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Theoretical Studies on the Stability of M_8C_{12} Clusters

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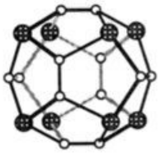
Abstract: Ab initio calculations with effective core potentials were completed on M_8C_{12} (M = Y, Zr, Nb, and Mo) clusters. Three different isomers (T_h, D_{3d}, and T_d) have been investigated. The T_h and D_{3d} isomers are derived from a dodecahedral geometry. In the former, the faces of a cube of the metal atoms are capped by ethylene-like C_2 units, while in the latter the 12 carbons form a cylindrical, closed chain capped by two M_4 units. In the T_d isomer, six acetylene-like C_2 units link the vertices of a tetracapped tetrahedral metal framework in a butterfly fashion. Our calculations show that the observed M_8C_{12} (M = Ti, Zr, Hf, V, Mo or W) clusters most likely adopt a structure similar to the T_d structure rather than one of the dodecahedral structures. The T_d structure is more stable than the T_h or D_{3d} structure by more than 200 kcal/mol. Molecular orbital analyses of the bonding in the T_d structure allow us to derive "magic numbers" of metal electrons, i.e., 18 and 36 when we formulate the cluster as $(M_8)^{12+}(C_2^{2-})_6$. The unique geometry and electronic structure are responsible for the observation of high stability of these metal–carbon clusters. In the group 4 clusters, a dicationic cluster, e.g., $[Ti_8C_{12}]^{2+}$, may be the best target to be isolated in the solid state as an ion.

Introduction

The discovery of C_{60} has prompted extensive studies in fullerenes and related carbon clusters.[1,2] Recently, a new class of highly stable 20-atom molecular clusters (8 transition-metal atoms and 12 carbon atoms) was reported. These clusters were formed when titanium (Ti), vanadium (V), zirconium (Zr), hafnium (Hf), molybdenum (Mo), or tungsten (W) was laser-vaporized in the presence of small hydrocarbon species, such as methane, acetylene, ethylene, and benzene.[3] A cage-like pentagonal dodecahedral structure with T_h symmetry **1** was proposed for the 20-atom clusters. Multicage structures were also proposed for Zr_mC_n.[4] In a previous communication,[5] the high stability in such a proposed structure was rationalized by assuming weak, rather than strong, metal–carbon d_π–p_π interactions. Thus, the transition-metal atoms would serve mainly to link the six ethylene-like units through M–C σ bonds. A similar valence-bond description for M_8C_{12} clusters was also proposed by Pauling.[6a] A larger number of other electronic structure calculations based on the proposed T_h symmetry have also been done.[6]



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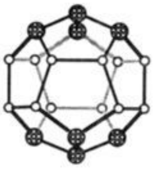
More recently, the hypothesis of a T_h **1** symmetry for M_8C_{12} clusters has been questioned.[6b,c,j] For example, a completely different D_{3d} structure **2** with direct metal–metal bonding was proposed as an alternative.[6c] This D_{3d} structure **2** is derived from a dodecahedral geometry by exchanging the positions of carbon and metal atoms. A particularly interesting geometry in which six C_2 units bridge the vertices of an M_8 tetracapped tetrahedron **3** has been proposed by Dance.[6b] In his local density functional calculation on Ti_8C_{12}, Dance found that this unique T_d isomer **3** is much more stable (ca. 351 kcal/mol) in energy than the proposed T_h isomer. Benard and his co-worker have also pointed out that the T_h structure has first-order Jahn–Teller instability.[6e]



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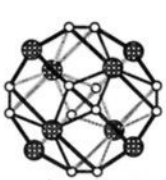

metal-metal bond is omitted from the structure for clarity

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In M_8C_{12} clusters, M is limited to certain transition-metal atoms: group 4 (Ti, Zr, and Hf), group 5 (V), and group 6 (Mo and W).[3] Although the V cluster is stable, the Nb and Ta clusters are not. Electronically, these results have special implications

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Table I. Selected Structural Parameters and Relative Energies of Different Geometries for M_8C_{12} Clusters

isomer		cluster			
		Y_8C_{12}	Zr_8C_{12}[a]	Nb_8C_{12}	Mo_8C_{12}
T_h	rel energy (kcal/mol)	0.00	0.00 (235.5)	0.00	0.00
	structural parameters (Å)				
	C–C	1.36	1.40 (1.45)	1.39	1.30
	M–C	2.38	2.24 (2.16)	2.16	2.13
	M–M	3.76	3.52 (3.36)	3.41	3.32
D_{3d}	rel energy (kcal/mol)	−20.1		3.6	
	structural parameters (Å)[b]				
	C_1–C_2	1.39		1.40	
	C_2–C_3	1.54		1.60	
	M_1–C_1	2.60		2.46	
	M_2–C_1	2.46		2.10	
	M_1–M_2	3.37		2.92	
T_d	rel energy (kcal/mol)	−176.2	−255.6		−203.0
	structural parameters (Å)[c]				
	C–C	1.31	1.36		1.34
	M_o–C	2.44	2.13		2.05
	M_i–C	2.62	2.37		2.23
	M_o–M_i	3.41	3.16		3.08
	M_i–M_i	3.36	3.24		3.00

