

Analysis of the Magic Numbers Observed for Metallocarbohedrane Clusters

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Abstract. A local-density approximation calculation is performed on various M_8C_{12} structures, including Ti_8C_{12} , V_8C_{12} , VTi_7C_{12} and $ScTi_7C_{12}$. It is found that the magic numbers observed during the experimental discovery of these species does not depend on the details of the electronic structure, but rather can be described as a chemical system derived from ethylene.

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1. Introduction

Mass spectral evidence for species formulated as M_8C_{12} , where $M = Ti, V, Zr$ or Hf , was recently reported by Castleman and coworkers.¹ They postulated that these species are metallocarbohedranes ("metcars"), i.e., closed polyhedra with dodecahedral symmetry. The proposed structure has 30 edges defining 6 C-C and 24 M-C nearest neighbor interactions. Alternately, the molecule can be described as a cube of metals with a C_2 unit centered above each face of the cube.

Most stunning about these structures is the well-defined stoichiometry that they assume. Like the fullerenes, among which C_{60} has particular stability, the M_8C_{12} compounds are greatly favored over other stoichiometries, especially for $M = Ti$ and V . This is what we term the magic number effect, and the primary purpose of this paper is to try to account for it.

The geometry proposed by Wei et al¹ is consistent with several different bonding interpretations, each of which can be supported by chemical precedent. For example, these species might be related to the interstitial carbides. The solid-state lattices of TiC , HfC and V_2C , consist of close-packed arrays of metals, with carbon atoms occupying the lattice interstices. However, interstitial

systems often exhibit variable stoichiometry, and hence the magic number should not be so well defined.²

A second possibility is an acetylide salt. Here the best-known analogy is calcium carbide, CaC_2 . This species is ionic, with discrete Ca^{+2} and C_2^{-2} ions. However, for M_8C_{12} , this model requires a non-integral charge (+1.5) on the metal ion.

A third approach is to consider M_8C_{12} a true cluster, held together by delocalized covalent bonds, analogous to the highly-stable fullerenes. (Since titanium has four valence electrons, Ti_8C_{12} would be valence isoelectronic with an all-carbon cluster.) However, the smallest stable fullerene has 32 atoms, so the metallocarbohedranes are too small to be directly related. Moreover, the valence electron count (80 and 88 for the Ti- and V- carbohedrane species, respectively) is inconsistent with expectations from the Wade-Mingos rules, commonly applied to small clusters.³

Very recently Grimes and Gale⁴ performed an *ab initio* study of Ti_8C_{12} and Si_8C_{12} . Our data generally confirm theirs, but we have more to say about the magic number effect. Section 2 presents the details of our method, results are presented in Section 3, and a brief conclusion appears in Section 4.

2. Method

The electronic structures of the clusters considered here were solved within the local-density approximation⁵ with the exchange-correlation formula of von Barth-Hedin.⁶ The LCAO formalism was then used to find the one-electron orbital eigenvalues and wave functions. The actual calculations were carried out using an SCF method.^{7,8} This *ab initio* method can find solutions for large electron systems with a reasonable amount of computing effort, especially if some additional approximations are made, as described below.

Only the minimal basis set was used, i.e., those atomic orbitals which are occupied in free atoms C, Sc, Ti and V. Furthermore, the core orbitals of these atoms were "frozen" to their atomic one-electron wave function forms, but otherwise fully accounted for in the solution of the molecular electronic structure. Thus the molecular orbitals of the clusters were built from the valence orbitals C: 2s, 2p; Sc, Ti, V: 3d, 4s. The deepest valence level included was the C 2s at -14 eV and the highest frozen core level was the Sc 3p at -34 eV. The minimal basis set used here provides satisfactory qualitative comparisons between different clusters. Where quantitative accuracy is required in what follows, we shall use the data provided by Grimes and Gale for Ti_8C_{12} .⁴

The geometry was optimized by minimizing the total energy for the system where both electronic spins were treated equally (spin-restricted). This corresponds to the singlet state of the cluster. The clusters tended to have a very small or zero gap between the HOMO and LUMO levels, resulting in instabilities. By using a low temperature Fermi-Dirac distribution for the occupations of the levels, stable solutions were obtained. This should have only a negligible effect on the electronic structure. The Ti_8C_{12} cluster was treated in D_{2h} symmetry but other clusters were allowed to find their conformations free from symmetry restrictions.

