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## Metallo-Carbohedrenes [ $M_8C_{12}^+$ ( $M = V, Zr, Hf$ , and $Ti$ )]: A Class of Stable Molecular Cluster Ions

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Findings of magic peaks corresponding to  $M_8C_{12}^+$  ( $M = V, Zr$ , and  $Hf$ ) formed from reactions of the respective metals with various small hydrocarbons, in conjunction with recent findings for the titanium system, establish metallo-carbohedrenes as a stable general class of molecular cluster ions. A dodecahedral structure of  $T_h$  point symmetry accounts for the stability of these ionic clusters.

We report findings of magic peaks corresponding to  $M_8C_{12}^+$  (where  $M$  is  $V, Zr$ , and  $Hf$ ) which, along with prior observations for  $Ti_8C_{12}^+$ , now establish metallo-carbohedrenes as a class of stable molecular cluster ions. The question of whether a general class of such species exists was raised following recent reporting (1) of a prominent (magic) peak in the distributions of titanium-carbon clusters generated through reactions of the metal with hydrocarbons using a laser vaporization source. In view of the nature of the species, we raised the issue of whether  $Ti_8C_{12}^+$  might be the first observed member of a new class of molecular clusters comprised of a cage-like network of carbon and metal atoms, possibly arranged in the form of a pentagonal dodecahedron. If metallo-carbohedrenes do exist, it is expected that other early transition metals should be capable of forming molecules of a similar type which would also display an unusual stability. A short while after the observation of  $Ti_8C_{12}^+$ , we extended our work to other transition metal systems, with particular attention to vanadium, and thereafter zirconium and hafnium. Like  $Ti_8C_{12}^+$ , all  $M_8C_{12}^+$  ( $M$  is  $V, Zr$ , or  $Hf$  elements) also are found to display an enhanced stability.

The experiments were conducted with both a double mass spectrometer (MS/MS) system (2) and a time-of-flight (TOF) mass spectrometer (3) coupled with a laser vaporization source. Ionic species comprised of transition metal atoms and carbons are produced with a versatile laser-induced plasma reaction concept (1). Employing a simple laser vaporization device (4, 5), the methodology enables the generation of pure met-

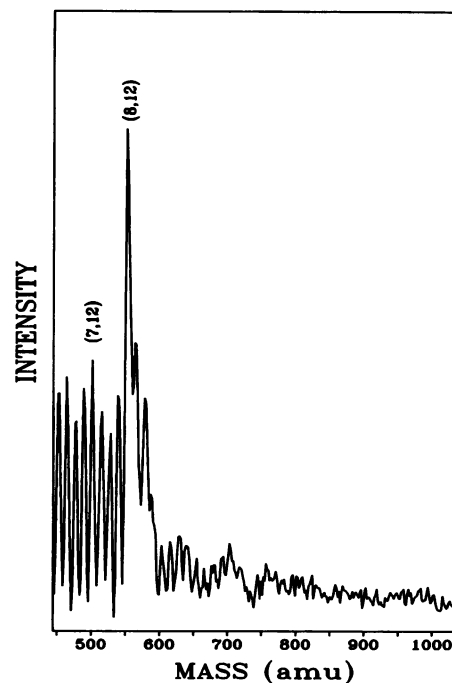
al-carbon and metal-nitrogen clusters in either neutral or ionized form. The details of the technique will be given elsewhere (6, 7). Briefly, a high power laser is used to irradiate the surface of the metal. In the presence of a plasma containing both neutral and ionic metal species, fast dehydrogenation reactions with hydrocarbons occur. As a result, in many cases the hydrocarbons lose all hydrogens and pure metal-carbon clusters are generated. The distribution of the ionic species are analyzed with a quadrupole or TOF mass spectrometer.

Figure 1 shows a typical mass spectrum of vanadium-carbon cationic clusters produced from reactions with  $CH_4$ . Other small hydrocarbons yield a similar cluster distribution. The TOF spectrum was obtained with an electric pulser to attract the ionic clusters from the source and analyze them via TOF mass spectrometry. It is evident in this spectrum that the peak at a mass of 552 atomic mass units (amu) (magic peak) displays enhanced abundance compared to proximate clusters. Because the reactions involve three elements, the molecule corresponding to the magic peak could, in principle, have the molecular formula  $V_aC_bH_c$ , where  $a, b$ , and  $c$  are the number of vanadium, carbon, and hydrogen atoms contained in the molecule, respectively. However, the isotope-labeling experiments made with hydrocarbons containing deuterium and  $^{13}C$  establish that the molecule has no hydrogen atoms at all and contains exactly 12 carbon atoms. Based on these facts and its mass position, the molecule is assigned as  $V_8C_{12}$ .

