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Reactivities of $Ti_8C_{12}^+$ at Thermal Energies

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Abstract: Reactivities of the Met–Car $Ti_8C_{12}^+$ toward various molecules have been examined at thermal energies employing a selected drift tube reactor coupled with a laser induced plasma source. It is observed that this cluster is quite reactive toward molecules with either large dipole moments or π-bonding systems. At room temperature $Ti_8C_{12}^+$ is found to take up 8 polar molecules but only 4 molecules with π-bonding systems. The Met–Car cluster ion reactions are observed to proceed mainly through association mechanisms leading to ligand attachment rather than those involving breaking and forming of new chemical bonds. In addition, $Ti_8C_{12}^+$ is seen to be inert even toward oxygen, which is known to be a good free radical scavenger. The assocition or attachment behavior of $Ti_8C_{12}^+$ reactions is explained in terms of a closed structure of the Met–Car and the presence of titaniums in the framework of $Ti_8C_{12}^+$. Hence, the observed reactivities of $Ti_8C_{12}^+$ provide further suggestive evidence supporting the argument that the Met–Car Ti_8C_{12} has a dodecahedral structure.

Introduction

Currently, there is extensive interest in the prospect of producing new materials comprised of molecular clusters. This is evidenced by the explosive research on C_{60}[1]. Interest in these materials has arisen due to the fact that molecular clusters often display unique physical and chemical properties unlike those of other forms of matter. Earlier last year, we discovered a remarkably stable cluster $Ti_8C_{12}^+$ [2] and postulated that its extraordinary stability was due to geometric and electronic properties inherent in a dodecahedral structure. Furthermore, we suggested that this molecule might be just one member of a new general class of molecular clusters named as metallo–carbohedrenes or Met–Cars which involve possible incorporation of early transition metals with carbon to construct a cage-like structure. Thereafter, our subsequent work confirmed this speculation and revealed that other early transition metals such as vanadium, zirconium, and hafnium can form similar stable metallo–carbohedrenes, M_8C_{12}, as well.[3,4]

The observation of Met–Cars and their proposed structure has received favorable response from the chemistry, physics, and materials science communities. Just a few months after our first report on Met–Cars, intensive theoretical investigations to verify our findings were made by a number of research groups.[5–14] These calculations suggest that Met–Cars with a cage-like structure are indeed very stable and that they are assembled by a framework comprised of metal–carbon and carbon–carbon bonds.

Despite active theoretical research on the stability and structure of Met–Cars, little is known about their chemical properties. To understand the chemistry of Met–Cars, it is instructive to examine the reaction behavior of Met–Cars toward various molecules. Reporting findings of studies of various reactions with $Ti_8C_{12}^+$ is the subject of the present paper which provides not only detailed knowledge of the chemistry of Met–Cars, but also further evidence for the cage-like structural model proposed for Met–Cars. Furthermore, it is expected that the findings from the recent work will also be valuable to those working in fields devoted to the synthesis of Met–Cars in bulk quantities.

2. Experimental Section

The experimental apparatus employed in the present work is a selected ion drift tube reactor (SIDT) coupled with a laser vaporization source. The details of the apparatus and experimental procedure have been published elsewhere.[15,16] Briefly, SIDT consists of four main parts. The first one is a laser vaporization source. Here, we employed a laser induced plasma reaction technique to generate titanium–carbon cluster cations.[17,18] After production, the titanium–carbon cluster cation beam passes through a skimmer of 0.5-cm diameter and then is focused and steered by the first group of three-element electrical ion lenses, and horizontal and vertical deflector plates, into the second part of the apparatus for mass selection via a quadrupole mass spectrometer. The function of this part is to select a specific size of cluster from a wide cluster distribution for the study of its reactivities. In the present work, $Ti_8C_{12}^+$ is selected by the first quadrupole mass spectrometer.

