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Beyond Metallo–Carbohedrenes: Growth and Decomposition of Metal–Carbon Nanocrystals

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Abstract: The recently discovered family of metal–carbon clusters, designated metallo–carbohedrenes or "met-cars" by Castleman and co-workers, are reinvestigated with a focus on titanium and vanadium systems. In addition to the stable $M_8C_{12}^+$ clusters reported previously, a family of larger metal–carbon systems are observed. Mass spectroscopy and mass-selected laser photodissociation measurements are used to investigate the structures and stabilities of these systems, which contain up to 60 atoms in the cluster framework. The larger metal–carbon species exhibit 1/1 M/C stoichiometries characteristic of cubic lattice structures and are therefore designated as "nanocrystals". The species $Ti_{14}C_{13}^+$ and $V_{14}C_{13}^+$, which are proposed to have the 3 × 3 × 3 cubic structure, are especially abundant and are believed to have stabilities comparable to those of the M_8C_{12} species. Photodissociation of larger nanocrystals produces both the 8/12 and 14/13 stoichiometries as abundant photofragments. Evidence is also presented for the formation of endohedral met–car clusters containing a central carbon atom, which are formed as photodissociation products from larger systems.

Introduction

Castleman and co-workers recently reported the formation of especially stable metal–carbon clusters designated "metallo–carbohedrenes", or "met–cars".[1–4] In their work, metal–carbon clusters having the formula M_8C_{12} form preferentially from plasmas containing a carbon precursor and transition metals (e.g., Ti_8C_{12} and V_8C_{12}). A structure consisting of a pentagonal dodecahedron with T_h symmetry has been proposed for these clusters. Larger zirconium clusters of this same family are proposed to have structures composed of multiple connected dodecahedron cages.[3] In recent work from our own laboratory, chromium, iron, and molybdenum met–car analogs were also produced and characterized.[5] The unusual bonding stability believed to be characteristic of these systems[6–10] has been theoretically investigated. These clusters are extremely interesting because of their potential for the production of catalytic or electronic materials with novel properties. They are also interesting for their possible relation to the "fullerene" family of carbon clusters,[11–15] where metal doping is a focus of intense activity.[16–23] In this report, we describe the formation and investigation of extended metal–carbon networks of titanium and vanadium beyond the M_8C_{12} species reported previously.

Previous investigations of met–car clusters have focused on the special M_8C_{12} stoichiometry (henceforth 8/12) exhibited in mass spectral distributions and on the ability of these clusters to chemisorb specific numbers of molecular ligands.[1–4] In recent studies from our laboratory, photodissociation experiments have also investigated the properties of the titanium, vanadium, and zirconium met–car systems first studied by Castleman,[24] as well as the chromium, iron, and molybdenum analogs synthesized in our laboratory.[5] These studies establish that the various met–car clusters have unique structure and bonding properties distinctly different from those of metal–carbon clusters in the metallo–fullerene family. In the studies here, both mass spectra and photodissociation mass spectra are examined for metal–carbon clusters containing titanium and vanadium which are larger than the 20-atom species reported previously (i.e., $M_xC_y^+$; $x + y > 20$).

A central question in the study of these larger metal–carbon clusters is their structure. In the dodecahedron structure proposed for the M_8C_{12} species, there are 12 five-membered rings, with each ring containing M_2C_3. However, it is geometrically impossible to extend this five-membered-ring pattern to cages having more than 20 atoms. Larger open cages or tube structures may be formed, as illustrated in the fullerenes and their related analogs, by the introduction of six-membered rings at symmetric positions in the wall of the cluster. It is conceivable, therefore, that the met–car growth pattern at small cluster sizes gradually transforms into substituted fullerene structures, with both five- and six-membered rings, at larger cluster sizes. It is also conceivable that larger clusters containing these same elements adopt fullerene or substituted-fullerene cage frameworks with some endohedral metal. On the other hand, as suggested by Castleman,[3] it is possible to grow larger clusters which do preserve the 2/3 metal–carbon ratio in five-membered rings by the

