LETTERS

Photoelectron Spectroscopy and Electronic Structure of Met-Car Ti$_8$C$_{12}$

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Photoelectron spectroscopy experiments are performed on a metallocarbohedre, Ti$_8$C$_{12}^-$, to obtain electronic
structure information. The Ti$_8$C$_{12}^-$ anion is produced by laser vaporization of a titanium carbide target. The
spectra of Ti$_8$C$_{12}^-$ consist of an intense threshold feature and two weaker features followed by a gap and
more higher energy features. The electron affinity of Ti$_8$C$_{12}$ is found to be 1.05 (±0.05) (adiabatic) and 1.16
(±0.05) eV (vertical). The surprisingly low electron affinity and the observed electronic features are interpreted
using theoretical electronic structure information. The current experiments provide hitherto the most direct
spectroscopic information on the Met-Car Ti$_8$C$_{12}$.

The discovery of the metallocarbohedrenes (Met-Cars) by
Castleman and co-workers represents a significant development
in cluster science following the discovery and subsequent bulk
synthesis of fullerences. The Met-Cars (M$_8$C$_{12}$) consisting of
8 early transition metal atoms and 12 carbon atoms are expected
to exhibit even richer chemical and physical properties that may
find applications in electronics, catalysis, and magnetic materials.
The original discovery has been followed by intensive theoretical
and experimental works. However, its structure is still the center of much contention. In particular, the
lack of direct spectroscopic information makes it difficult to
verify the various theoretical calculations.

Castleman et al. initially proposed a dodecahedral structure
($T_h$) for the Met-Cars. Chemical reaction studies are used to
support this structure. It can be viewed as a cubic M$_8$ cluster
with six C$_2$ units capping the six faces of the cube. Theoretical
considerations predict that Ti$_8$C$_{12}$ with $T_h$ symmetry will undergo
Jahn–Teller distortion. Several calculations have suggested
lower symmetry structures with much lower energies. The
most stable one is a tetrahedral cluster ($T_d$), which has received
the most theoretical attention recently. It involves distorting
the M$_8$ cube into a tetracapped tetrahedral M$_8$ cluster with
the six C$_2$ units along the six edges of the outer tetrahedron formed
by the four capping M atoms. Ion chromatography (IC)
experiments suggest that the $T_h$ Met-Car (Ti$_8$C$_{12}^+$) fits the IC
data best but cannot exclude the $T_d$ structure within the
experimental uncertainty. Recent chemical reaction experi-
ments on V$_8$C$_{12}^+$ and Nb$_8$C$_{12}^+$ seem to suggest that they are
consistent with the $T_d$ structure.

Theoretically, the $T_d$ structure is vastly more stable than the
$T_h$ structure by as much as 300 kcal/mol. Extensive theoretical efforts have been made on the $T_d$ structure with explicit predictions for its electronic structure. In principle, experimental electronic structure information can be used to test these predictions. Unfortunately, there are scarce experimental electronic structure information and few quantitative experimental data to test the different calculations. Chemical reaction studies of Ti$_8$C$_{12}^+$ with halogen
hydrocarbons found that Ti$_8$C$_{12}^+$ is able to abstract one halogen
atom to form Ti$_8$C$_{12}$(L)$^+$ (L = Cl, I), suggesting that Ti$_8$C$_{12}^+$
has one unpaired electron that can be donated to the halogen

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atom. Recent experiments on the ionization potentials (IP) of the Met-Cars find an anomalously low IP for Ti₈C₁₂ (4.9 ± 0.2 eV). Photoelectron spectroscopy (PES) of size-selected anions has been a powerful technique to probe the electronic structure of metal clusters. Here we present the first PES study on the Met-Car Ti₈C₁₂⁻, providing direct electronic structure information.

The apparatus used in this work has been described in detail previously. The key in the current experiment is how to produce the Met-Car Ti₈C₁₂⁻ anion. The Met-Car cation (Ti₈C₁₂⁺) was originally discovered by laser vaporization of pure titanium with a hydrocarbon seeded helium carrier gas. The plasma reactions between the laser-vaporized titanium atomic species and the hydrocarbons produce the magic Met-Car. Laser vaporization conditions: 3 mJ/pulse at 532 nm, 7 ns pulse width. (d) Negative ion mass spectrum of Ti₈C₁₂⁻ clusters under similar conditions as (c) (7 mJ/pulse), showing that the Met-Car anion Ti₈C₁₂⁻ is produced with significant abundance (see refs 16 and 18).