The selected $Ti_8C_{12}^+$ is refocused and adjusted by a second group of ion lenses and deflectors and then injected into the third part of the apparatus which is a drift tube reactor where reactions between $Ti_8C_{12}^+$ and reactant occur. The injection energy is less than about 1 eV.[15]

The drift tube reactor is comprised of a cylindrical copper tube, which is 2.9-cm long with a 9-cm inside diameter, and a pair of stainless steel plates which function as the entrance and exit plates; these each have a 1.0-mm-diameter orifice. The pressure in the reactor is measured by a capacitance manometer; typical pressures are about 0.7 Torr with helium as the buffer gas, and the drift field is less than 0.5 V/cm.

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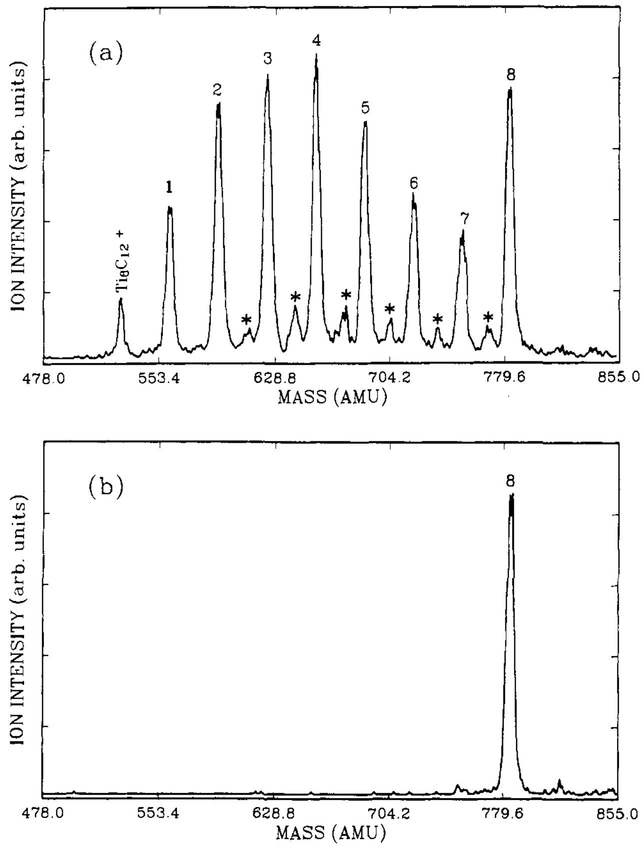

Figure 1. Mass spectra of products arising from reactions of $Ti_8C_{12}^+$ with methanol: (a) obtained at a very low partial pressure of methanol; (b) obtained at a much higher pressure of methanol. The number stands for the number of methanols associating onto $Ti_8C_{12}^+$. Note that association reactions terminate at the eighth step.

After undergoing thousands of collisions with buffer and reactant gases, a small fraction of selected ions, along with the product ions, diffuse through the exit orifice and into the high-vacuum chamber where a third group of ion lenses and deflectors focus and steer them into the fourth part of the machine. The fourth part contains the second quadrupole mass spectrometer affixed with a Channeltron electron multiplier (CEM). The final ion distribution is analyzed by the quadrupole mass spectrometer and detected by a CEM. The present experiments were conducted at room temperature. Hence, the reported results are the reaction behavior of $Ti_8C_{12}^+$ at thermal energies corresponding to room temperature.

3. Results

3.1. Reactions with Polar Molecules. As shown in what follows, $Ti_8C_{12}^+$ is very reactive toward the polar molecules CH_3OH, H_2O, and ND_3 studied in the present work at thermal energies. Measurement of the rate constants of polar molecule attachments to Met-Cars will be the subject of another paper. However, it is worthy of note that the rates have been found to proceed at surprisingly high values, near the collision rate in the case of all three ligands. Figure 1a displays the product distribution from reactions of $Ti_8C_{12}^+$ with methanol at a very low partial pressure of methanol in the reactor. The total reactor pressure is about 0.7 Torr. In the spectrum, the main peaks corresponding to products from the *n*th reaction step are labeled by an integer and indicate products that contain only methanol. Owing to water impurity in the sample or the buffer gas of helium, some minor peaks containing water also appear in the spectrum. These peaks are labeled by an asterisk. It is observed that the main reaction channels in both the primary and sequential reaction steps involve the attachment or association of methanols onto $Ti_8C_{12}^+$. The multiple-step attachment processes of polar molecules onto $Ti_8C_{12}^+$ can be expressed by following reactions