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aggregation of multiple dodecahedron cages. For example, mass spectra of zirconium–carbon clusters provide evidence for the formation of clusters with two, three, or four cages connected by shared faces.[3] These different patterns of cluster growth should be recognizable in the mass spectra of the larger metal–carbon clusters. As shown below, the mass spectra and fragmentation patterns of the larger titanium and vanadium metal–carbon clusters do provide distinctive patterns. However, these patterns are not consistent with either multiple dodecahedron cages or fullerene-type structures. Instead, the mass spectra are characteristic of crystalline fragment structures from a face-centered cubic (fcc) lattice, with a ratio of elements near 1/1. Additionally, the smaller met–car clusters and the larger fcc systems are found to be related in that the decomposition of the fcc crystal fragments produces the met–car M_8C_{12} species.

Experimental Section

Metal–carbon clusters are generated with a laser vaporization plasma reactor like that described by Castleman.[25,26] A rotating rod containing the metal of interest is mounted in a pulsed nozzle laser vaporization cluster source, and the expansion gas (helium) is seeded with methane or acetylene at a level of about 1%. The vaporization laser is either a XeCl excimer laser (308 nm) or the second harmonic of a Nd:YAG laser (532 nm). Vaporization of the metal sample ignites a plasma, and the hydrocarbon gas dissociates in this plasma. Mixed metal–carbon clusters grow as the plasma is quenched by collisions with excess expansion gas. Cation clusters formed in this process are cooled by the supersonic expansion and probed with a downstream reflectron time-of-flight mass spectrometer (RTOF). For measurements of mass distributions, the cation clusters formed in the laser vaporization process are extracted from the molecular beam into the RTOF with pulsed acceleration plates. For measurements of photodissociation mass spectra, the parent ion of interest is mass-selected and laser excitation occurs in the turning region of the reflectron field. The photodissociation laser for these experiments is a Nd:YAG laser (532 nm). The flight time through the remaining drift tube section provides mass analysis for the fragment ions. The operation of the RTOF instrument for these photodissociation experiments has been described previously.[27]

Results and Discussion

Figure 1 shows the mass spectrum of cation clusters produced for titanium–carbon and vanadium–carbon experiments. These spectra contain remarkable "magic number" mass peaks. The first intense peak, which is observed for both titanium and vanadium, is the $M_8C_{12}^+$ species reported previously.[1–4] Under higher vaporization laser power conditions, our source produces only this peak. However, lower vaporization laser power produces spectra like those shown here. A series of larger masses are produced for titanium, while only one larger mass is observed for vanadium. Clusters beyond the 8/12 stoichiometry have not been observed previously for these systems. We focus here on the identity and structural patterns in these larger clusters.

The second intense mass peak for titanium–carbon occurs at 828 amu. In principle, this mass could provide the stoichiometry of the cluster. However, this measurement is complicated by the mass coincidence of a titanium atom (48 amu) and four carbon atoms. There are therefore a number of stoichiometries having this mass. An isotopic experiment, using ^{13}C methane for the carbon precursor, confirms that this cluster has the formula $Ti_{14}C_{13}^+$. In the vanadium system, there is no mass coincidence. The second peak occurs at 870 amu, which determines the formula to be $V_{14}C_{13}^+$. Therefore, the second special cluster, like the first, corresponds to the same stoichiometry for both titanium and vanadium. The masses observed for both cluster peaks indicate that they contain no hydrogen, even though a hydrocarbon precursor is used in the cluster source. This surprising observation was also noted by Castleman and co-workers in their work.

