highest occupied molecular orbital.

The HOMO-LUMO energy gaps of the ground state geometries of \( Os_mC_n \) \((m+n\leq7)\) clusters are plotted in Fig. 5. Compared with pure Os and C-mixed clusters, the pure C clusters (except \( C_4 \)) have higher energy gaps, so pure C clusters have higher chemical stability than others, which coincides well with the result of the average binding energies and the second-order differences of total energies. It also can be found that most of the energy gaps of the C-mixed clusters are larger than those of the \( Os_n \) with the same cluster size; this result clearly indicates that the doping of C atom has lowered the chemical activity of
Fig. 6 — Corresponding HOMO and LUMO orbital isosurfaces of OsC$_2$, Os$_2$C$_5$, Os$_4$C$_2$, and Os$_2$C$_4$ clusters.

Fig. 7 — Partial density of states (PDOS) of s, p and d orbital and total density of states (TDOS) OsC$_2$, Os$_2$C$_5$, Os$_4$C$_2$, and Os$_2$C$_4$ clusters. The vertical line indicates the Fermi level.
Osₙ clusters. Among all the clusters, OsC₂, Os₂C₂, Os₃C₂, and Os₅C₄ display higher energy gaps as compared to their neighbours, which is coincident with the conclusions obtained from the average binding energy and the second-order differences of total energy.

3.3 Electronic properties of OsC₂, Os₂C₂, Os₃C₂, and Os₅C₄ clusters

In order to further explore the properties of OsₙCₙ (m+n≤7) clusters, the HOMO and LUMO orbital isosurfaces of OsC₂, Os₂C₂, Os₃C₂ and Os₅C₄ clusters are shown in Fig. 6 (because they are thought to be the most stable clusters in the present paper), from which one can see that both HOMO and LUMO states are mainly contributed by Os5d orbital and C2p orbital. This indicates that there exists d-p hybridization between Os atoms and C atoms, which are the dominating factor for decrease of doping of C atoms the energy gaps of pure Cₙ cluster but increase the energy gaps of pure Osₙ cluster. The corresponding total density of states (DOS) and partial density of states (PDOS) of these clusters are also calculated and shown in Fig. 7. The Fermi level is at zero energy presented as a vertical line, the upper side of the figure is related to DOS for electrons with upward spin, and the lower side is related to the electrons with downward spin. It is clear that in all the chosen clusters, all curves are discrete; this indicates that the energy levels for OsC₂, Os₂C₂, Os₃C₂ and Os₅C₄ clusters are discrete. It is also clearly seen from Fig. 7 that in the vicinity of the Fermi level, all the electronic states consist mainly of Os5d and C2p states, and the contribution of the s orbital electrons can be negligible as compared with p and d orbital electrons. There exist isolated peaks in the vicinity of the Fermi level of all the state density curves and in PDOS the peaks of all orbital are in one-to-one correspondents, this indicates that the d electrons of Os atoms and the s and p electrons of C atoms are relatively localized and there exist more or less spd hybridization in all of the selected clusters. For OsC₂, Os₂C₂ and Os₅C₄ clusters, both the PDOS and TDOS curves are symmetric, while for Os₃C₂ the situation is different. This indicates that there is a difference between the spin up electronic number and the spin down number in Os₃C₂, that is to say there exist unpaired electrons in this cluster. This result is consistent with the spin multiplicities of these clusters that previously mentioned.

4 Conclusions

Employed with PW91 functional within the generalized gradient approximation (GGA), the lowest energy structures of OsₙCₙ (m+n≤7) clusters are obtained. The lowest energy geometries show that most of small pure carbon clusters are in single state while pure osmium clusters have higher spin multiplicity and symmetry. For binary clusters, the singlet and triplet state structures are more stable than others. The preferred OsₙCₙ structures with size of m+n≤5 transform from chain-like geometries to ring-like structures except Os₅ which is a pyramid structure. As for those with size of m+n≥6, the C-rich clusters are still planar structures, while Os-rich clusters are three-dimensional structures and most of them tend to be capped pyramid or irregular prism.

The relative stabilities are determined by analyzing the average binding energies, the second-order differences of total energies and the energy gaps. The OsC₂, Os₂C₂, Os₃C₂ and Os₅C₄ show stronger stabilities than their neighbouring ones. HOMO and LUMO orbital isosurfaces and DOS analysis of OsC₂, Os₂C₂, Os₃C₂ and Os₅C₄ indicate that Os5d and C2p electrons play dominant roles in chemical reaction of mixed clusters. As the partial DOS described, the d electrons of Os atoms and the s and p electrons of C atoms are relatively localized and there exist more or less spd hybridization in all of the selected clusters.

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References