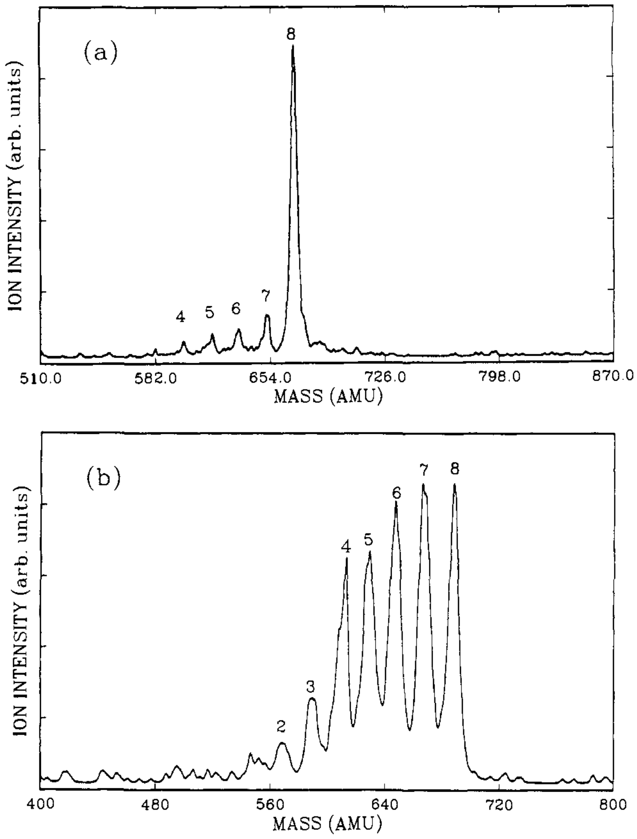

Figure 2. Mass spectra of products arising from reactions of $Ti_8C_{12}^+$ with (a) H_2O and (b) ND_3. The number indicates the number of H_2O (or ND_3) associating onto $Ti_8C_{12}^+$. Note that association reactions terminate at the eighth step.

$$Ti_8C_{12}^+(P)_{n-1} + P = Ti_8C_{12}^+(P)_n \qquad (1)$$

where P is a polar molecule.

Most importantly, it is seen from Figure 1a that sequential reactions terminate at the eighth reaction step. This result suggests that only 8 methanol molecules can bond to the first solvation shell of $Ti_8C_{12}^+$ at room temperature. In other words, the first solvation shell of this cluster ion can accommodate 8 methanols. In order to prove this point, we increased the partial pressure of methanol by more than one order of magnitude to see whether sequential reactions could result in further attachment of methanol molecules onto this cluster ion. The mass spectrum of Figure 1b reveals the effect of an increase in methanol pressure on the product distribution. This spectrum was obtained under conditions of a high methanol partial pressure. Obviously, the product distribution is still truncated at the eighth step, and the effect of an increase in the methanol pressure leads only to a conversion of the products formed from the first seven reaction steps into $Ti_8C_{12}^+(CH_3OH)_8$. In the same way, we also found that the first solvation shell of this cluster ion only takes up, individually, 8 water or 8 ammonia molecules as demonstrated in Figure 2, a and b, respectively. Hence, $n \leq 8$ in eq 1.

In order to ascertain whether the reactions with those molecules involve any dehydrogenation processes, we carefully examined the product distribution of the reactions with ND_3 using high-resolution mass spectra. It was found that the reactions only lead to the attachment of ammonia molecules, and no dehydrogenation products were observed at thermal energies.

3.2. Reactions with Benzene and Ethylene. Interestingly, $Ti_8C_{12}^+$ is also quite reactive toward molecules which do not have permanent dipole moments, but do have a π-bonding system.