3. Results and Discussion

We first inquire into the electronic structure of the metcars. More data is presented by Grimes and Gale.⁴ We find in all cases that the Fermi level is only partially occupied, implying that the clusters will have metallic or semi-metallic-like properties. For Ti_8C_{12} , the four orbitals around the Fermi level are separated by 0.16 eV and are populated by four electrons, distributed according to Fermi-Dirac statistics. The lowest substantially unoccupied level is 0.22 eV higher in energy. Hence adding or subtracting as many as four electrons should make relatively little difference in the stability of the cluster.

This is illustrated by Table I. The binding energy of Ti_8C_{12} is 0.73 eV lower than $\text{VTi}_7\text{C}_{12}$. In the latter case an additional electron has been added. However, it is known that because of the extra proton, vanadium is smaller than titanium, and the additional nuclear charge should help stabilize the molecule. Our previous study of boron- and nitrogen- doped fullerenes illustrates this point very well.⁹ There we show that doping with nitrogen (smaller than carbon) stabilizes the molecule, whereas doping with boron (bigger than carbon) destabilizes it. Analogously, doping with vanadium stabilizes and doping with scandium destabilizes the metcar cluster (by 0.97 eV).

Presumably, adding two vanadiums to the metcar would stabilize it even more, perhaps by 2×0.7 eV or so. However, Table I shows that the V_8C_{12} cluster is nowhere

near 8×0.7 eV more stable, and this must reflect the fact that the additional electrons are now populating orbitals of significantly higher energy.

Cluster	Binding energy
Ti_8C_{12}	122.4
$\text{VTi}_7\text{C}_{12}$	123.1
V_8C_{12}	123.6
$\text{ScTi}_7\text{C}_{12}$	121.5

Table I. Binding energies, in eV, for various metcar clusters.

It can in any event be argued that the magic number effect is not directly related to the electronic structure of the molecule. The open-shell nature of the species, along with the evidence presented in Table I, shows that metcars are unlike common fullerenes, which have well-defined band-gaps and closed-shell HOMO levels. This is partly because fullerenes have globally delocalized electrons throughout the molecule. The open-shell nature of the metcars implies that they are different - there may be dangling bonds or localized bonds with electrons largely fixed in one place. It is thus useful to consider what sort of chemical analogy most appropriately fits.

We first think of metcars as being "chips off the old block," i.e., a fragment from an interstitial carbide compound. Silicon clusters probably follow this pattern in that they probably assume bulk-like geometry even for relatively small species.¹⁰ However, while some sizes for silicon clusters seem to have special properties, there is nothing remotely resembling the magic number effect observed here. Relevant interstitial carbides include TiC and Ti_2C , both of which assume a NaCl-like lattice structure.² However, the carbons in the metcars are arranged in C_2 patterns, and this is not the case for the titanium carbides. Calcium carbide, however, does contain the C_2 moiety in the interstices of an fcc calcium lattice, so some precedent does exist. This is an ionic species, with the carbon existing as acetylide ions. Nevertheless, it seems the interstitial carbide model is not a good description of metcars.

However, the structure of CaC_2 indicates that metallocarbohedranes could exist as ionic species, with metal cations and acetylide anions. This was first proposed by Grimes and Gale.⁴ The Mulliken population analysis for Ti_8C_{12} partially supports this conclusion: it is found that titanium has a +1 charge and carbon a -0.7 charge, not too distant from what one might find in the idealized metal-acetylide structure. Several objections can be raised, however. First, such a model would predict an empirical formula of TiC_2 , rather than Ti_2C_3 . Secondly, even allowing for the latter stoichiometric ratio, an ionic model offers no compelling reason why the molecular formula

should be uniquely Ti_8C_{12} . Finally, the calculated C-C bond-length, shown in Table II, do not match acetylide, which is 120 pm.