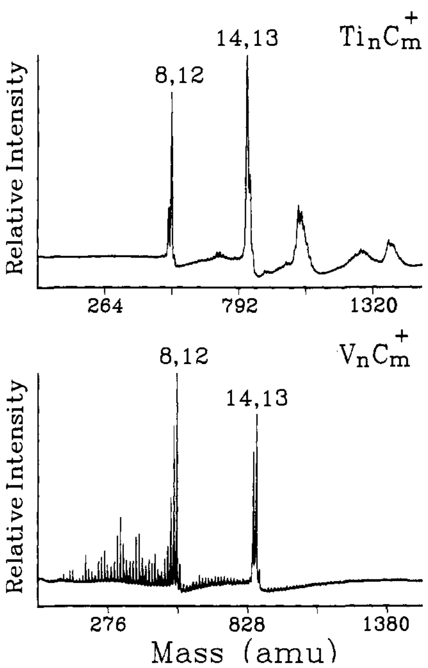
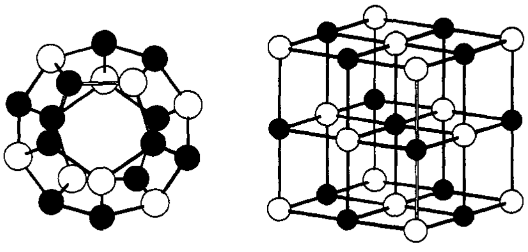


Figure 1. Mass spectra of titanium–carbon and vanadium–carbon cation clusters. The $M_8C_{12}^+$ and $M_{14}C_{13}^+$ clusters are formed preferentially. A series of larger clusters are observed for titanium.



8/12 **14/13**

Figure 2. The dodecahedron structure proposed by Castleman and co-workers for the M_8C_{12} clusters and the 3 × 3 × 3 fcc lattice fragment proposed here for the structure of the $M_{14}C_{13}^+$ clusters.

Castleman has observed larger met–car clusters for the zirconium–carbon system and has suggested that these species have structures composed of multiple dodecahedron cages.[3] However, 14/13 does not correspond to any stoichiometry reported for zirconium. It is therefore not consistent with a multiple-cage structure, and there can be no closed structure containing a single cage constructed from 27 atoms which preserves reasonable valence for the atoms. Instead, 14/13 is exactly the stoichiometry expected for a 3 × 3 × 3 fragment from a face-centered cubic (fcc) lattice. A 14/13 magic number has been reported for titanium–nitrogen clusters,[28] and this stoichiometry is well-known for alkali metal halide clusters.[29,30] A close-packed metal lattice with interstitial carbon atoms forming the fcc lattice is the bulk structure for TiC.[32] We therefore conclude that $Ti_{14}C_{13}^+$ and $V_{14}C_{13}^+$ probably have this same cubic structure, which is shown in Figure 2. A 1/1 metal/carbon cluster ratio, consistent with cubic crystalline growth, has been reported previously by

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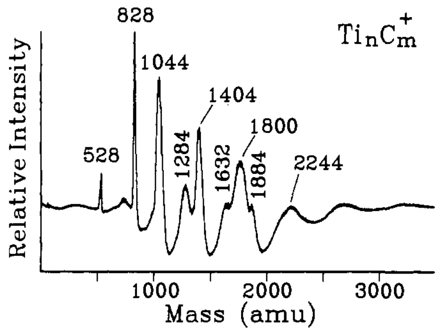

Figure 3. Mass spectrum of Ti–C clusters with the spectrometer focusing set for higher masses. Peaks indicated correspond to those listed in Table I.

Table I. Masses Observed in the Higher Molecular Weight Range Compared to the Predictions of Various Structural Schemes

		predicted masses for Ti_xC_y[b]		
obsd	multiple cages[a]	fcc	subst C_{60}	tubes
1044 ± 12		1080(1044) 18/18(17/19) 3 × 3 × 4	1044 9/51	1056 16/24
1284 ± 24	1212, 1320	1332(1296) 22/23(21/24) 3 × 3 × 5	1260 15/35	1320 20/30
1404 ± 12	1476	1440(1404) 24/24(23/25) 3 × 4 × 4	1404 19/31	
1632 ± 24	1716	1620 27/27 3 × 3 × 6	1620 25/35	1584 24/36
1800 ± 24		1800 30/30 3 × 4 × 5	1800 30/30	1848 28/42
1884 ± 24		1920(1884) 32/32(31/33) 4 × 4 × 4	1872 32/28	1848 28/42
2244 ± 100		2160 36/36 3 × 4 × 6	2232 42/18	

[a] "Multiple cages" refers to face-shared dodecahedra. [b] fcc ideal lattices are given for $x = y$ with nonstoichiometric values in parentheses. The tube and substituted-C_{60} patterns are described in the text. Stoichiometries corresponding to each mass and the fcc lattice patterns are given below it.