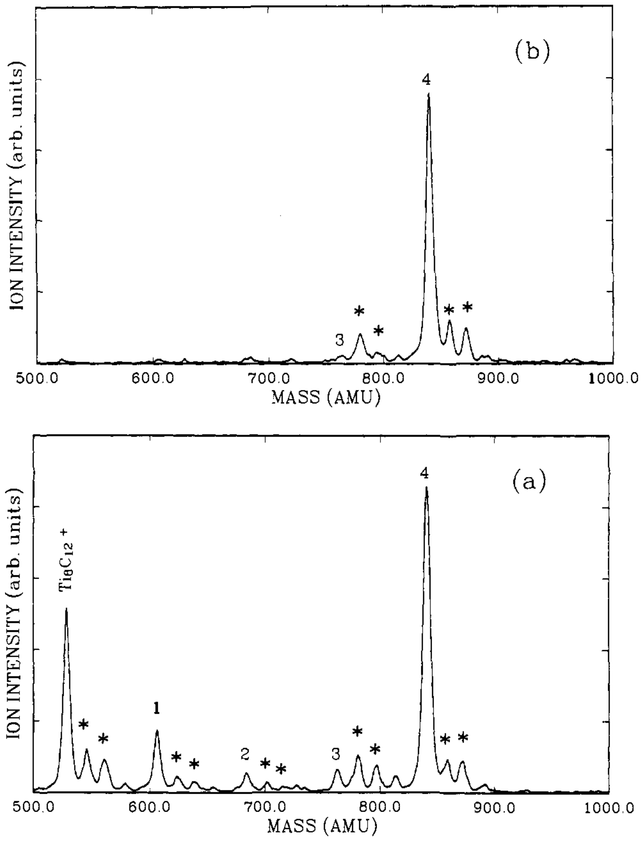

Figure 3. Mass spectra of products arising from reactions of $Ti_8C_{12}^+$ with benzene: (a) obtained at a very low partial pressure of benzene (0.14 m Torr); (b) obtained at a much higher partial pressure of benzene. The number stands for the number of benzenes associating onto $Ti_8C_{12}^+$. Note that association reactions terminate at the fourth step.

This is evidenced by reactions which we have investigated with benzene and ethylene. For instance, Figure 3a displays the typical product distribution from the reactions with benzene molecules at a benzene pressure of 0.14 mTorr. As in the case of methanol, aside from the major peaks labeled by an integer, there are two or three minor peaks labeled by an asterisk which are located on the right side of the major peaks. These minor peaks correspond to products containing both benzene and water molecules. Once again, the water impurities come mainly from the helium buffer gas; the products corresponding to the major peaks contain only benzenes. From the dependence of the peak intensity on the benzene partial pressure, we can estimate that its primary reaction is slower than that with polar molecules reported above. It is seen that both primary and sequential reactions with benzene and ethylene also correspond to attachment or association reactions. These attachment reactions of molecules contained π-bonding systems follow the reaction paths

$$Ti_8C_{12}^+(M)_{n-1} + M = Ti_8C_{12}^+(M)_n \qquad (2)$$

where M is a molecule containing a π-bonding system.

Surprisingly, it is seen from Figure 3a that the reactions with benzene molecules terminate at the fourth reaction step rather than the eighth, which is different from the case of reactions with polar molecules. This suggests that only four benzenes attach in the first solvation shell of $Ti_8C_{12}^+$ at room temperature. In the same way, to verify this, we increased the partial pressure of benzene to see whether more benzenes could become accommodated to $Ti_8C_{12}^+$. Figure 3b is the spectrum obtained at a much higher benzene partial pressure. As seen from Figure 3b, the majority of the products in the early reaction steps were converted into the reaction products of the fourth step at much higher pressures of benzene, but the reaction still terminated at the fourth molecular addition. In the case of the reactions with ethylene, we also find that the reactions with this molecule involve attachment of ethylene onto $Ti_8C_{12}^+$, and most importantly, only four ethylene molecules could bond onto $Ti_8C_{12}^+$ at room temperature. Therefore, $n \leq 4$ in eq 2.

3.3. Reactions with Oxygen and Methane. Aside from those molecules mentioned above, we also investigated the thermal energy reactions of $Ti_8C_{12}^+$ with oxygen and methane. Neither of these molecules have either permanent dipole moments or a π-bonding system. The motivation for using these reactants was to test whether $Ti_8C_{12}^+$ can undergo, besides association reactions, chemical reactions that involve breaking and forming chemical bonds. We find that unlike the reactions discussed above, $Ti_8C_{12}^+$ is inert toward the two molecules. No "real" chemical reaction occurs as evidenced by the failure to observe any product at low pressures. Even at very high pressures of oxygen and methane (ca. 0.1 Torr), only a small fraction of $Ti_8C_{12}^+$ is observed to attach oxygen or methane to form an association or addition product.

