The Structure and Growth Mechanism of Small Titanium Carbide Clusters: A Competition between C_2 and C_4 Carbon Chains

Jordi Muñoz,[†] Marie-Madeleine Rohmer,[‡] Marc Bénard,*,[‡] Carles Bo,[†] and Josep-M. Poblet*,[†]

Departament de Quimica Física i Inorgànica, Universitat Rovira i Virgili, Pc. Imperial Tarraco 1, 43005-Tarragona, Spain, and Laboratoire de Chimie Quantique, UMR 7551 CNRS and Université Louis Pasteur, 4 rue B. Pascal, F-67000 Strasbourg, France

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DFT calculations have been carried out on the titanium carbide clusters Ti_3C_8, Ti_4C_8, Ti_6C_{13}, and Ti_7C_{13} and their anions, in relation with the recent experimental and theoretical report by L.-S. Wang and his group on those clusters (Wang, L.-S.; Wang, X.-B.; Wu, H.; Cheng, H. *J. Am. Chem. Soc*. **1998**, *120*, 6556). The small clusters Ti_3C_8 and Ti_4C_8, characterized by a C/Ti ratio higher than or equal to 2, favor conformations in which the carbon phase is assembled into *cis*-butadiene-like C_4 chains without bond length alternation. The 19- and 20-atom clusters Ti_6C_{13} and Ti_7C_{13} prefer structures which are reminiscent of the very stable metallocarbohedrene (MetCar) Ti_8C_{12} T_d structure. An analysis of the structure most probable for $Ti_7C_{13}^-$ suggests that this conformation cannot be a precursor to multicage clusters. The layer-by-layer growth pathway proposed by Wang et al. therefore appears susceptible to account for the formation and stability of high nuclearity titanium carbide clusters. However, the existence of multicage structures cannot be ruled out with other metals. The surprising absence of the MetCar species $Ti_8C_{12}^-$ and $Zr_8C_{12}^-$ from the mass spectrum of anionic clusters, as observed by Wang under specific experimental conditions, is tentatively explained by the formation of unstable molecular Rydberg states.

1. Introduction

In 1992, Castleman and co-workers carried out laser vaporization experiments of early transition-metal samples in hydrocarbon-seeded carrier gases. The obtained mixture of carbide cations was analyzed at the mass spectrometer and revealed the remarkable predominance of the $M_8C_{12}^+$ species (M = Ti, V, Zr, Hf), characterized as a “supermagic” peak.[1,2] The term “metallocarbohedrene” or MetCar was coined to designate the new class of stable clusters.[1] It has been established that the special stability of MetCars is related to a structure of highly symmetric cage, but the exact conformation of the structure remains controversial.[1−6] Most recent theoretical studies[3,7] together with the interpretation of the spectroscopic properties[8] and of the chemical reactivity of met-cars,[9] however, suggest that the preferred structure of the metal backbone could be that of a tetracapped tetrahedron giving rise to the cage structure with T_d symmetry represented in Figure 1. The quest for other magic numbers in metal carbide clusters M_xC_y (M = Ti, V, Zr, Ta,...) and investigations on the formation and growth mechanisms of MetCars have led to a series of fascinating discoveries and hypotheses. On one hand, the characterization by Pilgrim and Duncan of magic peaks for high nuclearity titanium and vanadium carbide cluster cations with 1/1 M/C stoichiometries produced evidence for the growth of cubic lattice structures designated as “nanocrystals”.[10] On the other hand, Wei et al. produced a series of magic peaks corresponding to the carbon-rich zirconium carbide clusters $Zr_{13}C_{22}^+$, $Zr_{18}C_{29}^+$, and $Zr_{22}C_{35}^+$.[11] Those magic numbers were tentatively assigned to an unusual growth pattern of the MetCar structure leading to multiple face-sharing M_8C_{12} cages.[11,12] Both series of magic numbers therefore seemed associated with separate growth paths selected as a function of the metal−carbon ratio.[13] However, recent investigations carried out by Wang et al. on the metal carbide *anions* provided a quite different distribution of the magic numbers, characterized by the unexpected lack of $Ti_8C_{12}^-$ and $Zr_8C_{12}^-$ under certain experimental conditions.[8b,14] The absence of Ti_8C_{12} anions made improbable a double-cage structure for the abundant species $Ti_{13}C_{22}^-$. A cubic structure with $8C_2$ dimers at the cube corners was rather proposed and confirmed from anion photoelectron spectroscopy and DFT calculations.[15] This led to the assumption of a novel layer-by-layer growth pathway for the large carbide clusters, involving metal backbones similar

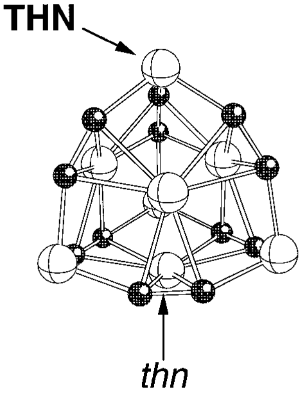

Figure 1. The M_8C_{12} MetCar structure based upon a tetracapped tetrahedron arrangement of the eight metal atoms (T_d symmetry) and generally assumed to be the most stable form of those clusters.[3] **THN** and *thn* represent the capping and the capped tetrahedra of metal atoms, respectively.