Figure 1. (a) Positive ion mass spectrum of Ti₈C₁₂⁺ clusters when a titanium target is vaporized with a 5% CH₄ seeded helium carrier gas, showing the “magic” Ti₈C₁₂⁺ Met-Car. Laser vaporization conditions: 10 mJ/pulse at 532 nm, 7 ns pulse width. (b) Negative ion mass spectrum of Ti₈C₁₂⁻ clusters under similar conditions as (a), showing that the anticipated Met-Car anion Ti₈C₁₂⁻ is not produced (see text). (c) Positive ion mass spectrum of Ti₈Cₓ⁺ clusters when a solid TiC target is vaporized with neat helium carrier gas, showing the “magic” Ti₈C₁₂⁺ Met-Car. Laser vaporization conditions: 3 mJ/pulse at 532 nm, 7 ns pulse width. (d) Negative ion mass spectrum of Ti₈Cₓ⁻ clusters under similar conditions as (c) (7 mJ/pulse), showing that the Met-Car anion Ti₈C₁₂⁻ is not produced (see text).

With the TiC target, the Ti₈C₁₂⁻ anion is still not magic, it is produced with significant abundance (see refs 16 and 18). The Ti₈C₁₂⁻ clusters are produced by laser vaporization of a solid TiC target with neat helium carrier gas. Figure 1c shows a positive mass spectrum when only 3 mJ/pulse vaporization power is used. We find that the TiC target yields more abundant Ti₈Cₓ⁺ clusters and the magic Ti₈C₁₂⁺ is easily made. Higher vaporization power is required in the pure Ti/CH₄ case to produce an intense plasma for the dehydrogenation reactions necessary to produce the Ti₈Cₓ clusters. Figure 1d shows the negative ion mass spectrum with the TiC target under similar conditions as in Figure 1c. It is quite different from Figure 1b. Even though here the Ti₈C₁₂⁻ cluster is not magic, it is produced with significant abundance. We will show below that the low abundance of Ti₈C₁₂⁻ is due to the unusually low electron affinity of Ti₈C₁₂⁻.

With the TiC target, the Ti₈C₁₂⁻ cluster anions are produced at every 12 amu starting from TiCᵩ⁻. We have obtained PES spectra for all the mass channels starting from TiCᵩ⁻ up to Ti₈C₁₂⁻. Figure 2 displays the spectra of Ti₈Cₙ⁻ (y = 10–14) taken at two different photon energies, 3.49 and 4.66 eV. The Ti₈C₁₂⁻ spectrum is quite special with an intense threshold peak, from which we obtain the electron affinity (EA) of Ti₈C₁₂⁻, 1.05 (±0.05) (adiabatic) and 1.16 (±0.05) eV (vertical). The Ti₈C₁₂ cluster has the lowest EA among the species shown in Figure 2. In fact, it is among the lowest EA species of all the Ti₈Cᵧ⁻ clusters that we have measured from TiC₄ up to Ti₈C₁₂⁻. This anomalously low EA for Ti₈C₁₂⁻ is at least partially responsible for the low mass abundance of Ti₈C₁₂⁻ (Figure 1d).
be viewed as an acetylene-like unit (C_2^2)

signals at higher binding energies are also observed. These
electrons too many to make the
2t_2 orbital. The filling of the nine bonding orbitals

The anomalous EA and the well-defined spectral features of
three different photon energies are compared in Figure 3. At 3.49 eV, three features are clearly
A (1.16 eV) and B (1.81 eV). More transitions are
6.42 eV spectrum but are not well resolved due to poor signal-to-noise ratio. The features A and B are barely
visible in the 6.42 eV spectrum due to poor resolution and lower signals at this photon energy. It can be seen from the 6.42 eV
spectrum that the spectral features may be divided into two groups, the lower energy features (X, A, B) followed by a small
electron gap (0.7 eV) and more transitions at higher BE (C and D).

The anomalous EA and the well-defined spectral features of

Under the T_d structure, the six C_2 units are end-on bonded to the four outer Ti atoms through σ bonding and side-on bonded to the four inner Ti atoms through π bonding. Each C_2 may be viewed as an acetylene-like unit (C_2^2). Each metal atom

Figure 3. Comparison of the photoelectron spectra of Ti_8C_{12^-} at three
photon energies: top, 355 nm (3.49 eV); middle, 266 nm (4.66 eV); bottom, 193 nm (6.42 eV).