[a] The numbers not in parentheses were calculated from an electronic configuration of $(a_g)^1(T_u)^3(T_g)^3(a_u)^1$ while the numbers in parentheses were calculated from a configuration of $(a_g)^2(t_u)^6(t_g)^0(a_u)^0$ (see text for details). [b] See **4** for the details of atomic numbering. [c] M_o and M_i denote the outer and inner tetrahedral atoms, respectively.

with respect to high stability for certain electron counts. In this paper, we will study the relative stabilities of these different isomers (structures). Furthermore, we will extend Dance's work further to study the high stability of the T_d structure, to analyze the bonding in this newly proposed structure, and to understand the magic number (metal-carbon combination) observed experimentally.[3]

Theoretical Details

Ab initio effective core potentials (ECP)[7] were employed in all calculations. Geometries were optimized at the restricted Hartree–Fock level. In the geometry optimizations, double-ζ basis sets were used for C atoms[7b] while a double-ζ representation of 4d orbitals and a single-ζ representation of 5s/5p orbitals were employed for second-row transition-metal atoms.[7a] The use of second-row transition metals diminishes the need for electron correlation in the geometry optimizations.[8]

All calculations were performed with GAMESS and Gaussian 92 software[9] at the Cornell National Supercomputer Facility (CNSF) on an IBM ES9000, at the Supercomputer Center of Cray Research, Inc., Minnesota, on a Cray Y-MP8I/8128-2, and on a Silicon Graphic Iris Indigo workstation.

Results and Discussion

Geometry optimizations have been completed on T_h **1**, D_{3d} **2**, and T_d **3** structures for Y_8C_{12}, Zr_8C_{12}, Nb_8C_{12}, and Mo_8C_{12}. Table I lists selected structural parameters and the relative energies of these three isomers for these clusters. As we can see from Table I, the T_d isomer is vastly more stable than the T_h and D_{3d} isomers. The T_h and D_{3d} isomers are comparable in stability. Apparently, the extremely high stability of the T_d isomer, when compared to others, arises because it has numerous additional metal–metal and metal–carbon interactions. In the following sections, we will briefly discuss results of the two less stable isomers and then focus our attention on the bonding analysis of the T_d structure (the most stable isomer).

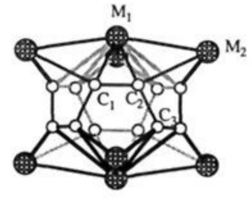
T_h Isomer. Because of the weak metal–metal interaction in the proposed T_h structure (no metal–metal bonds, see **1**), there are a large number of electron configurations that could be chosen for the ground stable configuration. Based on our previously developed model,[5] where the transition-metal atoms serve mainly to link the six ethylene-like units through M–C bent σ bonds, one can appreciate the starting configurations used for the T_h dodecahedral structure of M_8C_{12} described below. In the Y_8C_{12} cluster, each Y uses up all of its three valence electrons to form each of the three Y–C σ bonds. Thus, the electronic configuration for Y_8C_{12} satisfies this bonding description and may be viewed formally as d^0 Y^{3+} ions connected by C_2^{4-} units.

In the Zr_8C_{12} cluster, the Zr uses three electrons to form three Zr–C σ bonds. Thus, each metal has a remaining valence electron, which is most likely localized in the metal centers. The highest spin multiplicity ($2S + 1 = 9$) corresponds to an electronic configuration with each remaining d^1 valence electron occupying a radially outpointing orbital on each metal atom. Therefore, a geometry optimization with the restricted HF open shell calculation was performed for the Zr_8Cl_{12} cluster with the valence electron configuration $[Y_8C_{12}](a_g)^1(t_u)^3(t_g)^3(a_u)^1$ in T_h symmetry. The a_g and t_u molecular orbitals correspond to metal–metal in-phase combinations while the t_g and a_u molecular orbitals are the out-of-phase combinations. The calculated structural parameters for the T_h Zr_8C_{12} with this configuration are shown in Table I (numbers not in parentheses). To examine the possibility of metal–metal interactions in the T_h Zr_8C_{12} cluster, we also optimized the zirconium cluster with the closed-shell configuration $[Y_8C_{12}](a_g)^2(t_u)^6(t_g)^0(a_u)^0$, in which the Zr–Zr bonding orbitals are occupied and the antibonding ones are not. The results are also listed in Table I (in parentheses).