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* Authors to whom correspondence should be addressed.

[†] Departament de Química Física i Inorgànica.

[‡] Laboratoire de Chimie Quantique.

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TABLE 1: Total Binding Energies and Binding Energies per Atom (eV) for Titanium Carbide Clusters in the Conformations Studied in the Present Work

	Ti_3C_8	Ti_4C_8	Ti_6C_{13}	Ti_7C_{13}(*thn*)	Ti_7C_{13}(**THN**)	Ti_8C_{12}
cation	59.4	67.0	115.2[b]	122.8		126.9
neutral	66.7	73.2	121.2[b]	129.5	129.9	131.6
Wang et al.[14] [a]	(65.4)	(70.9)	(116.4)	(121.2)		
anion	69.0	74.8	123.0[b]	131.5	131.2	132.9
B.E./atom[c]	6.07	6.10	6.38[b]	6.48	6.50	6.58
Wang et al.[14] [a]	(5.95)	(5.91)	(6.12)	(6.06)		

[a] Binding energies calculated at the same level of theory for the neutral form of the structures advocated by Wang et al.[14] are given in parentheses. [b] Conformation of lowest energy, referred to in Figure 4 as Ti_6C_{13}(**THN**). [c] Neutral form.

to those of the cubic nanocrystals but surrounded by C_2 dimers at the periphery of the crystallite.[15]

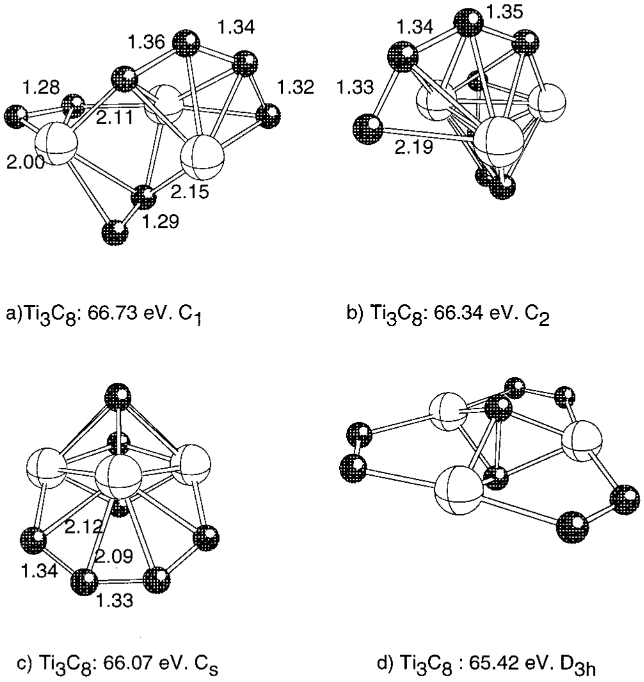
The distribution of the small Ti_xC_y anions ($x < 10$) showed the predominance of the following cluster ions: $Ti_3C_8^-$, $Ti_4C_8^-$, $Ti_6C_{13}^-$, $Ti_7C_{13}^-$, and $Ti_9C_{15}^-$.[14,15] Very recently, Wang et al.[14] proposed structures for each of those clusters, based upon DFT geometry optimizations and supported by the agreement obtained with experiment for the calculated electron affinities and for the single particle density of states. However, the authors acknowledged that the selection of the initial conformations taken to start the geometry optimization processes had been guided by the structural features validated for high nuclearity clusters, namely: (i) the important role of C_2 dimers in the carbon-rich clusters, and (ii) the existence of a cubic structural motif in both series of large clusters exemplified by $Ti_{14}C_{13}$ ($3 \times 3 \times 3$ cubic lattice) and by the C_2-decorated cubic $Ti_{13}C_{22}$ cluster.[14] We thought that those prerequisites were susceptible to introduce a bias in the optimization process. It is well-known that the topology of very small clusters may follow an erratic behavior, quite unrelated with the more regular growth path established for larger species. For species of intermediate size (Ti_6C_{13}, Ti_7C_{13}), we were surprised to notice that the optimal structures proposed by Wang et al.[14] are quite dissimilar to that of Ti_8C_{12} or to that of its endohedral adduct Ti_8C_{13}. We are inclined to believe that the remarkable stability of the met-car T_d structure − at least for cations and neutrals − can persist for stoichiometries that differ from Ti_8C_{12}/Ti_8C_{13} by the substitution or by the loss of one, or possibly two atoms. The goal of the present work is therefore to use the DFT formalism to optimize for Ti_6C_{13}, Ti_7C_{13} and their anions cluster structures derived from the topology of the MetCar T_d structure and compare their stabilities at the same level of theory with the conformations proposed by Wang et al.[14] For the smaller clusters, Ti_3C_8, Ti_4C_8 and the corresponding anions, new structures were also investigated without any prerequisite concerning either the cluster symmetry or the organization of the carbon ligands. Finally, the problem of the surprising absence of $Ti_8C_{12}^-$ and $Zr_8C_{12}^-$ in the mass spectrum will be discussed and tentatively explained in correlation with the energy of the highest occupied orbital in a spin-unrestricted scheme.

