

Metal–Polyhydride Molecules Are Compact Inside a Fullerene Cage

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Abstract: Quantum chemical calculations show that metal–hydride molecules are more compact when they are placed inside a fullerene cage than when they are isolated molecules. The metal–hydrogen bond distance in ZrH_4 becomes 0.15 Å shorter when it is placed inside a C_{60} cage. Metal–polyhydride molecules with a large number of H atoms such as ScH_{15} and ZrH_{16} , which are not bound as isolated molecules, are predicted to be bound inside a fullerene cage. It is also shown that two TiH_{16} clusters are bound inside a bicapped (9,0) carbon nanotube. Possible ways to make metal–hydrides inside C_{60} and nanotubes are suggested.

Introduction

Metal–hydrides are of considerable interest as potential hydrogen storage systems. A design target of 6.5 weight (wt)% has been regarded as adequate.¹ Species of MH_n type, with $n = 9$, as for example ReH_9^{2-} , are known experimentally.^{2,3} We have recently predicted the existence of some MH_{12} molecules, where M is a group 6 atom, Cr, Mo, and W.⁴ The isoelectronic ions VH_{12}^- , TiH_{12}^{2-} , and MnH_{12}^+ also turned out to be stable. In a hypothetical solid $\text{Li}(\text{VH}_{12})$, the hydrogen weight percentage would be 17. This study suggested that the number of hydrogen atoms, bound to a metal atom, could be increased from the previously known $n = 9$ to $n = 12$. The CrH_{12} species has six H_2 moieties, while MoH_{12} and WH_{12} have four H_2 moieties and four M–H σ bonds. The H–H distance in the H_2 moieties is larger than 0.8 Å in all species, while a calculation on isolated H_2 gives an H–H bond distance of 0.77 Å. These values for the H–H bond distances can be considered a fingerprint of the fact that the H_2 moieties are effectively bound to the central metal.

The possible existence of MH_n species with n greater than 12 has also been investigated. Examples are TiH_{14} , ZrH_{14} , ScH_{15} , and ZrH_{16} . Calculations indicate that such species have long metal–hydrogen bonds (greater than 2.0 Å). It should be noted that TiH_{14} , ZrH_{14} , and ScH_{15} fulfill the 18-electron rule, while ZrH_{16} would be a 20-electron species. ZrH_{16} turns out not to be stable and, instead, dissociates to ZrH_{12} and 2H_2 . Moreover, TiH_{14} , ZrH_{14} , ScH_{15} , and ZrH_{16}

are not more stable than $\text{TiH}_4 + 5\text{H}_2$, $\text{ZrH}_4 + 5\text{H}_2$, $\text{ScH}_3 + 6\text{H}_2$, and $\text{ZrH}_4 + 6\text{H}_2$, respectively. It thus seems unlikely that MH_n species with n larger than 12 will exist as isolated molecules.

The following question was then posed: is there an alternative way to store hydrogen in its molecular form. A conceptually new route to stabilize hydrogen-rich metal–polyhydride clusters would consist in placing a metal–hydride inside a C_{60} fullerene cage. The inside sphere of a fullerene is large enough to enclose atoms and small molecules. A variety of endohedral complexes, having metal fragments, noble gases, and atoms inside the cage, have been synthesized and characterized.^{5–10} Recently, encapsulation of molecular hydrogen into an open-cage fullerene having a 16-membered ring orifice has been investigated.¹¹

Would the C_{60} cage have the effect of stabilizing the MH_n cluster or would dissociation or reaction occur? We performed quantum chemical calculations on the supermolecular systems $\text{MH}_n + \text{C}_{60}$. To our knowledge, this is the first study on metal–hydrides inside a fullerene.

A recent paper by Zhao et al.¹² proposes to use transition-metal atoms bound to fullerenes as adsorbents for storage of hydrogen. Compounds such as $\text{C}_{60}[\text{ScH}_2(\text{H}_2)_4]_{12}$ have the Sc atoms bound externally to the fullerene cage. Here we propose a completely different approach, consisting of placing both the metal and the hydrogen inside the fullerene cage. We report results of a computational study on the species $\text{ZrH}_4@ \text{C}_{60}$, $\text{ScH}_{15}@ \text{C}_{60}$, and $\text{ZrH}_{16}@ \text{C}_{60}$. While ZrH_4 is experimentally known as a single molecule¹³ and has been

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Table 1. Typical Bond Distances (Å) for the MH_n Species^a

	M–H(σ)	M–H(H ₂)	H–H(H ₂)	H–C
ZrH ₄	1.859			
ZrH ₄ @C ₆₀	1.706			2.095–2.633
ScH ₁₅	1.865	2.018–2.232	0.806–0.861	
ScH ₁₅ @C ₆₀	1.739	1.775–1.891	0.802–0.875	1.848–2.643
ZrH ₁₆	1.871–1.882	2.124–2.136	0.827–0.829	
ZrH ₁₆ @C ₆₀	1.753	1.807–1.853	0.807–0.917	1.841–2.635

^a M–H(σ) is the distance between M and a nonbound H atom. M–H(H₂) is the distance between M and H in a H₂ molecule. H–H is the distance in the H₂ moiety. See Figures 1–3.

previously predicted by Pykkö and Desclaux,¹⁴ ScH₁₅ and ZrH₁₆, on the other hand, are unknown. All these MH_n @C₆₀ species turned out to be stable with all real harmonic frequencies. We extended the idea by considering also two TiH₁₆ clusters inside a bicapped (9,0) carbon nanotube, C₁₁₄. This system also turned out to be stable.