For Nb_8C_{12}, the geometry optimization was done with the configuration $[Y_8C_{12}](a_g)^2(t_u)^6(t_g)^6(a_u)^2$; the eight molecular orbitals discussed above are fully occupied. In Mo_8C_{12}, eight electrons are added (when compared to Nb_8C_{12}). For theoretical simplicity, we chose a closed-shell configuration, $[Y_8C_{12}](a_g)^2(t_u)^6(t_g)^6(t_u)^6(e_g)^4$, in which the a_u is not occupied and extra electrons occupy the t_u and e_g molecular orbitals. The results for these latter two systems are also shown in Table I.

Here, we comment briefly on the calculated T_h structures since we are more interested in the vastly more stable T_d isomers. As we can see from Table I, the M–C and M–M distances decrease from group 3 (Y) to group 6 (Mo). This trend does not indicate changes in the extent of delocalization or metal–metal bonding in these clusters, but it does reflect the decreasing sizes of transition metals, e.g., the metallic radii of Y, Zr, Nb, and Mo are 1.82, 1.60, 1.47, and 1.40 Å, respectively.[10] The C–C bond distances in the Mo_8C_{12} cluster are the shortest in these dodecahedral (T_h) clusters, but they depend heavily on the configuration.

D_{3d} Isomer. Recently, a D_{3d} **2** alternative, which is a different dodecahedral geometry with direct metal–metal bonding, was proposed by Ceulemans and Fowler.[6c] Based on this proposed structure, we optimized the geometries of Y_8C_{12} and Nb_8C_{12} clusters. The resulting geometry is shown in **4**, and can be described as a 12-carbon chain with alternating single and double



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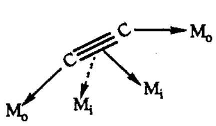
bonds linked by two M_4 units (C_1–C_2 are double bonds and C_2–C_3 are single bonds; see the selected structural parameters in Table I). The optimized strucutres differ significantly from the dodecahedral ones and the short C–C bond distances again show the importance of carbon–carbon interactions. The Y_8C_{12} cluster has much longer M–C and M–M bond lengths than the Nb_8C_{12} cluster. These differences are again closely related to the sizes of the relevant metals. These metal–metal distances are also much shorter than those in the T_h dodecahedral clusters, further evidence of the lack of direct metal–metal bonds in the T_h dodecahedral clusters **1**.

The calculated D_{3d} conformation for Y_8C_{12} is 20.1 kcal/mol lower in energy than its T_h conformer while for Nb_8C_{12} it is 3.6 kcal/mol higher than its T_h conformer. Attempts to obtain another D_{3d} structure with a different pattern of C–C single–double bond alternation (C_1–C_2 as single bonds and C_2–C_3 as double bonds) did not result in a local minimum.

T_d Isomer. Examining the structural feature of the T_d isomer **3**, one can see that the eight transition metals form a tetracapped tetrahedron. Six C_2 units are aligned along the six edges of the outer tetrahedron formed by the four capping metal atoms. In other words, the six C_2 units are end-on bonded to the four capping metals and are side-on to the inner metal tetrahedron. For theoretical simplicity, one can describe the structure and bonding of the T_d cluster as six acetylene-like units (C_2^{2-}) bonded to the four outer capping metal atoms through 12 σ bonds and the inner tetrahedral metal unit bond to the six C_2 units through the side-on (η^2-C_2) π bonding electrons. A schematic illustration of such bonding is shown in **5**. Although such a bonding description is, of course, an oversimplification, it must represent a major resonance contribution because the calculated structural parameters in Table I show that the M_o–C bond is shorter than the M_i–C bond, where M_o and M_i stand for atoms of the outer and inner tetrahedron in the T_d cluster (see **3**).



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Based on this simplified description for the C–C and M–C bonding, one can easily extract the metal–metal bonding orbital interaction and the metal electron count. In the optimized structures (T_d) for the three clusters lised in Table I, each inner metal is coordinated by three acetylene-like ligands which are arranged in a pseudotriangular plane while each outer metal also has three ligands bonded to it in a pyramidal arrangement (C–M_o–C is about 95.0° from the optimized structures). Therefore, each metal center can be taken as a ML_3 fragment. Without considering the metal–metal bonding, the inner metal atom is coordinated side-on to its three adjacent C_2 units in a trigonal planar fashion and the outer metal atom is coordinated end-on to its three adjacent C_2 units in a C_{3v} pyramidal manner, a familiar fragment derived from an octahedron.