2. Computational Details

All calculations have been carried out by means of density functional calculations including gradient corrections. We used the local spin density approximation characterized by the electron gas exchange ($X\alpha$ with $\alpha = 2/3$) together with Vosko−Wilk−Nusair[17] parametrization for correlation. Becke's nonlocal corrections to the exchange energy[18] and Perdew's nonlocal corrections to the correlation energy[19] have been added. The choice of this model is justified by its efficiency and accuracy in the evaluation of bond energies for a variety of metal−ligand and metal−metal bonds, as documented by Rosa and colleagues.[20] The calculations have been carried out with the ADF program.[21] A frozen core, composed of the 1s shell for carbon, of the 1s and 2sp shells for titanium, is modeled by means of a minimal Slater basis. The valence electrons of carbon are described by means of a triple-ζ + polarization Slater basis set. For the valence shell of titanium, 3s and 3p electrons are described by double-ζ Slater functions, 3d and 4s by triple-ζ functions, and 4p by a single orbital.[22,23] No f-type polarization function is added. A basis set of the same quality was used for zirconium. Spin-unrestricted calculations were used for the open-shell configurations. The total binding energies are calculated with respect to the sum of the energies computed for the isolated atoms in their ground-state configuration. The geometry optimization processes were continued until all of the three following convergence criteria were fulfilled: (i) the difference in the *total energy* between two successive gradient optimization cycles is less than 0.001 hartree, (ii) the difference in the *norm of the gradient* between two successive cycles is less than 0.01 hartree $Å^{-1}$, and (iii) the maximal difference in the *Cartesian coordinates* between two successive cycles is less than 0.01 Å.

3. Cluster Structures

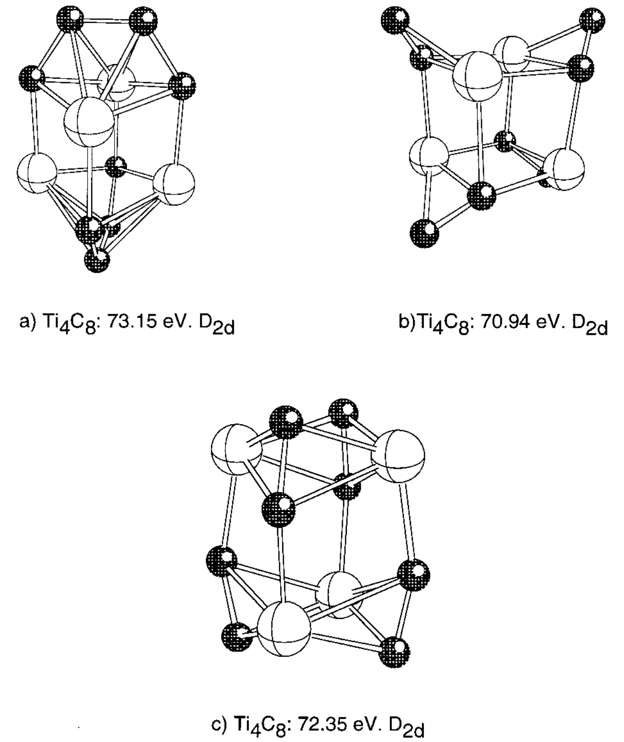
3.1 Low Nuclearity Clusters. The structures of the clusters optimized in the present work are represented in Figures 2−5, with their binding energies in the neutral form. Next to those conformations are presented the structures of lowest energy proposed by Wang et al.[14] and reoptimized at the same level of theory for the sake of comparison. The total binding energies and the binding energies per atom calculated for the neutral clusters and for their anions, both in their optimal geometries, are displayed in Table 1. For the lowest nuclearity clusters, energy minima were obtained for structures involving two bent chains of four carbon atoms each accommodated in two perpendicular planes. For Ti_3C_8, however, the lowest energy minimum (−66.73 eV) was obtained for a totally nonsymmetric conformation in which one such C_4 chain has been broken into two C_2 fragments (Figure 2a). For Ti_3C_8 and Ti_4C_8, all reported conformations containing at least one C_4 chain are more stable than structures exclusively composed of C_2 fragments connecting the metal atoms (Figures 2 and 3). Although it may be hazardous to correlate the relative stabilities of small clusters with their structures, it should be noticed that the presence of one or two C_4 chains increases the number of stable carbon−carbon bonds without reducing the potentiality for metal−ligand stabilizing interactions. This latter condition is fulfilled because of the high C/Ti ratio observed in low nuclearity "magic" clusters. For clusters with more than four metal atoms, the C/Ti ratio decreases to values lower than 2, with the notable exception of $Ti_6C_{13}^-$ which retains most of the stability associated with the MetCar structure. This decrease of the C/metal ratio will obviously favor the dispersion of the carbon phase in high nuclearity clusters, thus explaining the marked predominance of very small carbon fragments such as C_2 dimers and single carbon atoms. For the most stable form of Ti_3C_8, a formal



a) Ti_3C_8: 66.73 eV. C_1 b) Ti_3C_8: 66.34 eV. C_2

c) Ti_3C_8: 66.07 eV. C_s d) Ti_3C_8 : 65.42 eV. D_{3h}

Figure 2. (a,b,c) Optimized conformations of lowest energy for neutral Ti_3C_8; (d) conformation proposed by Wang et al.[14] reoptimized at the present level of calculations. Total bonding energies (eV) are given with respect to free atoms in their ground state.