Castleman for the tantalum–carbon system,[3] and we have observed similar ratios for iron–carbon[5] and niobium–carbon[31] systems.

Figures 1 and 3 show that clusters even larger than 14/13 are produced for the titanium–carbon system. The deflection plates in the mass spectrometer are at their normal focusing for Figure 1, while for Figure 3 they are set to enhance masses beyond 500 amu. The larger masses are consistently reproducible for the titanium system, but they are not observed for vanadium. Unfortunately, the titanium isotope distribution, the instrument resolution, and overlapping peaks make these higher mass peaks appear broad and poorly defined. Therefore, the mass cannot be assigned exactly, and it is difficult to determine the stoichiometries for these clusters. Nevertheless, considerable insight into the cluster growth process is possible.

Table I provides a list of the higher masses observed. The table also includes masses which are predicted by several possible patterns of larger cluster growth. We compare the approximate masses observed to see if there is any correlation with those predicted by simple patterns. Four possible growth patterns are investigated: the multiple dodecahedron cage structures, the fcc lattice family, substituted C_{60}, and a family of tube structures based on the dodecahedron framework. The multiple-cage structures observed previously had up to four cages formed by dodecahedra sharing common faces.[3] Of the numerous stoichiometries predicted for fcc lattice fragments,[29,30] we indicate only those in the correct mass range. $C_{60-N}Ti_N$ species have masses of 720 + 36*N*. We consider also a family of tube structures, which could conceivably be built by beginning with a dodecahedron hemisphere and elongating this pattern in much the same way that "bucky-tubes" have been constructed.[33,34] The waist of this structure contains five six-membered rings, and additional sections would increment the system by M_4C_6, establishing a regular pattern which can be truncated with a dodecahedron hemisphere. There is no reason to expect the formation of tubes, but they are highly symmetric and they preserve the characteristic met–car M_2C_3 bonding ratio. We know of no other families of cluster structures with reasonable bonding arrangements for these elements.

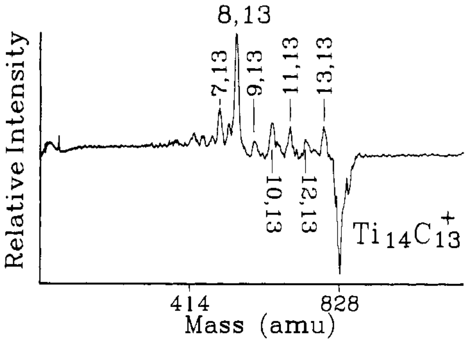

Figure 4. Photodissociation spectrum for $Ti_{14}C_{13}^+$ at 532 nm. The fragmentation pattern indicates a sequence of metal atom losses, and the most intense fragment is $Ti_8C_{13}^+$.