Bond	Length A	Length B	Source
Ti-Ti	306	238	Ti solid
Ti-C	198	196	Ti+C radii
C-C	140	142	graphite

Table II. Bond lengths, in pm, of various bonds in metcar clusters. Length A refers to the bond as calculated in the Ti_8C_{12} cluster in Ref. 4. Length B refers to the bond length as found in the system shown in the fourth column.

It appears that a strict ionic model is also inappropriate, so some sort of covalent structure must be hypothesized. The obvious choice is an ethylene-like arrangement, with titaniums replacing the hydrogen atoms. In this case the carbon atoms are sp^2 hybridized, for which the C=C bond length should be 134 pm. It is obviously longer, and also the titaniums are not coplanar with the carbons. Finally, the charge density is such that each carbon has a charge of -0.7, much larger than for ethylene.

We now point out that for covalent systems, Mulliken analysis yields somewhat arbitrary results, since it depends on how the bond is split between the two atoms, and thus on the precise nature of the basis set. Therefore, if the covalent model is accepted, the Mulliken population data should not be taken literally. On the other hand, the ethylene moiety must be strained, and it is certainly sensible to think of the Ti-C bond as being polar covalent. The strain reduces the bond order from 2 to about 1.5, and thus the bond length is comparable to that found in graphite.

Let us estimate the bond energies for the different bonds. The C-C bond energy is taken from graphite, and the C-Ti bond strength is obtained from subtraction from the total energy of the cluster. This data is shown in Table III. Now the magic stoichiometry can be explained. If a carbon is replaced by a titanium atom (Ti_9C_{11}), then a C-C bond and 2 C-Ti bonds are lost, and a C-Ti and 2 Ti-Ti bonds are gained. The net cost is about 6.7 eV. On the other hand, if a titanium is replaced by a carbon atom, then the added trivalent carbon would disrupt the adjacent C=C π interactions, weakening the overall system. Our calculations suggest that the average C-C bond strength would be reduced by over 2 eV.

Bond	Bond Order	Bond Strength
Ti-Ti	1.0	1.4
Ti-C	1.0	3.5
C-C	1.5	6.0

Table III. Bond strengths of relevant bonds, in eV. C-C and Ti-Ti are taken from graphite and titanium solid, respectively. The Ti-C bond strength is calculated by subtraction from the binding energy of the cluster.

4. Conclusion

We have shown that a covalent, or at least polar covalent, model for metcar systems can account for the magic number effect. We now ask the question: to what extent are metcar systems analogous to fullerenes? On the one hand, the bond structure of the molecule is fullerene-like; there are 30 bonds in the molecule, and it thus consists of 12 pentagonal rings, whereas if the structure were ionic, then it would make no sense to talk about bond topology at all. On the other hand, as we have already pointed out, the metcar electronic structure must be localized to a much greater extent. The billions of Kekule structures that exist for bucky ball are absent here, and it is probably more accurate to think of this structure as being made up of ethylene units.

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References

1. Wei, S., Guo, B. C., Buzza, S., Castleman, A. W., *J. Phys. Chem.* **96**, 4166 (1992).
2. See Wells, A. F., *Structural inorganic chemistry*, 5th ed., pp. 947-952. Oxford. New York. Clarendon 1984.
3. Wade, K., *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976); Mingos, D. M. P., *Chem. Soc. Rev.* **15**, 31 (1986).
4. Grimes, R. W., Gale, J. D., *Chem. Comm.*, in press.
5. Kohn, W., Sham, L. J., *Phys. Rev. A* **140** 1133 (1965).
6. Von Barth, U., Hedin, L., *J. Phys. C* **136**, 864 (1964).
7. Rantala, T. T., Wästberg, B., Rosén, A., *Chem. Phys.* **109**, 261 (1986).
8. DMol Version 2.2, BIOSYM Technologies, San Diego, CA, USA (1992).
9. Xia, X., Bowser, J. R., Jelski, D. A., George, T. F., *J. Amer. Chem. Soc.* **114**, 6493 (1992).
10. For example, see Jelski, D. A., Swift, B. L., Rantala, T. T., Xia, X., George, T. F., *J. Chem. Phys.* **95**, 8552 (1991).