a) Ti_4C_8: 73.15 eV. D_{2d} b) Ti_4C_8: 70.94 eV. D_{2d}

c) Ti_4C_8: 72.35 eV. D_{2d}

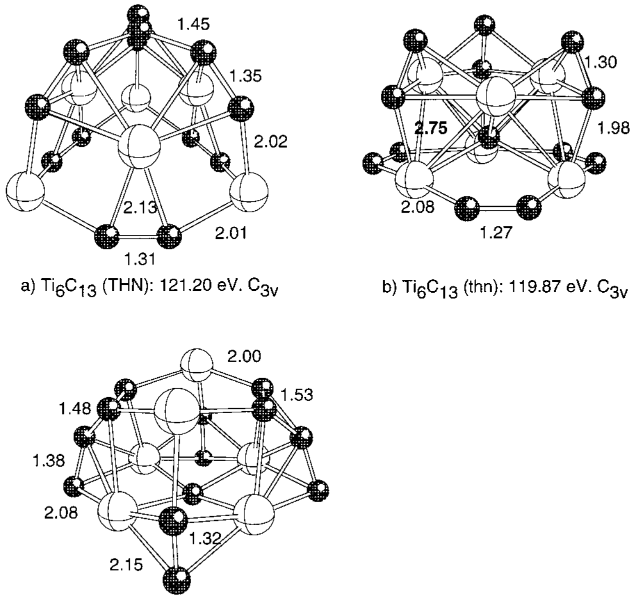
Figure 3. (a) Optimized conformation of lowest energy for Ti_4C_8; (b) and (c) conformations proposed by Wang et al.[14] and Ge et al.,[24] respectively, reoptimized at the present level of calculations. Bonding energies (eV) as in Figure 2.

electron count based upon two acetylene-like $(C_2)^{2-}$ and a butadiene-like $(C_4)^{6-}$ fragments would assign two electrons to the titanium backbone, then offering possibilities for back-bonding interactions. At variance from that, the structure with D_{3h} symmetry composed of three peripheral C_2 dimers and two capping carbon atoms separated by 1.61 Å could involve titanium atoms with oxidation state IV if the central carbon dimer is considered as a $(C_2)^{6-}$ fragment with a single s bond. The Mulliken population analysis seems to support this picture since the charge of the Ti atoms is $+0.95e$ in the D_{3h} form compared to an average value of $+0.63e$ in the unsymmetrical form of lowest energy. A similar electron counting would also assign the oxidation state IV to titanium structures involving *two* butadiene-like C_4 chains arranged in a conformation with either C_2 or C_s symmetry (Figure 2b,c). This could explain why those conformers were found less stable by 0.39 and 0.67 eV, respectively, than the structure with lowest energy.

In Ti_3C_8 and Ti_4C_8, the C_4 chains display the same bent conformation as in *cis*-butadiene, but the bond alternation characteristic of the free hydrocarbon has practically disappeared. In the C_4 chain of the unsymmetrical Ti_3C_8 cluster, the average length of the terminal C−C bonds is 1.34 Å, same as the length of the central bond. In the more regular Ti_4C_8 cluster (D_{2d} symmetry), the C−C distances are somewhat longer ($C-C_{term} = 1.41$ Å; $C-C_{cent} = 1.38$ Å) but the small trend toward bond alternation is opposite to what is observed in butadiene. This equalization of the C−C bond lengths should be assigned first to the metal to carbon back-donation which populates the p^* orbitals and then lengthens the terminal C−C bonds, and second to the overlap of the in-plane p orbitals of carbon which tends to reduce the central distance. The orbital analysis of the highly symmetrical (D_{2d}) conformer optimized for Ti_4C_8 shows that two closed-shell orbitals have a metal weight higher than 60%. The corresponding oxidation state of the metal atom, Ti(III), is in agreement with a butadiene-like representation of the C_4 chains with formal charges of 6−. The Mulliken charge of the metal is $+0.67e$, somewhat less than in the conformation proposed by Wang et al.[14] ($+0.74e$, $+0.77e$). The charges on the carbon atoms are $-0.47e$ (terminal) and $-0.21e$ (central). In Ti_4C_8, two electrons are accommodated in a degenerate orbital with *E* symmetry, which implies a triplet ground state if the D_{2d} symmetry is to be retained. Various attempts to optimize a singlet closed shell structure with lower symmetry resulted in energies higher by ~0.2 eV.