Figure 4. Schematic orbital diagram showing the valence molecular orbitals resulting from the metal–metal interactions for a tetracapped Ti_8C_{12^-} Met-Car (from ref 6a). It is used to interpret the observed photoelectron spectra of Ti_8C_{12^-}. In the anion, Ti_8C_{12^-}, the extra electron resides in the 2t_2 orbital.

has three d orbitals for metal–metal interactions that form the valence orbitals of the Met-Car. Figure 4 shows a schematic orbital diagram for these interactions,6a where 1a_1, 1t_2, 1e, and 1t_1 are bonding orbitals and 2a_1, 2t_2, 3t_2, 2e, 2t_1, and 4t_2 are antibonding orbitals. The filling of the nine bonding orbitals is expected to make an especially stable cluster. Among the 32 valence electrons on the Ti atoms in Ti_8C_{12^-}, only 20 are available for the metal–metal interactions (12 are donated to the 6 C_2 units). These are two electrons too many to make the stable 18-electron configuration. The two extra electrons fill the higher energy 2a_1 orbital. This is consistent with the low IP measured for the Ti_8C_{12^-} Met-Car since the 2a_1 electrons are expected to be easily ionized. In fact, it has been suggested that the dication [Ti_8C_{12}^{2+}] might be specially stable and may be the best target for synthesis in bulk form.6a Figure 4 is also consistent with the halogen abstraction experiments that suggest that the Ti_8C_{12}^+ cation has one unpaired electron.10 Our PES spectra shown in Figure 2 can be understood on the basis of this orbital diagram.

In the anion, the extra electron enters the 2t_2 orbital. Since the 2t_2 orbital is further up in energy, a low EA for Ti_8C_{12} is easily understandable. The occupation of the 2t_2 orbital leads to a ^2T_2 degenerate ground state for Ti_8C_{12^-}, which is subject to Jahn–Teller distortion. Within the single-particle picture, the detachment of the electron from the 2t_2 orbital yields the ground state PES feature (X, Figure 3). The width of this feature suggests that there is a geometry change from the anion to the neutral transition. This may be due to the anticipated Jahn–Teller effect. The removal of a 2a_1 electron will produce the two low-lying states (A and B, Figure 3) due to the singlet–triplet coupling. The A feature with lower energy is likely to be the singlet state by removing a spin-up 2a_1 electron, while the B state is the triplet state due to the removal of the spin-down 2a_1 electron. The A–B energy separation yields a singlet–triplet coupling energy of ~0.25 eV. Following an energy gap of ~0.7 eV, the C and D features are from removal of electrons from the highest occupied bonding orbitals (1t_1). Even higher energy features seen in the 6.42 eV spectrum are then due to removal of electrons from other bonding orbitals. The relative intensities of the spectral features support the various orbital characteristics. The A and B features have the lowest intensities because their orbital origin (2a_1) is nondegenerate.
Thus the electronic structure of the $T_d$ Ti$_7$C$_{12}$ is not only consistent with several experimental observations, such as low IP (high cation abundance), chemisorption of only four $\pi$-bonding molecules, low EA (lower abundance of anion), and halogen abstraction reactions, but also allows a detailed interpretation of the current PES spectra. These lend considerable credence to the validity of this structure. More accurate ab initio calculations that can consistently predict precise IP and EA values in agreement with the experimental measurements should provide the definitive structure for the Met-Cars.

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References and Notes


(16) The apparent continuous mass distribution is caused by the mass coincidence between one Ti and four C. When a ZrC or CrC target is used, we observe that the cluster distributions are grouped according to a given number of metal atoms. For the CrC case, we observe a slightly magic Cr$_{12}$ mass peak along with Cr$_{2}$C$_{5}^{-}$ ($y = 10, 11, 13, 14$). The clusters with likely stoichiometry to overlap with Ti$_{12}$C$_{5}^{-}$ and Ti$_{7}$C$_{5}$ are Ti$_{15}$C$_{5}^{-}$ and Ti$_{14}$C$_{5}^{-}$. From the range of metal–carbon compositions for the M,C$_{y}$ clusters observed for the Zr or Cr systems, these compositions are unlikely.


(18) The special nature of the PES spectrum of Ti$_{7}$C$_{12}^{+}$ suggests that it has little or no contamination from other Ti$_{x}$C$_{y}$ clusters. Additionally, the Ti$_{7}$C$_{5}^{-}$ cluster produced using Ti/CH$_{4}$ gives a very different PES spectrum with much higher electron binding energies.

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