

oxygen isotopic composition, as do meteorites of different classes. Mars, in contrast to Earth, lacks plate tectonics, the mechanism by which isotopic homogenization occurs on Earth. For example, Muehlenbachs and Clayton (26) found that terrestrial oceans are buffered to a relatively constant oxygen isotopic composition by exchange between seawater and basalt at midocean ridges where the plates are being generated. Thus the whole ocean is cycled through the oceanic crust in a few million years; as a result, any isotopic anomalies that might have been present between the hydrosphere and lithosphere on Earth were quickly erased.

Alternatively, the hydrosphere on Mars could initially have been in equilibrium with the lithosphere but changed its composition over time as a result of the influx of isotopically distinct material such as comets. A change in the isotopic composition of the atmosphere (and hydrosphere) may also have resulted from photochemical processes leading to loss of oxygen from the planet. Some such processes are known to have anomalous oxygen isotopic behavior (27) and may lead to non-mass-dependent isotope fractionation in the ozone chemistry of Earth's atmosphere (28). Again the two reservoirs could have remained separate because an efficient mixing mechanism such as plate tectonics was lacking.

A discussion of such processes, in the context of a comprehensive model for interpretation of hydrogen, carbon, and oxygen isotope abundances in the martian surface reservoir, has been presented by Jakosky (29). The present work provides some of the necessary input data for further development of such models.

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## Ti<sub>8</sub>C<sub>12</sub><sup>+</sup>-Metallo-Carbohedrenes: A New Class of Molecular Clusters?

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During the course of studying the dehydrogenation reactions of hydrocarbons by titanium atoms, ions, and clusters, an exceptionally stable and abundant cluster which contains 8 titaniums and 12 carbons was discovered. "Titration" reactions with ND<sub>3</sub> reveal the uptake of eight molecules, pointing to the fact that the titanium atoms are at exposed positions of similar coordination. A dodecahedral structure of T<sub>h</sub> point group symmetry is proposed to account for the unusual stability of this molecular cluster. The Ti<sub>8</sub>C<sub>12</sub><sup>+</sup> dodecahedron has 12 pentagonal rings and each of the rings is formed by two titanium and three carbon atoms, where each titanium is bound to three carbons. Based on the model, it is expected that neutral Ti<sub>8</sub>C<sub>12</sub> would be a stable metallo-carbododecahedral molecule and may comprise one member of a new class of molecules, namely metallo-carbohedrenes.

HEREIN WE REPORT EVIDENCE OF a class of cage-like molecular clusters, namely metallo-carbohedrenes. During the course of detailed studies made in our laboratory to investigate dehydrogenation reactions of hydrocarbons induced by metal ions, atoms, and clusters (1), we discovered the formation of an unusually abundant and stable cationic species with a molecular weight of 528 atomic mass units (amu), which we have now established as containing 8 titanium atoms and 12 carbons. The evidence for our findings and a suggested structure (see Fig. 1) are the subject of this report.

The reported observation of the molecule C<sub>60</sub> (2) has prompted extensive activity in fullerenes and related carbon-cluster research (3, 4). A group at AT&T Bell Laboratory reported the successful doping of alkali metal atoms into C<sub>60</sub> crystals to produce a new superconductive material (5).

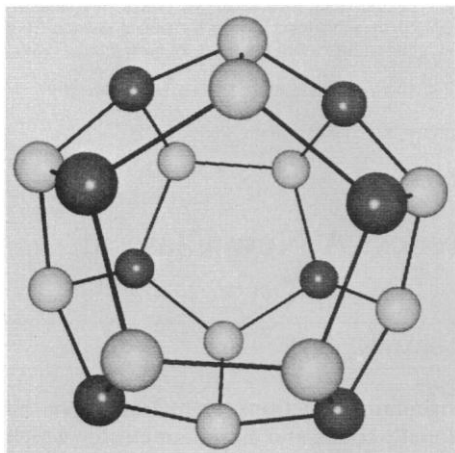
Smalley and co-workers obtained evidence for the incorporation of lanthanum in the interior of C<sub>60</sub> (6), a structure that has been born out by more extensive studies. Also, other researchers have reported the ability to incorporate He<sup>+</sup> within the fullerene ball (7). In addition to the above doping, Smalley's group (8) has found that a few carbon atoms in C<sub>60</sub> can be replaced by nonmetal boron elements in the C<sub>60</sub> cage without substantially destabilizing the entire fullerene. However, to the best of our knowledge, cage-like molecules that we term metallo-carbohedrenes, in which a number of metal atoms incorporate with carbons to form a symmetrical network, have not been reported heretofore.