When the masses observed are compared to those predicted by these models, several observations are apparent. None of the first four intense peaks are predicted by the multiple-dodecahedron-cage pattern. Likewise, the tube pattern does not fit. The substituted-C_{60} pattern predicts many of the masses observed. However, the ^{13}C isotope mass shift for the 1044-amu peak is far too small for a cluster with 51 carbon atoms, thus ruling out the substituted fullerene stoichiometry for this mass. ^{13}C isotope shifts are inconclusive for clusters higher in mass than the 1044-amu peak. However, the fcc crystalline pattern predicts all of the masses observed and also is consistent with the isotope shifts which can be measured. For example, mass 1044 is explained by a 3 × 3 × 4 lattice with 36 total atoms. The ideal stoichiometry is $Ti_{18}C_{18}^+$ at mass 1080, but replacement of one titanium by carbon (i.e., $Ti_{17}C_{19}^+$) produces the observed mass with a slightly nonstoichiometric ratio of the elements. Likewise, mass 1404 is explained by a slightly nonstoichiometric 23/25 species, with the 3 × 4 × 4 lattice. The final intense peak at 1800 amu is predicted by an exact-stoichiometric 30/30 cluster having the 3 × 4 × 5 lattice. All the masses observed correspond to exact or near-stoichiometric fcc lattice fragments. Moreover, each of the intense peaks corresponds to a symmetric lattice fragment with near-equal *x,y,z* proportions. Interestingly, the larger fcc fragments are the same as those observed for Ti–N clusters[28] and Ta–C clusters.[3] This evidence, and the confirmed 14/13 species above, suggests that the growth pattern for larger Ti–C clusters is the fcc lattice. Using the now-popular terminology, we therefore designate these larger clusters as "nanocrystals".

Additional insight into the structures of these clusters can be obtained through their *decomposition* patterns, as measured by photodissociation mass spectra (Figures 4 and 5). These data are accumulated with a difference method which averages the spectrum with and without the fragmentation laser. The plotted data show depletion of the parent ion as a negative peak and fragment ions as positive peaks. Photodissociation is accomplished here with an unfocused Nd:YAG laser operating at 532 nm with a pulse energy of about 20 mJ/cm². These are moderately high

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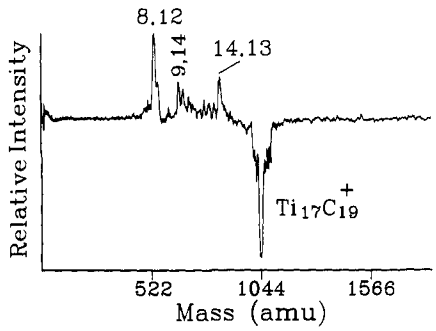

Figure 5. Photodissociation mass spectrum of $Ti_{17}C_{19}^+$. The main fragments are $Ti_{14}C_{13}^+$ and $Ti_8C_{12}^+$.

laser powers, and we believe that the signals observed are the result of multiphoton absorption.

Figure 4 shows the photodissociation spectrum of $Ti_{14}C_{13}^+$ obtained under these conditions. There are peaks corresponding to a series of metal atom losses, with an intense fragment at $Ti_8C_{13}^+$ corresponding to the loss of six metal atoms. $V_{14}C_{13}^+$ has the same dissociation pattern. This pattern is fascinating when one considers the structure of the 14/13 fcc lattice and its possible relationship to the 8/12 dodecahedron. The 14/13 lattice has eight metal atoms at cube vertices, 12 carbon atoms on cube edges, six metal atoms in cube faces, and one central carbon atom. One scenario which explains the fragmentation is that the six metal atoms which are eliminated come from the faces of the cube. When this occurs, carbon atoms on opposite edges can join to form a C_2 unit which spans a fcc cube face in place of the missing metal. Elimination of six metal atoms leads to the formation of six such C_2 units, leaving eight remaining metal atoms: exactly the numbers present in the 8/12 dodecahedron. However, the photofragment is not the 8/12 species—it is the 8/13 species, which contains an extra carbon atom. The source of this "extra" carbon atom may be the central carbon in the 14/13 cube which has no counterpart in the normal dodecahedron. It is conceivable that this central atom in the fcc structure can be trapped as the crystal reconstructs to form the dodecahedron, explaining the preferred fragment $Ti_8C_{13}^+$. This scenario is compelling because of its consistency with the fragmentation pattern and the small reorganization of atom positions. *Ab initio* calculations indicate that the dodecahedron internal diameter ($\approx$5 Å) is sufficiently large to accommodate a caged carbon atom.[35] We therefore suggest that there is reasonable circumstantial evidence for the existence of a stable endohedral carbon met–car cluster for both the titanium and vanadium analogs.