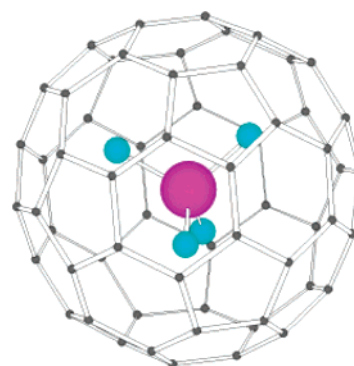
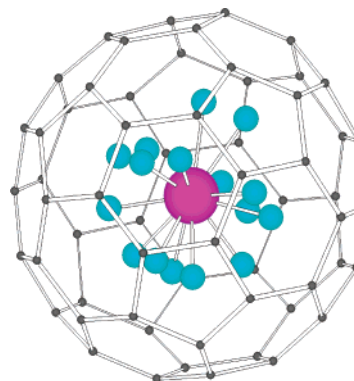
Details of the Calculations

The program TURBOMOLE^{15–17} was employed. The calculations were performed using density functional theory, DFT, with the Becke–Perdew, BP86, exchange–correlation functional. For the Zr metal, the energy-adjusted Stuttgart ECPs were used in order to take into account relativistic effects.¹⁸ The number of valence electrons is 12. The basis sets accompanying the ECPs 5s3p2d were used.¹⁹ For Sc, Ti, H, and C an all electron, split-valence basis set, contracted to 5s3p2d, 5s3p2d, 2s, 3s2p, respectively, was used. Equilibrium geometries and harmonic frequencies were computed for all species at the BP86/DFT level of theory, using the resolution-of-the-identity (RI) variant available in the TURBOMOLE package^{15–17} to make the calculations feasible. The auxiliary basis set of split-valence plus polarization type, available in the TURBOMOLE library, were used for all atoms. Comparative equilibrium geometry calculations on some selected structures were performed at the second order perturbation theory level with the RI variant, RI-MP2, to check if possible weak interactions between the H atoms and the fullerene cage would imply a substantial rearrangement of the structures. Since the RI-MP2 structure of ZrH₁₆@C₆₀ turned out to be very similar to the BP86 structure, with a slightly shorter Zr–H bond distance at the RI-MP2 level, only BP86 structures will be discussed below. Frequency calculations, on the other hand, were not performed at the RI-MP2 level of theory.

Results

The calculations show that the MH_n systems have shorter M–H bonds when placed inside the C₆₀ cage than as isolated molecules. All supersystems turn out to be local minima, having all harmonic frequencies real. The M–H bonds are significantly shorter when the MH_n species are placed inside the C₆₀ cage, and the H–H bonds in the H₂ moieties are much longer than in a H₂ isolated molecule.

The M–H and H–H bond distances are reported in Table 1. In general the M–H bond distances become about 0.15 Å shorter when the MH_n cluster is inside the fullerene than when it is an isolated molecule.

**Figure 1.** The structure of ZrH₄@C₆₀.**Figure 2.** The structure of ScH₁₅@C₆₀.

ZrH₄ has a tetrahedral structure both as an isolated molecule and in C₆₀. The Zr–H bond distance is 1.86 Å in an isolated ZrH₄ molecule and 1.70 Å in ZrH₄@C₆₀. In ZrH₄@C₆₀ (Figure 1) the carbon–hydrogen distances vary between 1.69 and 2.63 Å. The infrared spectrum of ZrH₄ in solid argon has been observed by Chertihin and Andrews.¹³ They measured an antisymmetric stretching frequency of 1623.6 cm^{–1}. Our calculation on isolated ZrH₄ gives a value of 1648.4 cm^{–1} in the harmonic approximation. The same mode for ZrH₄@C₆₀ is calculated to be 1119.5 cm^{–1}.

Isolated ScH₁₅ has one Sc–H σ bond (1.86 Å) and seven Sc–H₂ bonds (2.00–2.22 Å). In C₆₀, ScH₁₅ undergoes a significant structural rearrangement: the Sc atom is not at the center of the fullerene cage, surrounded symmetrically by the hydrogen atoms, as one might expect. Instead, the hydrogen atoms are all on one side of the Sc atom, and the Sc–H bonds are in the center of the fullerene cage (Figure 2). The Sc–H σ bond reduces to 1.74 Å and the Sc–H₂ bonds to 1.78–1.89 Å.