Because of the high 4d–5p promotion energy, the importance of p orbital involvement in the metal–metal bonding will be omitted from the metal–metal orbital interaction argument below. When the *z* axis is perpendicular to the plane of the inner-metal pseudo-ML_3, the $d_{x^2-y^2}$ and d_{xy} are used to form σ bonds with the π bonding pairs of the acetylene-like C_2 units. Thus, for each inner metal atom, there are three d orbitals (d_{z^2}, d_{xz}, and d_{yz}) available for metal–metal interaction. For each outer metal atom, there are again three available orbitals, which are often referred to as the "t_{2g}" set from a ML_3 fragment derived from an octahedron.[11] The orbitals of the "t_{2g}" set are usually taken as metal–metal nonbonding in most carbonyl clusters.[12] However, they are very important in the metal–metal bonding in other noncarbonyl clusters such as octahedral $M_6(\mu_2\text{-}X)_{12}L_6$ and $M_6(\mu_2\text{-}X)_8L_6$ (M = Zr, Mo, or W, X = halide, and L = phosphine or halide) clusters.[13]

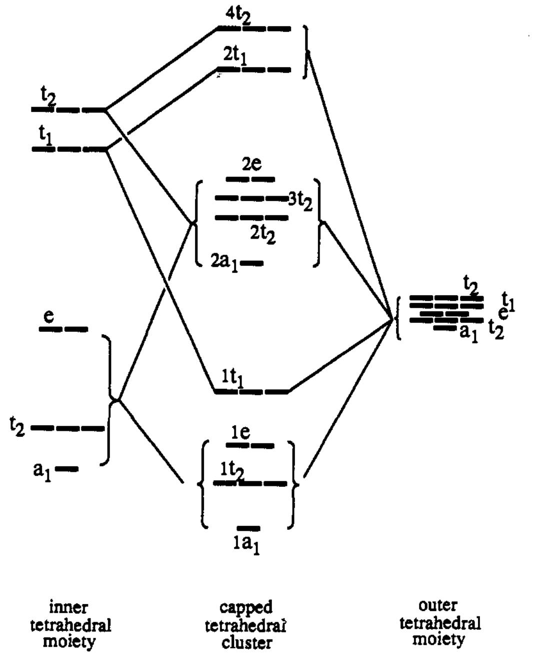

Figure 1. A schematic orbital interaction for a tetracapped tetrahedral metal cluster (M_8C_{12}).

At this stage, we can easily develop the metal–metal orbital interaction in the tetracapped tetrahedral cluster. In the inner tetrahedral unit, the interaction among the twelve metal orbitals (d_{z^2}, d_{xz}, and d_{yz} from each metal atom in the local coordinate assignment) results in six bonding ($a_1 + t_2 + e$) and six antibonding ($t_1 + t_2$) orbitals which are shown in the left column of Figure 1. The right column of Figure 1 shows the linear combinations of the outer metal orbitals ($a_1 + t_2 + e + t_1 + t_2$), a total of 12 orbitals that have the same symmetry as those in the inner tetrahedron. They are located together at an intermediate energy because the interactions among them are weak. As a result of strong interaction between the inner and outer tetrahedrons, the six original bonding orbitals from the inner unit are stabilized further. In addition, three extra bonding orbitals are obtained from the interaction of the two t_1 sets of orbitals (the antibonding set from the inner metals and the nonbonding set from the outer metals). The interaction also gives rise to 9 weakly antibonding orbitals ($2a_1$, $2t_2$, $3t_2$, and 2e, see Figure 1). The $2a_1$ molecular orbital is bonding in nature within the inner tetrahedron, but antibonding between the inner and outer tetrahedral moieties. A similar situation prevails for the 2e. The location of the two t_2 ($2t_2$ and $3t_2$) molecular orbitals in the weakly antibonding region is a result of four-orbital interaction (two nonbonding orbitals from the outer tetrahedron, one bonding and one antibonding from the inner tetrahedron). The orbital energy ordering in the center column is based on the result of the ab initio calculation on the T_d Mo_8C_{12} cluster.