Figure 5 shows the photodissociation mass spectrum of the 1044-amu peak, for which the best assignment is the 17/19 cluster corresponding to the 3 × 3 × 4 fcc fragment. The fragments are 14/13 and 8/12. There is no evidence here for a caged carbon atom, presumably because the dissociation/reconstruction mechanism in the larger cluster allows central carbons to escape. We have been unable to photodissociate clusters larger than 17/19 because of insufficient parent ion intensity. However, we can already conclude that the 14/13 species and the 17/19 species are related to each other and to the dodecahedron species. This is additional evidence consistent with the fcc structures proposed for these larger clusters. It is difficult to imagine a grossly different structure for the 17/19 species (for example, a multiple-dodecahedron cage or a substituted fullerene) which could produce the 14/13 fcc fragment.

In conclusion, the mass spectroscopy and photodissociation data indicate that the 14/13 clusters observed for titanium and vanadium, and the larger Ti–C clusters, have symmetrical fcc lattice structures. The formation of fcc clusters is itself not surprising because several other cluster systems exhibit this growth pattern. However, these structures are revealed here to be structurally related to the dodecahedron, in that they decompose to produce it. It is remarkable that the 14/13 species is the only fcc fragment observed at low mass, where many other fcc fragments are statistically possible. Likewise, at higher mass only a few symmetric fcc crystal fragments are formed out of many possible structures. The high symmetry of these specific structures must result in enhanced bonding stability. Recent theoretical calculations agree with this proposition. Reddy and co-workers have found that Ti_8C_{12} has an average binding energy of 6.1 eV per atom,[10] consistent with its enhanced stability. However, similar calculations have predicted, prior to our work, that $Ti_{14}C_{13}$ is also especially stable.[10] The optimized structure is the 3 × 3 × 3 fcc lattice proposed here, with an average binding energy of 6.74 eV per atom.[10] Thus, the 14/13 nanocrystal is predicted to be more stable than the 8/12 met–car cluster. While the stability of the 14/13 cluster and other symmetric lattices is understandable, one remaining puzzle is the preference for nonstoichiometric occupation observed for these lattices in the larger fcc clusters. This is an issue which could be addressed by future theoretical work.

If the binding energies in these clusters are indeed on the order of 5–6 eV per atom, it is unlikely that photodissociation could occur on a microsecond time scale after the absorption of only a few (two or three) 532-nm (2.3-eV) photons. Internally cold clusters with many strong bonds would require far greater energy to dissociate this quickly. The observation of dissociation therefore implies either that the bonds are not so strong or that the clusters produced by our source are not internally cold. The latter option seems to be more reasonable, considering that the heat deposited into growing clusters is considerable when strong bonds are formed. Complete cooling of this internal energy is unlikely, even in a supersonic expansion. It therefore seems likely that our clusters have a significant amount of internal energy and that photoexcitation provides the final increment of energy needed to accomplish dissociation. This scenario has been used previously by Mandich and co-workers to explain the dissociation behavior of strongly-bound semiconductor clusters.[36]

Efforts are presently ongoing in many other laboratories to synthesize and isolate macroscopic quantities of metallo–fullerene materials. The results here would suggest that metal–carbon clusters of titanium and vanadium prefer instead to form structures other than the endohedral C_{60} systems. However, it seems that in both the Castleman experiments and ours the vaporized densities of metal and carbon are roughly equal. In fact, it may be small differences in the metal–carbon densities which explain the formation of met–car clusters under some conditions and nanocrystals under other conditions. Even though the fcc structures or dodecahedron structure are both very stable for metal–carbon mixtures, it may still be possible to synthesize metallo–fullerenes from these elements using careful control of the relative metal density in the growth process. Castleman recently reported the isolation of macroscopic quantities of the titanium and vanadium 8/12 met–car clusters discussed here.[37] If the stability patterns indicated here are valid, similar experiments with variations in the metal density may be able to isolate not only the 8/12 species but also the 14/13 and/or some of the larger crystalline fragments discussed here. These nanocrystals may be as interesting for cluster-based materials as the dodecahedron met–car clusters or the metallo–fullerenes.

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