The experimental method employed in the present work is based on our newly developed MS/MS system which we have described elsewhere (1). The new molecular cluster that we report here was generated through reactions of titanium with any of the following vapors: CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, or C<sub>6</sub>H<sub>6</sub>. The details of the experiments will be given elsewhere (9).

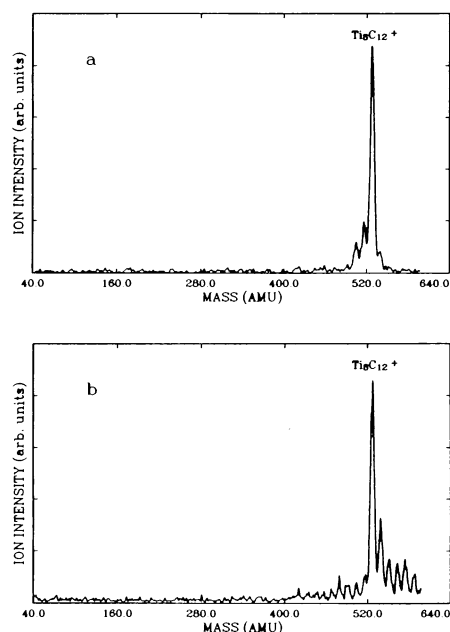
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Figure 2 shows mass spectra of clusters containing titanium metal atoms and carbons formed from reactions of titanium with two of these five different hydrocarbon molecules: Fig. 2a obtained with methane and Fig. 2b with acetylene. As seen from Fig. 2, a peak at 528 amu is totally dominant ("super magic") in both mass spectra. No other prominent peaks are observed in the mass range below 1200 amu. Reactions with ethylene, benzene, or propylene gener-



**Fig. 1.** Idealized pentagonal dodecahedron structure,  $T_h$  point group, proposed to account for the observed stability and  $\text{ND}_3$  uptake by  $\text{Ti}_8\text{C}_{12}^+$ . Note that the eight titanium atoms (dark spheres), which appear at the edge of a cube-like arrangement, are similarly coordinated to three-carbon atoms (light balls) at all equivalent positions.



**Fig. 2.** (a) Mass distribution of  $\text{Ti}_m\text{C}_n^+$  clusters generated from the reactions of titanium with  $\text{CH}_4$ . Note the "super magic" peak corresponding to  $\text{Ti}_8\text{C}_{12}^+$ . (b) Mass distribution of  $\text{Ti}_m\text{C}_n^+$  clusters generated from the reactions of titanium with  $\text{C}_2\text{H}_2$ . Note the super magic peak corresponding to  $\text{Ti}_8\text{C}_{12}^+$ .

ate similar cluster distributions.

In order to definitively establish the identity of this unusually stable species, we undertook a series of studies with hydrocarbons of varying isotopic composition. Isotope labeling experiments with deuterium show that the clusters corresponding to the "super magic" peak do not contain any hydrogen atoms, while  $^{13}\text{C}$  labeling establishes that the cluster accommodates exactly 12 carbon atoms. Therefore, the magic peak was assigned as  $\text{Ti}_8\text{C}_{12}^+$  based on the mass and isotope labeling experiments. Furthermore, high-resolution isotope distribution pattern analyses support the assignment of eight Ti atoms as well.