Figures 2 and 3 display the mass spectra of zirconium and hafnium-carbon cluster cations, respectively. These spectra were obtained under the same experimental conditions used to obtain Fig. 1, except the use of the zirconium or hafnium rods instead of the

vanadium rod. Interestingly, the two spectra are seen to truncate at  $Zr_8C_{12}^+$  and  $Hf_8C_{12}^+$ . It is well established that the intensity anomalies (magic numbers) observed in a mass spectrum of clusters reflect the stability of the corresponding cluster (8). Magic numbers do not always become manifested as prominent peaks, but more typically as a discontinuity, namely truncation in the present case, in an otherwise smoothly varying distribution, indicating the formation of geometric structures of special stability. Hence, the truncation seen in Figs. 2 and 3 indicates that  $Zr_8C_{12}^+$  and  $Hf_8C_{12}^+$  also display magic behavior.

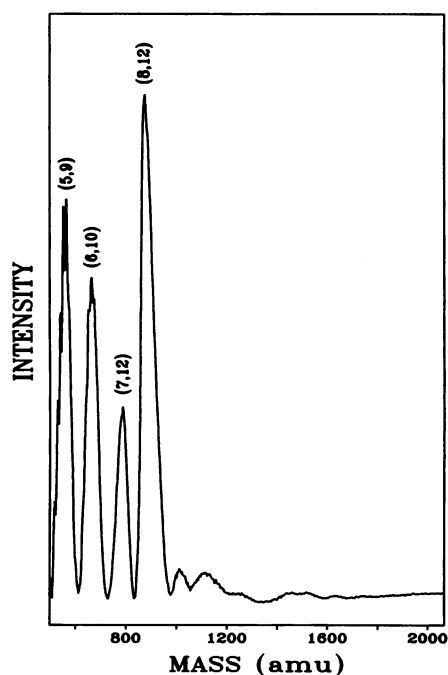
Because  $Zr$  and  $Hf$  have a similar electronic structure to that of  $Ti$ , it is expected that the dodecahedron model proposed for  $Ti_8C_{12}^+$  can rationalize the magic nature of the corresponding species,  $M_8C_{12}^+$ . As for the ionic form of  $V_8C_{12}$ , although the vanadium atom has one more electron than  $Ti$ , we believe that its geometric structure should also be dodecahedral, in which the vanadium atoms occupy eight unique positions. In order to gain supporting evidence for the proposed structure, we conducted titration experiments with  $ND_3$  under thermal reaction conditions. In conducting



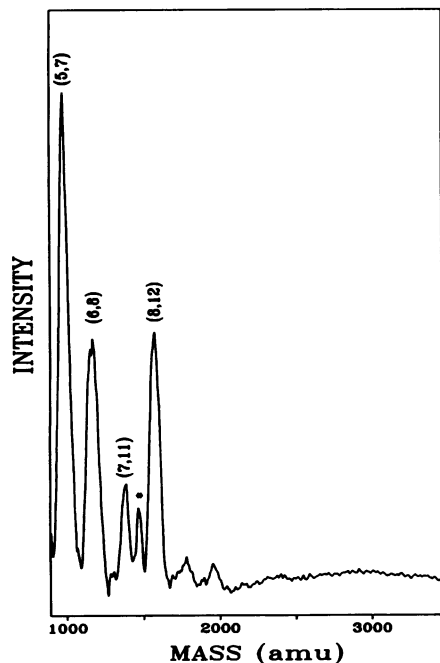
**Fig. 1.** Time-of-flight mass spectrum of vanadium-carbon cluster cations. The labeled magic peak is  $V_8C_{12}^+$ . Note that there are other prominent peaks preceding the magic  $M_8C_{12}^+$  which are precursors involved in the mechanism of formation of the cage-like metallo-carbohedrenes. Species with one- and two-carbon atoms attached to  $M_8C_{12}^+$  are also visible, where some carbons remain on the magic structure upon its closing (9). Other precursors to the magic peak are seen, such as (7, 12).

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**Fig. 2.** Time-of-flight mass spectrum of zirconium-carbon cluster cations. The magic peak  $Zr_8C_{12}^+$  is labeled. Other precursors to the magic peak are seen, such as (5, 9), (6, 10), (7, 12), and (8, 12).