Recently, Ge et al.[24] have reported a local DFT study on the $(TiC_2)_n$, ($n = 1-6$) clusters. Those authors suggest that cyclic structures formed of TiC_2 units could participate in the MetCar formation. We think, however, that the very high energies of those cyclic structures rule out their participation in the growth mechanism of the MetCars. The same authors reported a cage structure for Ti_4C_8 which deserves more attention. Figure 3c shows a representation of this D_{2d} structure and its binding energy with respect to the atoms computed using the Becke−Perdew functional. The structure found by Ge et al. differs basically from the D_{2d} cluster described above in that the C_2 units are not connected forming C_4 chains. We can observe again that the formation of C_4 chains stabilizes significantly the clusters of low nuclearity, in this case by 0.8 eV.

3.2 Ti_6C_{13} and Ti_7C_{13}. Magic numbers in the spectrum of cluster anions with intermediate sizes are observed for $Ti_6C_{13}^-$ and $Ti_7C_{13}^-$. The conformations proposed by Wang et al.[14] for those clusters are based on a two-layer, cubic-like structure with one complete layer composed of four metal atoms (A-type layer) and one incomplete, B-type layer composed of two, or three metal atoms instead of five. The carbon phase has the same arrangement in both structures, composed of a single carbon atom at the center of the A layer, two C_2 dimers, and two bifurcated C_4 chains connecting the two layers (Figures 4c and 5d). Those structures correspond to average binding energies per atom of 6.12 and 6.06 eV for Ti_6C_{13} and Ti_7C_{13}, respectively. We think that conformations reminiscent of the MetCar T_d geometry could provide those clusters a higher stability. We



a) Ti_6C_{13} (THN): 121.20 eV. C_{3v}

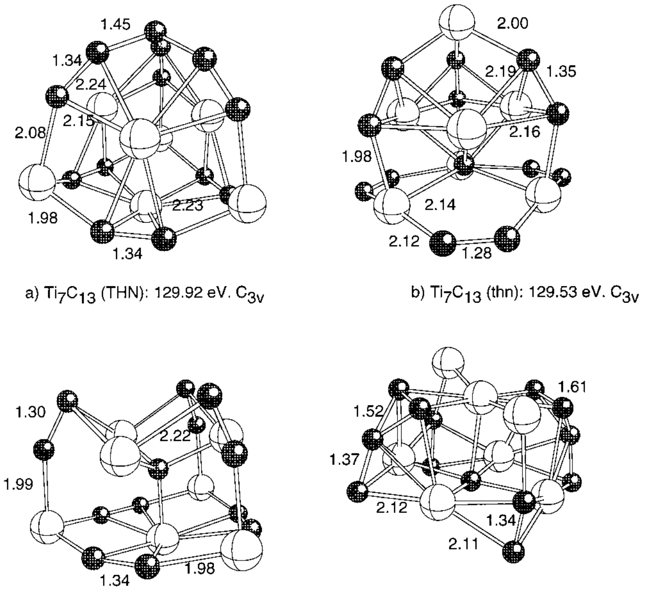
b) Ti_6C_{13} (thn): 119.87 eV. C_{3v}

c) Ti_6C_{13}: 116.35 eV. C_{2v}

Figure 4. (a,b) Optimized conformations of lowest energy for Ti_6C_{13}; (c) conformation proposed by Wang et al.[14] reoptimized at the present level of calculations. Bonding energies (eV) as in Figure 2.

had investigated in a previous work MetCar-like structures for clusters resulting from the dissociation of one or two metal atoms from Ti_8C_{12}.[16] Binding energies per atom of 6.47 and 6.24 eV were obtained for Ti_7C_{12} and Ti_6C_{12}, respectively, showing that the Dance-like structure retains a large part of its original stability (B.E./atom = 6.58 eV) despite the considered alterations.

The starting geometries of our MetCar-like structures for Ti_7C_{13} were obtained by just replacing one titanium atom by one carbon in the optimal conformation of tetracapped tetrahedron obtained for Ti_8C_{12}. This exchange can occur in two positions, either by removing a metal atom from the inner tetrahedron, symbolized by *thn*, or by discarding a titanium atom from the large, capping tetrahedron, referred to as **THN**. The optimized structures derived from those starting points are referred to as Ti_7C_{13}(*thn*) and Ti_7C_{13}(**THN**), respectively, and are displayed in Figure 5a−c. In Ti_7C_{13}(**THN**), the shape of the original tetracapped structure has been maintained with one carbon atom as the fourth "capping" site, bonded to three C_2 fragments (Figure 5a). In another structure, also corresponding to a local energy minimum, but less stable by 2.54 eV, the capping carbon has moved from its keystone position to an endohedral location where it is bonded to four metal atoms (Figure 5c). For Ti_7C_{13}(*thn*), the optimization process has led to a single structure characterized by a migration of the extra carbon atom to an endohedral position from where it can interact with six out of the seven remaining metal atoms (Figure 5b). Both the Ti_7C_{13}(**THN**) and the Ti_7C_{13}(*thn*) conformations are extremely stable in the neutral form, with binding energies per atom amounting 6.50 and 6.48 eV, respectively. Those values are considerably higher than those obtained either for smaller nuclearity clusters (6.07−6.10 eV/atom) or for the optimal structures obtained for Ti_6C_{13} or Ti_7C_{13} assuming the cubic structural motif (6.06−6.12 eV/atom, Table 1). They approach, in fact, the value of 6.58 eV/atom obtained for Ti_8C_{12}, then substantiating the special stability associated to the T_d cage motif. It should be noticed that such a high order of magnitude for the binding energy per atom has been obtained only for the MetCar-like structures and for the layered-cubic conformations of Ti_9C_{15} and $Ti_{13}C_{22}$.[14] Those latter conformations are characterized by the presence of two or three *complete* layers of metal atoms. The production of a regular structure of metal layers therefore seems a prerequisite for the cubic-like structures to compete with MetCar cages.