Why is  $\text{Ti}_8\text{C}_{12}^+$  in Fig. 2 so abundant compared with all other species representing possible combinations of Ti and C? Our rationalization of this result is that  $\text{Ti}_8\text{C}_{12}^+$  and its corresponding neutral molecule may have a pentagonal dodecahedron structure as illustrated by Fig. 1, where the Ti atoms occupy eight unique positions that are similarly coordinated. In this structure, there are 12 pentagonal rings and each of the rings contains two titaniums and three carbons. Each of the titanium atoms can bond to three carbon atoms through Ti-C  $\sigma$ -bonds, and each of the carbons may bond to its adjacent carbon through a C-C  $\sigma$ -bond in addition to bonding to two titanium atoms. Those Ti-C and C-C  $\sigma$ -bonds connect all atoms together and form the network of the dodecahedral titanium-carborene. As for the remaining valence electrons, since titanium is viewed as being carbon-like in the model, the " $\pi$ -bonding" structure of  $\text{Ti}_8\text{C}_{12}^+$  is similar to that which might be envisioned for  $\text{C}_{20}$ , although in the present case  $d$ -electrons of Ti are involved in the bonding. The metal-carbon double-bonding structure has been widely seen in metal-carbene and metal-carbyne complexes (10–12). Of particular importance to the present work are theoretical considerations by Hoffmann and co-workers regarding electron-deficient transition-metal carbene complexes (11). (An alternative consideration of the bonding for the remaining valence electrons is that the pairs of adjacent carbon atoms form six  $\pi$ -bonds, and that the titaniums in the corners of the cube-like geometry may undergo some metal-metal interactions. However, this is less likely due to much weaker metal-metal bonding compared to the metal-carbon interactions allowed by the proposed structure.) It is also worth noting that there have been several reports of molecules and clusters that assemble into dodecahedral structures such as  $\text{C}_{20}\text{H}_{20}$  (13) and  $(\text{H}_2\text{O})_{20} \cdot \text{H}_3\text{O}^+$  (14) and that are relatively stable.

Owing to the severe strain and the degen-

eracy of " $\pi$ -bonding," the dodecahedral  $\text{C}_{20}$  is not expected to be a stable molecule (15). How can  $\text{Ti}_8\text{C}_{12}^+$  become so stable? The question can be answered in light of characteristics of titanium. Since Ti can participate in  $\sigma$ -bonding through  $d$ - $sp$  hybridized orbitals (12), the incorporation of two titaniums into the pentagonal ring may somewhat reduce the strain of the ring. On the other hand,  $d_\pi$  metal orbital and  $p_\pi$  carbon orbital may have better overlap in the dodecahedral structure to form " $\pi$ -bonding." Furthermore, Ti is more electropositive than carbon. This would suggest a " $\pi$ " dodecahedron with eight electropositive atoms for which simple Hückel calculations (16) indicate that all electrons would be paired. As a result, the dodecahedral  $\text{Ti}_8\text{C}_{12}$  molecule and its cation are expected to be very stable in terms of both spherical geometry and a satisfied electron-bond structure. Collision-induced dissociation studies made in our laboratory (9) indicate that, indeed,  $\text{Ti}_8\text{C}_{12}^+$  is remarkably stable.

In order to provide supporting evidence for the proposed structure, we have conducted experiments to "titrate" the metal atoms that are available for bonding. The  $\text{Ti}_8\text{C}_{12}^+$  molecular cluster was mass-selected and injected into the thermal reaction cell containing  $\text{ND}_3$ . Importantly, the species accommodates eight ammonia molecules, one for each Ti site. This finding shows that the titaniums are exposed at the cluster surface and indicates that they are similarly coordinated. This is strong evidence for the proposed dodecahedral structure.

Other clusters such as  $\text{Ti}_7\text{C}_{13}^+$ ,  $\text{Ti}_6\text{C}_{14}^+$ , and so on can also form a dodecahedral structure, but replacement of titaniums by carbons would be expected to destroy this structure of high symmetry. In turn, this would necessitate the direct connection of at least three of the pentagonal rings, each of which would have only one metal, or less. It is unlikely that one metal atom can sufficiently reduce the strain of the pentagonal rings to stabilize the cluster. Therefore, in the reactor such clusters would undergo further reactions with hydrocarbons to form more stable products (such as  $\text{Ti}_8\text{C}_{12}^+$ ), thereby leading to a reduction in their abundance. In accordance with our findings,  $\text{Ti}_8\text{C}_{12}^+$  would be expected to survive in the reactor once formed. If one considered that  $\text{Ti}_8\text{C}_{12}^+$  does not have a dodecahedral structure, but instead a planar one, the cluster would have many dangling bonds at the edges and it would be much more reactive with other species in the reactor than observed. Consequently, such a  $\text{Ti}_8\text{C}_{12}^+$  species would not be expected to display the "super magic" peak shown in Fig. 2.