4. Discussion

Indeed $Ti_8C_{12}^+$ displays a unique chemical behavior. Although the titanium containing Met–Car is very reactive toward molecules with either large dipole moments or π-bonding systems, its reactions proceed mainly through associations or attachments of ligands rather than via chemical reactions involving molecular rearrangements. Even for the association of ligands, the number of ligands bonding onto $Ti_8C_{12}^+$ depends on the type of molecules involved. $Ti_8C_{12}^+$ is found to take up 8 polar molecules, while only 4 molecules with π-bonding systems are accommodated. It is also observed that this cluster ion is inert toward oxygen and methane at room temperature.

At first glance, the experimental evidence that $Ti_8C_{12}^+$ is not only very reactive toward various molecules but can also adsorb a number of these molecules might be taken as evidence against the closed shell structure model proposed for Met–Cars. Because this model suggests that $Ti_8C_{12}^+$ can adopt a dodecahedral structure without dangling bonds, one would expect that this cluster should be resistant to chemical attack by virtually all molecules. However, a careful examination of the proposed structure shows that the experimental results are not in opposition to this model, but are actually supportive of it. As pointed out earlier,[2] the frame of the cage-like structure of $Ti_8C_{12}^+$ is constructed by not only carbons but also titanium atoms with unfilled d-shells. The observed reactivities of $Ti_8C_{12}^+$ might just be the characteristics of a dodecahedral structure containing transition metals in its molecular framework. We rationalize this argument in what follows.

First, considerations of bonding[5,10] suggest the existence of well-defined C_2 dimers whose orbitals bind with the d-orbitals of Ti and that the unoccupied states above the Fermi energy are nearly pure Ti in character. Although all the valence electrons of the titaniums in the dodecahedral Ti_8C_{12} are satisfied, the titaniums have unoccupied d-orbitals.[13] As in the formation of typical transition metal ligand complexes it is very likely that polar ligands such as methanol, which have lone pairs of electrons on one of their atoms, can provide their lone pair of electrons to the unoccupied d-orbitals of the titaniums to form coordination bonds. As a result, $Ti_8C_{12}^+$ can be very reactive toward those polar molecules and each of the titanium atoms can accommodate one polar molecule. Hence, products from the reactions with polar molecules should be able to form $Ti_8C_{12}^+$ coordination complexes containing polar ligands bound to each transition metal atom.

Second, titanium is quite different from carbon in terms of electronegativity. It is expected that there is a formal transfer of electrons from the titanium atoms to the C=C units. As a result, titanium should be more electropositive than carbon in the Ti–C bonds. As a matter of fact, this argument has been borne out by recent calculations from a number of research groups.[5-10] For instance, the calculations of Gale and Grimes[6] indicate that each of the titaniums in the dodecahedral Ti_8C_{12} bears ca. 0.75 positive charge, and each of the C=C units has about 0.50 negative charge, while Reddy et. al.[5] find respective values ranging from +0.66 to +1.07 and –0.44 to –0.71, depending on the basis set used in the calculations. As a result, each of the titaniums on $Ti_8C_{12}^+$ can attract polar molecules through electrostatic interactions. Hence, from either of the above points of view, it is not suprising that $Ti_8C_{12}^+$ can react with polar molecules to form adducts.

Although the ion–dipole force is normally the dominant term in electrostatic interactions, other interactions such as ion–quadrupole and ion–induced dipole forces can, sometimes, be sufficiently strong to hold ions and ligands together at room temperature, if the polarizabilities and quadrupole moments of the ligand are large and result in a favorable interaction.[19] In fact, ion complexes stabilized by those interactions have been observed at room temperature.[20] Both benzene and ethylene have fairly large polarizabilities.[21] In this regard, the fairly strong electrostatic interactions are expected to be sufficient to enable $Ti_8C_{12}^+$ to form small adducts at room temperature.