a) Ti_7C_{13} (THN): 129.92 eV. C_{3v}

b) Ti_7C_{13} (thn): 129.53 eV. C_{3v}

c) Ti_7C_{13} : 127.38 eV. C_{3v}

d) Ti_7C_{13} : 121.24 eV. C_{2v}

Figure 5. (a,b,c) Optimized conformations of lowest energy for Ti_7C_{13}; (d) conformation proposed by Wang et al.[14] reoptimized at the present level of calculations. Bonding energies (eV) as in Figure 2.

The binding energy calculated for $Ti_7C_{13}^-$ still approaches more closely that of the MetCar anion, but contrary to the order of the relative stabilities computed for the two conformations of neutral Ti_7C_{13}, $(Ti_7C_{13})^-$(*thn*) is now more stable by 0.23 eV than the other anionic conformer (Table 1). It is important to determine which of the two MetCar-like conformations of $Ti_7C_{13}^-$ is responsible for the peak observed on the mass spectrum of cluster anions, since the structure of the selected form may have consequences concerning the crystal growth mechanism and the structure of higher nuclearity clusters. The layer-by-layer growth pathway proposed by Wang and Cheng[15] has been first assessed on the impossibility of obtaining multicage structures as soon as the single $Ti_8C_{12}^-$ was missing in the mass spectrum. However, if Dance-like structures are substantiated for $Ti_7C_{13}^-$, then the growth of multicage clusters cannot be abruptly ruled out. This possibility would become especially attractive if the **THN** form was shown to be the preferred conformation for $Ti_7C_{13}^-$. In such a case, a double cage similar to that represented by Wang and Cheng in Figure 1c of ref 15 could be generated from two Ti_7C_{13}(**THN**) clusters sharing a face composed of one Ti atom and four atoms belonging to the bifurcated carbon chain and including the apex. The generation of a double cage with the stoichiometry $Ti_{13}C_{22}$ appears less probable from the *thn* conformer of Ti_7C_{13} because of the higher dispersion of the carbon phase: the definition of a shared face composed of one Ti and four C atoms would appear somewhat arbitrary from that structure.

The calculation of the adiabatic electron affinity assuming the structure optimized for the anion fortunately provides a discriminating property. Those values are 1.39 and 1.96 eV for Ti_7C_{13}(**THN**) and Ti_7C_{13}(*thn*), respectively. Only the latter value agrees with the experimental electron affinity reported by Wang et al. which is 2.1 eV.[14] We therefore conclude that the $Ti_7C_{13}^-$ cluster detected at the mass spectrometer has a MetCar-like structure corresponding to the *thn* conformer (Figure 5b). This structure is computed to be most stable by ∼0.2 eV *for the anion*, but not for the neutral form (Table 1). Since the *thn* conformer does not provide an easy way to generate multicage complexes, we think that the layered cubic structures proposed by Wang and Cheng[15] remain most probable for $Ti_{13}C_{22}^-$ and other high nuclearity titanium carbide *anions*. However, the change in the relative stabilities of the two conformers when considering the *neutral* form of Ti_7C_{13} suggests that the formation of multicage structures from that cluster cannot be excluded, depending upon the experimental conditions. It should be remembered that, according to the calculations of Wang and Cheng, the double cage structure for $Ti_{13}C_{22}$ is no more than marginally destabilized with respect to the C_2-decorated cubic form (DE = 1.33 eV; DE/atom = 0.04 eV) at a level of theory that does not account for the gradient corrections.[15] The delicate energetical balance obtained between the two MetCar-like conformations of Ti_7C_{13} on one hand, between the C_2-decorated cubic and the double-cage structures on the other hand, suggest that multiple cage structures cannot be excluded either for high-nuclearity M/C clusters obtained with other early transition metals such as Zr or Nb.

The conformations optimized for Ti_6C_{13} are also deduced from the tetracapped MetCar cage from which two opposite metal atoms have been removed, one belonging to *thn*, the other to **THN**. In the structure of lowest energy, the extra carbon atom occupies a **THN** site and forms the apex of a bifurcated carbon chain similar to that of Ti_7C_{13}(**THN**) (Figure 4a). The total binding energy is ∼5 eV below that of the cubic-like form proposed by Wang et al.,[14] but the decrease of the B.E. per atom (6.38 eV) with respect to the 20-atom T_d structures (Table 1) illustrates the alteration of the MetCar motif. In another structure reminiscent of Ti_7C_{13}(*thn*), the extra carbon occupies an endohedral position and is bonded to the six remaining titanium atoms (Figure 4b). The neutral cluster in that conformation is, however, less stable by 1.3 eV.

