

# Metallo-carbohedrenes: Recent advancements

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The recently discovered family of molecular clusters, metallo-carbohedrenes (metcars), have generated considerable excitement in cluster chemistry. Metcar research has spread into a large number of transition metals and mixed metals and recent investigations point to the complexity and variety of metcar chemistry. The structure and electronic properties are vigorously studied by various methods of theory. Many of the earlier assumptions have been proved wrong by carefully planned experiments and detailed computational studies. Metcar research will certainly intensify in the years to come in view of their predicted novel properties.

SOME of the most interesting experiments in contemporary chemistry are centered around molecular clusters. Clusters are aggregates of ions, atoms or molecules that are weakly bound together, having properties in-between those of gaseous and condensed states of matter<sup>1</sup>. Most of the available chemistry of molecular clusters is investigated by mass spectrometry. The discovery of buckminsterfullerene<sup>2</sup> in mass spectrometric experiments has added greater impetus to molecular cluster chemistry; the associated physics and materials science also attracted attention. Recently the observation of a peak at 528 amu in the mass spectrum of a laser evaporation experiment culminated in the discovery of yet another class of cage-like molecules called metallo-carbohedrenes, shortly 'metcars'<sup>3</sup>. Castleman and co-workers made this discovery while studying the dehydrogenation reaction of hydrocarbons using metal ions, atoms and clusters<sup>3</sup>. The experimental setup they employed for this discovery was a mass spectrometry/mass spectrometry (MS/MS) system coupled with a laser vapourization source. By performing isotopic labelling experiments and reactions with NH<sub>3</sub>, they came to the conclusion that the elemental composition corresponding to 528 amu is Ti<sub>8</sub>C<sub>12</sub>. They proposed a pentagonal dodecahedron structure to explain its stability (Figure 1 a). They later extended the investigations to other early transition metals<sup>4</sup>, V, Zr and Hf and obtained clusters of the same composition, M<sub>8</sub>C<sub>12</sub><sup>+</sup>. In the case of Zr there is also multicage formation<sup>5</sup>. Pilgrim and Duncan<sup>6</sup> showed that metcar is also possible with Cr, Mo and Fe; face-

centered cubic (fcc) structures beyond metcars (which exists in the cubic form) called nanocrystals<sup>7-10</sup> were also observed. Binary metal metcars of Ti, Y, Nb, Mo, Ta and W have been produced by direct laser vaporization of mixtures of the metal carbide and the metal<sup>11</sup>. Studies related to the mechanism of formation suggest that metal-carbon clusters first develop through multiple ring structures via the successive addition of MC<sub>2</sub> units<sup>12,13</sup>. Photodissociation and metastable decomposition experiments were performed on metcars<sup>7-10</sup> and it was found that the decomposition channel for Ti<sub>8</sub>C<sub>12</sub><sup>+</sup> is through the loss of Ti atom. Castleman *et al.* studied the reaction of metcar with H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>3</sub>OH which resulted in the formation<sup>14</sup> of M<sub>8</sub>C<sub>12</sub>(H<sub>2</sub>O)<sub>8</sub>, etc. With  $\pi$ -bonding molecules such as benzene it resulted in the formation of M<sub>8</sub>C<sub>12</sub>(benzene)<sub>4</sub>. Reaction of metcar with acetone is an association process whereas abstraction takes place with iodine to form M<sub>8</sub>C<sub>12</sub>-I (ref. 15). The metcar research until early 1995 was summarized in an earlier review<sup>16</sup>. Since then, many new experiments have been performed and our understanding of these unusual clusters has improved substantially and many of the earlier assumptions have been proved to be untrue. We present here the state-of-the art of the subject matter.

Theoretical investigations on metcars focused mainly on the structure and stability of the cluster. Castleman *et al.* proposed a dodecahedral structure (T<sub>h</sub> point group) for metcars<sup>3</sup>. It can be viewed as a cubic M<sub>8</sub> cluster with six C<sub>2</sub> units capping the six faces of the cube<sup>17-30</sup> (Figure 1 a). Hay subsequently showed that the electronic configuration with lowest energy for the T<sub>h</sub> cage of Ti<sub>8</sub>C<sub>12</sub> corresponds to a nonet state with one unpaired electron each localized on the Ti atoms<sup>31</sup>. Calculations predicted that Ti<sub>8</sub>C<sub>12</sub> with T<sub>h</sub> symmetry will undergo Jahn-Teller distortion<sup>32-34</sup>. Another structure which has received considerable theoretical attention with less experimental evidence is the tetracapped tetrahedron of T<sub>d</sub> symmetry (and the closely related structure of D<sub>2d</sub> symmetry), proposed by Dance<sup>35</sup> (Figure 1 b). Geometrical optimizations carried out using either density functional approach or *ab-initio* Hartree-Fock methodology show that a 45° rotation of all dicarbon fragments with respect to the underlying skeleton of metal atoms leads to a cage structure with 36 metal-carbon bonds which is much more stable than the pentagonal dodecahedron<sup>35-40</sup>.

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