Another important fact is that we are able

to observe anions with the same metal-carbon composition as for the cation. Based on this fact, as well as the dominant intensity of  $\text{Ti}_8\text{C}_{12}^+$  in Fig. 2 and the nature of the dodecahedral structure, we expect that neutral  $\text{Ti}_8\text{C}_{12}$  would also have a high abundance in the neutral cluster distribution. If our speculation and the proposed model are correct, there are many important implications of the existence of such a stable metallo-carbohedrene. Owing to limitations of our current mass spectrometer, we have not yet been able to mass-analyze ions with masses larger than 1200 amu. However, radio frequency-only operation of our quadrupole mass spectrometer indicates that there are numerous species in the higher mass range.

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## Extraction and STM Imaging of Spherical Giant Fullerenes

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High-temperature, high-pressure extracts of soot produced by the Krätschmer-Huffman technique (KH carbon) were characterized by mass spectrometry and imaging with scanning tunneling microscopes (STMs). The mass spectra of these samples are similar to those of ambient-pressure, high-boiling-point solvent extractions, supporting the idea that solvent temperature and possibly pressure are key parameters in extraction of the giant fullerenes. The STM images show that the giant fullerenes in these samples are roughly spherical in shape and range in diameter from approximately 1 to 2 nanometers, corresponding to fullerenes containing 60 to 330 atoms. No evidence of bucky tubes was found.

RECENT REPORTS (1, 2) OF THE EXTRACTION from KH-carbon and mass-spectroscopic characterization of the so-called giant fullerenes ( $C_n$ ,  $n \geq 100$ ) have sparked considerable interest in their properties. These mass spectra, along with some intriguing transmission electron microscopy images published by Wang and Buseck (3) and Iijima (4), have given rise to speculations that the canonical form of the giant fullerenes is the bucky tube. In the simplest case (5), the wall of such a structure is thought to resemble a portion of a single graphitic plane that has been curled until it forms a tube. The tube is capped on each end with a fullerene-like hemisphere, thus leaving no dangling bonds. Before the current work was begun, the sole evidence that seemed to contradict the bucky tube model of the structure of the giant fullerenes was a single STM image published by Wragg *et al.* in a study of solid  $C_{60}$ - $C_{70}$  (6). This image appeared to show a spherical giant fullerene with a diameter of  $\sim 1.5$  nm, corresponding to a molecule with 180 to 240 carbon atoms. The authors noted, however, that since this was the only such image to appear in their data set, which contained images of many thousands of smaller fullerenes, identification of this object as a giant fullerene was highly speculative. We report the extraction of giant fullerenes from KH carbon using a low-boiling-point solvent in a high-pressure, high-temperature vessel and STM imaging of these molecules. The images show only spherical giant fullerenes, with no evidence of tubular structures.

In previous work on extraction of the giant fullerenes, high-boiling-point solvents,

such as 1,2,3,5-tetramethylbenzene (1) or 1,2,4-trichlorobenzene (2), were used in standard extraction procedures at ambient pressures. The starting material in these experiments was KH carbon, which previously had been thoroughly washed with low-boiling-point solvents such as toluene (2) or benzene followed by pyridine (1). The effect of these prior extractions was to remove as much of the readily soluble  $C_{60}$  and  $C_{70}$  as possible. After the high-temperature extractions, the solvent was removed and mass spectrometry was performed on the residue. Although high-boiling-point solvent, ambient-pressure extractions are quite favorable in terms of solvating the giant fullerenes, these approaches require solvents that are unpleasant to work with and that are hard to remove without heating the sample under vacuum. Also, there is concern that some combination of air, ambient light, and the boiling solution may lead to the formation of unwanted compounds (2). These considerations, together with evidence that the key parameter governing extraction of the higher fullerenes under ambient pressure might be the solvent temperature (2), and a preliminary report of successful high-pressure, high-temperature xylene extractions of the higher fullerenes (7), led us to investigate extractions with toluene at high pressure and temperature.

The starting material was KH carbon (8), which had first been solvent-extracted with toluene at ambient pressure to remove as much of the  $C_{60}$  and  $C_{70}$  as possible. The high-pressure, high-temperature extractions were then carried out in simple pressure bombs built out of 30-cm lengths of 1.2-cm outside-diameter stainless-steel thick-wall tubing, capped on the ends with stainless-steel compression fittings. (Warning: Great care should be used in this procedure, because failure of the vessel may result in an explosion.) Each bomb was loaded with  $\sim 5$  g of the preextracted KH carbon and  $\sim 20$  ml of toluene. The bombs were filled to

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