4. Electron Affinities

The structures proposed by Wang et al.[14] for titanium carbide clusters were validated by the excellent agreement obtained with experiment for the computed adiabatic electron affinities. For the four investigated clusters with lowest nuclearity (Ti_3C_8, Ti_4C_8, Ti_6C_{13}, and Ti_7C_{13}), the average gap between the experimental and the computed values did not exceed 0.21 eV. This average deviation increases slightly (up to 0.26 eV) when the electron affinities are computed at the level of the theory used in the present work. Since we propose markedly different structures for those clusters, the criterion of the total binding energy is clearly insufficient; we have to prove that the agreement obtained by Wang et al.[14] concerning the physical properties could have been fortuitous, and that an agreement of similar or even better quality is obtained with the structures of lowest energy. We have therefore calculated the adiabatic electron affinities, based on the structures optimized for the anions. The results are displayed in Table 2. The average discrepancy with experiment amounts 0.15 eV for the four considered clusters. If this agreement is not sufficient by itself to fully validate the proposed structures—the proof is given that such an agreement can be fortuitous—it shows that the conformations optimized in this work are compatible with the presently available experimental data and that the indications provided by the relative binding energies should be considered seriously.

TABLE 2: Adiabatic Electron Affinities (E.A.) and Ionization Potentials (I.P.) Calculated for Titanium Carbide Clusters in the Conformations Studied in the Present Work[a]

	Ti_3C_8	Ti_4C_8	Ti_6C_{13}	Ti_7C_{13}(*thn*)	Ti_8C_{12}
E.A. (this work)	2.52	1.52	2.05[b]	1.96	1.30
E.A.[c]	2.33	2.12	2.3	2.34	
E.A.[d]	2.55	2.08	2.46	2.46	
E.A. (expt)[14]	2.5	1.8	2.2	2.1	1.05
I.P. (this work)	7.30	6.15	6.04[b]	6.73	4.43

[a] Experimental values reported by Wang et al.[14] and theoretical estimates proposed by the same authors assuming C_2 decorated layered cubic structures are remembered; all values are in eV. [b] Conformation of lowest energy, referred to in Figure 4 as Ti_6C_{13}(**THN**). [c] Electron affinities reported by Wang et al.[14] [d] Computed electron affinities for the Wang et al.[14] structures at the level of theory used in the present work.

There is no real guarantee that a structure optimized by means of energy gradient minimization correlates with the conformation of the real cluster because the optimization process carried out on a complex potential hypersurface will not necessarily converge toward the deepest energy minimum. It is at least possible to check that the obtained conformation corresponds to a real energy minimum for the considered electronic state and not to a saddle point obtained because of the symmetry constraints. Such artifacts can be detected by the presence of imaginary frequencies in the force field. We have checked for the presence of imaginary frequencies in all the conformations reported in the present work for the neutral clusters. No such frequencies were detected for Ti_3C_8, Ti_4C_8, Ti_6C_{13}, and Ti_7C_{13}(**THN**). For Ti_7C_{13}(*thn*), three weakly negative frequencies were found (−87, −87, and −68 cm^{-1}). These three negative frequencies are associated with small rotations of the three C_2 units that do not participate in π interactions in the *thn* structure. The energy of this structure decreases slightly (∼1 kcal mol^{-1}) when the constraints of symmetry are removed and the geometry is previously distorted according to displacement vectors associated to the three negative frequences. The only noticeable difference between the C_{3v} and C_1 geometries appears in the three above-mentioned C_2 units. Hence, while the distances of the six carbons to the inner carbon are equal to 2.97 Å in the symmetric structure, these distances range between 2.83 and 3.05 Å in the distorted conformation. Although, the number of atoms and the lack of symmetry makes impracticable the calculation of the vibrational frequences for the C_1 structure, we think that the energy lowering confirms that the structure has evolved from a stationary point in the C_{3v} symmetry toward a minimum of the potential surface. Imaginary frequencies were also found for several of the symmetric structures proposed by Wang et al[14]: Ti_3C_8(3), Ti_4C_8(3), Ti_6C_{13}(1), and Ti_7C_{13}(3). Most of those frequencies have an absolute value lower than 100 cm^{-1}. This order of magnitude is more important, however, for the largest imaginary frequency obtained for Ti_7C_{13} (−207 cm^{-1}) and especially for Ti_4C_8 (−517 cm^{-1}). This suggests that the associated structures could correspond to saddle points constrained by symmetry.

5. $Ti_8C_{12}^-$: A Rydberg Ground State?