**Fig. 3.** Time-of-flight mass spectrum of hafnium-carbon cluster cations. The species indicated by \* corresponds to  $Hf_7ZrC_{12}^+$ . Other precursors to the magic peak are seen, such as (5, 7), (6, 8), (7, 11), and (8, 12). It should be noted that, depending on experimental conditions, abundant small metal-carbon clusters which play a role as building blocks, can also be detected. Nevertheless, invariably, truncation (magic behavior) is found at  $M_8C_{12}^+$ .

these experiments,  $V_8C_{12}^+$  was mass-selected by a first quadrupole mass spectrometer, and thereafter injected into a thermal reaction cell containing 0.7 torr of helium buffer gas. The products arising from the reactions within the reactor are analyzed by a second quadrupole mass spectrometer located at its exit. Figure 4 shows the product distribution obtained from attachment reactions of mass-selected  $V_8C_{12}^+$  with  $ND_3$  at an  $ND_3$  partial pressure of about 0.006 torr. Obviously, the reactions reveal the uptake of eight  $ND_3$  molecules, pointing to the fact that the vanadiums are similarly coordinated and located at exposed positions rather than inside the cage. This evidence strongly supports the proposed dodecahedral structure.

As for the electronic structure of the ionic form of  $V_8C_{12}$ , each of the vanadiums is proposed to be bound to three carbons through V-C  $\sigma$ -bonds, while each of the carbons is bound to an adjacent carbon through a C-C  $\sigma$ -bond in addition to V-C  $\sigma$ -bonds. These strong  $\sigma$ -bonds combine all atoms together and construct the basic framework of the dodecahedron. For the remaining valence electrons, it is proposed that they contribute to a delocalized  $\pi$ -system (9). Alternatively, in order for all valence electrons to be satisfied, it is possible that the remaining electrons in the vanadiums participate in metal-metal bonds instead of delocalized  $\pi$ -bonding.

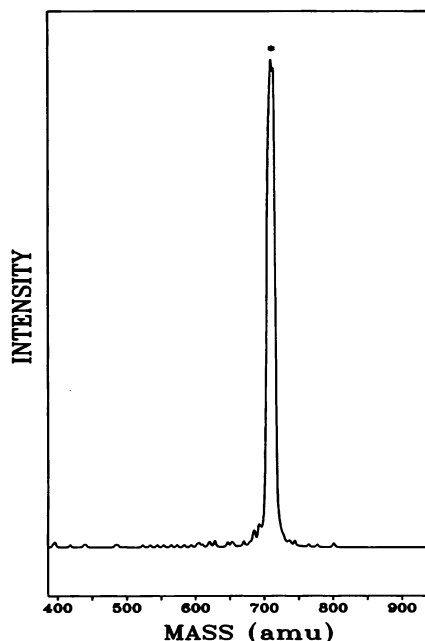
One may ask that if the valence electrons are fully satisfied in the dodecahedron structure, how can  $V_8C_{12}^+$  bond to eight ammo-

nia molecules? This question can be answered in light of the characteristics of transition metals. Although all the valence electrons of the vanadiums in the dodecahedral  $V_8C_{12}$  are satisfied, the vanadiums have unoccupied  $d$ -orbitals. Like typical transition metal complexes, the lone pair electrons of the ligands can interact with unoccupied  $d$ -orbitals of the transition metals to form coordination bonds.

In the initial report on the stability of  $Ti_8C_{12}^+$  (1), we speculated that  $Ti_8C_{12}$  may comprise one member of a metallo-carborene family, and that other early transition metals could also form stable  $M_8C_{12}$  in both neutral and ionized forms. All the results obtained so far for the ionic clusters are very supportive for the suggestion that metallo-carborenes do, in fact, comprise a new class of clusters. The work addressed in this report pertains to cationic species. Other preliminary investigations were made in our laboratory to determine whether the anions would also display prominent magic numbers. Importantly, studies for the vanadium system are also very positive, showing the enhanced abundance of  $V_8C_{12}^-$ . Moreover, in very recent experiments using laser photoionization methods, we have confirmed the existence of prominent neutral species of the same compositions as those of the magic numbers for the ionic species discussed herein (10). Additionally, the detection of small neutral cluster species is providing important clues about the formation processes of the precursors to the magic cage structure and the mechanisms involved in cage closure. In order to definitively confirm the model of metallo-carborenes, one has to establish the existence and stability of the neutral species (9), and make macroscopic quantities of the metal-carbon cluster molecules for analyses via such methods as  $^{13}C$  nuclear magnetic resonance and x-ray diffraction.

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**Fig. 4.** Mass spectrum of the products arising from the titration reactions of  $V_8C_{12}^+$  with  $ND_3$ . The single peak labeled by \* is  $V_8C_{12}(ND_3)_8^+$ . Data taken with quadrupole double mass spectrometer apparatus.

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