According to Figure 1, one should expect an especially stable cluster with 18 metal d electrons, i.e., when the $1t_1$ is fully occupied. A total number of 36 metal electrons will satisfy the next significant orbital gap, up to the occupation of the 2e orbitals. In the latter case the $1a_1^2 1t_2^6 1e^4 1t_1^6 2a_1^2 2t_2^6 3t_2^6 2e^4$ configuration

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corresponds to formation of 18 metal–metal (edge) bonds in the tetracapped tetrahedron (one along each edge). Although the $2a_1$ up to 2e are somewhat antibonding, they can be stabilized through mixing with high-lying p orbitals which have been omitted from our discussion. From Figure 1, we can also exclude those clusters with more than 36 electrons, because electrons would need to occupy the very strongly antibonding $2t_1$ or $4t_2$.

From the discussion above, one comes to the conclusion that, if the T_d isomer represents the structure of M_8C_{12} clusters, the obvious magic numbers must be 18 or 36 electrons. Now, let us examine the number of metal electrons in the observed M_8C_{12} clusters. Since the C_2 units are taken as acetylene-like, the formal charge of each is −2, i.e., C_2^{2-}. The six C_2 units take 12 electrons from transition metals to satisfy the acetylene-like formula. Therefore, Y_8C_{12} has only 12 metal electrons, while Ti_8C_{12}, Zr_8C_{12}, and Hf_8C_{12} clusters have 20 metal electrons. V_8C_{12} has 28 electrons and Mo_8C_{12} (or W_8C_{12}) has 36 electrons.

From the analysis above, we can see that Mo_8C_{12} (or W_8C_{12}) satisfies the magic number of 36 electrons while the group 4 clusters have 2 metal electrons in excess of the magic number of 18. Our calculations indicate that the two extra electrons in the group 4 clusters occupy the slightly antibonding $2a_1$ orbitals. Here, one may raise a question why the group 4 M_8C_{12} clusters are stable as they have two extra electrons in excess of the magic number of 18. One should realize the fact that with only one type of metal, group 4 clusters are those clusters which have the closest electron count to 18. Furthermore, the $2a_1$ molecular orbital has spherical-like symmetry and is delocalized extensively over the entire cluster. Therefore, the occupation of this slightly antibonding molecular orbital simply increases the volume of cluster evenly. The stability of the V_8C_{12} cluster may be due to the weaker metal–metal bonds for first-row as opposed to second- or third-row metals. Thus, a high-spin state which corresponds to a configuration of $[Zr_8C_{12}]2t_2{}^3 3t_2{}^3 2e^2$ (see Figure 1 for a reference of orbitals) could be particularly stable. The instability of Nb_8C_{12} and Ta_8C_{12} clusters[3d] can be explained through their more diffuse d orbitals which cause significant splittings among the eight singly occupied orbitals of the V cluster.

Conclusions

Our calculations suggest that the observed M_8C_{12} (M = Ti, Zr, Hf, V, Mo, and W) clusters adopt a T_d-like structure which has a tetracapped tetrahedral metal framework linking six C_2 units in a butterfly fashion. This T_d structure is 200 kcal/mol more stable than a dodecahedral structure (T_h). One can, for theoretical simplicity, describe the structure as having six acetylene-like C_2^{2-} units linked end-on by the four capping metal atoms and side-on by the inner tetrahedral metal unit. Molecular orbital analyses on such a T_d structure allow us to derive the magic numbers of metal electrons, i.e., 18 and 36 when we formulate the cluster as $(M_8)^{12+}(C_2^{2-})_6$. The unique geometry and electronic structure are responsible for the observation of high stability of these metal–carbon clusters which correspond closely to those magic numbers. In the group 4 clusters, a dicationic cluster, e.g., $[Ti_8C_{12}]^{2+}$, may be the best target to be isolated in the solid state as an ion.

Usually, stable metal systems have a full coordination sphere of ligands. Therefore, we would expect that these clusters with exposed metals are highly reactive. Furthermore, we expect that they would be difficult to isolate in the solid state unless extra ligands are introduced to protect the metal centers from reacting with other species. The extra ligands can be neutral ligands (such as NH_3 and PR_3), which can bond to metal centers to form a protecting coordination sphere. In fact, the $Ti_8C_{12}(H_2O)_8$, $Ti_8C_{12}(NH_3)_8$, and $Ti_8C_{12}(CH_3OH)_8$ clusters have been detected.[3] Each metal atom in T_d structure **3** does have an open site to coordinate one extra ligand. In the T_d structure, one can also distinguish two types of transition-metal atoms (4:4). Therefore, one would expect two different coordination sites in the T_d structure. The four capping metal atoms apparently have larger open coordinate sites. It has indeed been reported that only four molecules of larger nonpolar organic molecules coordinate to the metal–carbon clusters.[3d,14] This can be easily explained from the T_d structure discussed in this paper.

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