One might wonder how the number of polar and π-bonding molecules bonding onto $Ti_8C_{12}^+$ can be different. This could be due to the differences in the interaction orientation and strength between $Ti_8C_{12}^+$ and the ligands. For molecules containing π-bonding, it is very likely that their interactions with this cluster ion are mainly ion–quadrupole or ion–induced dipole electrostatic forces, whereas for polar molecules, their interactions could be coordination bonds, or ion–dipole electrostatic interactions, or a combination of both. In terms of the nature of polar molecules, it is expected that their interactions with $Ti_8C_{12}^+$ should be much stronger than those of π-bonding molecules. More importantly, in the case of polar molecules, only the atom containing lone electron pairs will point toward the titanium so that the repulsive interaction of the ligands with the C=C units of $Ti_8C_{12}^+$, or the ligands with each other, will become minimized. In contrast, if the plane of the π-bonding molecular frame would point toward the metal atoms of $Ti_8C_{12}^+$, the repulsive interaction of the π-bonding molecules with C=C bonds would likely be large. Consequently, the attraction between the ion and the π-bonding molecules could be diminished if the molecules approach the ion edge-on; moreover, the repulsion among the ligands would be rapidly increased by such an arrangement. If repulsion is stronger than attraction, there will be no further attachment of ligands onto $Ti_8C_{12}^+$. Therefore, the number of molecules bonding onto $Ti_8C_{12}^+$ should be different, depending on the nature of bonding and ligands. Steric hindrance may enable only atoms with non-occupied nearest-neighbor metal atoms to accommodate ligands, which would lead to the accommodation of only four molecules with large π-bonded molecular frameworks, as observed.

The fact that the observed maximum number of polar molecules bonding onto $Ti_8C_{12}^+$ is equal to the number of metal atoms of which the Met-Cars $Ti_8C_{12}^+$ are comprised has implication regarding its structure. It is believed that this number is indicative that eight titanium atoms are located in similar positions, similarly coordinated, and that all of them are exposed at the surface of the cage rather than within its interior.

Although $Ti_8C_{12}^+$ is very reactive toward many molecules, it appears that its reactions proceed mainly through the association of ligands and do not involve the breaking of any original chemical bonds. If this cluster did not have a closed shell structure, Ti_8C_{12} would have dangling bonds around the edges. These dangling bonds should behave similarly to reactive radicals, and the atoms in dangling positions are likely to undergo "real" chemical reactions with the reactant molecules especially with oxygen which is a good free radical scavenger.

Taken all together, it appears that the observed reactivities of $Ti_8C_{12}^+$ are fully in accord with expectations for a closed cage-like structure containing transition metals, and that the postulated dodecahedral structure for Ti_8C_{12} is supported by these experimental results.

Finally, it is worth briefly discussing the possible implications of the present results on the synthesis of Met-Cars in bulk quantities. As pointed out earlier,[2] our ultimate goal is to develop Met-Cars into a new material. To achieve this goal, one has to make Met-Cars in bulk quantities. If the Met-Car Ti_8C_{12} can be held together by van der Waals forces to form a crystal as in the case of C_{60}, the present work certainly is of significance to those working on the synthesis of Met-Cars in bulk quantities. For instance, the results from the present work indicate that there is a strong interaction between polar molecules and $Ti_8C_{12}^+$. This might suggest that bulk Ti_8C_{12} can be solvated by polar solvents. Considering this fact, it is expected that it might be possible to use polar solvents to extract Ti_8C_{12} from samples which might contain other impurities. In addition, evidence that $Ti_8C_{12}^+$ does not undergo chemical reactions with oxygen at thermal energies (room temperature) suggests that bulk Ti_8C_{12} may also be very stable in air and that samples containing Met-Cars could be handled in air.

Just as this paper was being completed, new experiments from the Duncan group[22,23] revealed that gas-phase Met-Cars of Cr, Mo, and Fe can also be produced by using a plasma reactor technique similar to the one we used in our original work. This adds further excitement to the chemistry which is expected to unfold for this new class of molecular cluster compounds.

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