A puzzling question remains unanswered: how can one explain the lack of $Ti_8C_{12}^-$ in the mass spectrum of titanium carbide anions while the binding energy of the MetCar anion (132.9 eV) is calculated to be larger than that of the “magic” $Ti_7C_{13}^-$ (131.5 eV)? Wang, Li, and Wu discussed the problem and proposed to link the vanishing of the MetCar peak in the anion spectrum with the exceedingly low value observed for the electron affinity of Ti_8C_{12} (1.05 eV).[8] An analysis of the energies obtained for the highest occupied orbital of the

TABLE 3: Electronic State and Energy of the Highest Occupied Kohn−Sham Orbital (eV) Obtained for Titanium Carbide Clusters and Their Anions in the Conformations Studied in the Present Work

	Ti_3C_8	Ti_4C_8	Ti_6C_{13}	Ti_7C_{13}(*thn*)	Ti_7C_{13}(**THN**)	Ti_8C_{12}
neutral state	singlet	triplet	triplet	singlet	singlet	triplet
HOMO	−4.94	−3.90	−4.13	−4.92	−3.48	−3.19
anion state	doublet	quartet	doublet	doublet	doublet	quartet
HOMO	−0.34	+0.55	+0.02	−0.16	+0.30	+0.29

investigated clusters allows us to clarify this hypothesis. Those orbital energies are displayed in Table 3. For most cluster anions, the HOMO has an energy which is either negative or very close to zero ($Ti_6C_{13}^-$), which can be interpreted as the sign of a certain stability for the anionic form of the cluster. Moreover, this negative or zero eigenvalue can be correlated with a relatively high electron affinity, accounting for the relaxation of the electron density, and suggests that the additional electron can be adequately described by means of the standard valence basis set. However, the MetCar anions $Ti_8C_{12}^-$ and $Zr_8C_{12}^-$ do not follow that way. The lowest electronic configuration of those anions is a quartet state with an energy of +0.29 eV ($Ti_8C_{12}^-$) or +0.36 eV ($Zr_8C_{12}^-$) for the triply degenerate orbital. Those positive values suggest that the description of $Ti_8C_{12}^-$ by means of valence orbitals only is inadequate and that the additional electron will tend to populate a very diffuse orbital—if available in the basis set—thus giving rise to a molecular Rydberg state. An attempt has been made to supplement the basis set with a single diffuse Slater orbital originating at the center of symmetry of the cluster. Preliminary results indicate that the transfer of the additional electron to the diffuse orbital (exponent 0.111, maximum density at ~4.2 Å from the center) yields a significant decrease of the energy, but technical and theoretical problems remain to be solved for the DFT calculation of molecular Rydberg states.

The hypothesis of a molecular Rydberg ground state for $Ti_8C_{12}^-$ and $Zr_8C_{12}^-$, based upon the positive energy obtained for the HOMO, obviously explains the very low value obtained for the electron affinity. The presence of a loosely attached electron could also elucidate the observed instability of the MetCar anions. This electron might easily be detached or captured in the supersonic cluster beam from where anions are extracted.[8] Those MetCar anions will therefore be lacking in the mass spectrum, despite their overwhelming global stability.

It is interesting to notice that some of the cluster conformations investigated in the present study are also characterized by a positive HOMO value for the anion. This is the case for the **THN** conformation of $Ti_7C_{13}^-$, which had been already ruled out because of the very low value, incompatible with experiment, computed for its electron affinity. The case of $Ti_4C_8^-$ is more puzzling. Assuming the same D_{2d} symmetry as for the neutral form, the cluster anion has a HOMO with a highly positive energy (+0.55 eV). The electronic ground state is a quartet, followed by a doublet state at +0.24 eV. The computed adiabatic electron affinity associated with the quartet ground state (1.52 eV) is rather low compared to the experimental value of 1.8 eV. A distortion toward a conformation with lower symmetry therefore seemed probable, but could not be evidenced from the calculations.

6. Summary and Conclusions

DFT calculations and geometry optimizations have been carried out on some of the titanium carbide clusters characterized as "magic peaks" on the mass spectrum of Ti/C cluster anions. Those calculations have led us to propose new structures for the ground states of Ti_3C_8, Ti_4C_8, Ti_6C_{13}, and Ti_7C_{13} and their anions. The two smallest nuclearity clusters are characterized by the presence of one or two C_4 chains that can be described as altered *cis*-butadiene backbones without bond alternation. The conformations proposed for Ti_6C_{13} and Ti_7C_{13} are strongly reminiscent of the structure of tetracapped tetrahedron assumed by most recent theoretical treatments to be optimal for M_8C_{12} MetCar clusters. An analysis of the conformation most probable for the $Ti_7C_{13}^-$ precursor suggests that the higher nuclearity clusters observed in the mass spectrum of Ti/C anions should display the C_2-decorated layered cubic structure recently proposed by Wang and colleagues.[14,15] However, the multicage growth path advocated by Castleman's group[11,12] cannot be ruled out for high nuclearity metal carbide clusters involving zirconium, niobium, or even titanium if obtained from neutral or cationic precursors. Finally, the puzzling absence of $Ti_8C_{12}^-$ and $Zr_8C_{12}^-$ from the mass spectrum of anionic clusters is interpreted by the existence of MetCar anions as molecular Rydberg species in which the loosely attached electron can be easily removed despite the overall stability of the MetCar anion.

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