As already mentioned, our calculations predict isolated ZrH₁₆ not to be stable and, instead, exist as ZrH₁₂ and 2H₂. ZrH₁₂ has four Zr–H σ bonds of 1.88 Å and four Zr–H₂ bonds of 2.13 Å. In C₆₀, ZrH₁₆ is bound (Figure 3), and it has two Zr–H σ bonds of 1.75 Å and seven Zr–H₂ bonds of 1.83 Å. The H–H bonds are longer than in an isolated H₂ molecule (0.82 Å compared with 0.77 Å).

ZrH₄@C₆₀, ScH₁₅@C₆₀, and ZrH₁₆@C₆₀ have all harmonic frequencies real. The calculated values of the frequencies are available upon request.

In all cases, placing the MH_n cluster inside a fullerene cage leads to a significant shortening of the M–H bond

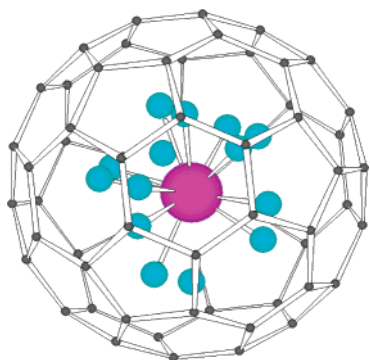


Figure 3. The structure of $\text{ZrH}_{16}@\text{C}_{60}$.

distances. The large clusters (ScH_{15} and ZrH_{16}) change from a M–H nonbonding situation (the M–H bond distances are larger than 2 Å) to a bonding situation (the bond distances are about 1.8 Å). One possible explanation for the structural rearrangement is that the fullerene repels the electrons of the metal–polyhydride cluster and pushes the cluster as far as possible from its surface, i.e., toward the center of the sphere. One may have expected that the metal–hydride cluster would break the fullerene cage, but this does not seem to be the case.

The reason for the polarization of the ScH_{15} cluster in C_{60} is not clear to us. One possibility is the formation of a dipole that can interact favorably with the polarizability of the C_{60} unit. This could be the case if the energy difference between the symmetric and the polarized structure is small. For the isolated clusters the polarized structure (Sc on the side) has a dipole moment of ca. 3.95 D, while the symmetric structure has a dipole moment of 1.87 D.

As previously mentioned, ScH_{15} is an “18-electron” species, while ZrH_{16} is a “20-electron” species. Even if the results are not reported here, structural optimization had also been performed for $\text{TiH}_{14}@\text{C}_{60}$ and $\text{ZrH}_{14}@\text{C}_{60}$, as other “18-electron” species, and they also are bound local minima.

Up to now it has been shown that the MH_n systems here considered are more compact when placed inside a C_{60} than as isolated molecules. The next step is trying to understand if these systems are energetically stable inside C_{60} . Thermodynamical stability implies these species to be lower in energy than other isomers of the same molecules. In the $\text{ZrH}_4@\text{C}_{60}$ case, we considered two other isomers besides the one previously discussed (Figure 1): the first isomer is a Zhao¹²-style $\text{ZrH}_4@\text{C}_{60}$ species, with ZrH_4 attached to the external C_{60} surface (structure A), and the other isomer has ZrH_4 inside the C_{60} , but close to the C_{60} internal surface in order that one H atom is van der Waals bonded to C_{60} (structure B). Both structures A and B are significantly higher in energy (more than 150 kcal/mol) than the original $\text{ZrH}_4@\text{C}_{60}$ structure (Figure 1). The optimization of A leads to separated ZrH_4 and C_{60} fragments, while the optimization of B leads to the original $\text{ZrH}_4@\text{C}_{60}$ structure (Figure 1). These results confirm the original $\text{ZrH}_4@\text{C}_{60}$ isomer to be a global minimum.

Kinetic stability of these systems, on the other hand, would imply that they are stable with respect to one or more dissociation pathways. Possible ways of forming/dissociating the supermolecular systems were investigated. It seems

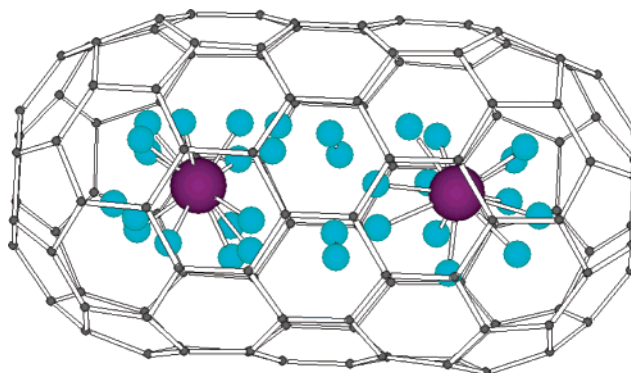


Figure 4. The structure of two TiH_{16} inside C_{114} .

unfeasible to ‘put’ an already formed metal–hydride inside a fullerene cage. Simple energetic balances (differences between calculated electronic energies) show that the formation of $\text{ZrH}_4@\text{C}_{60}$ from ZrH_4 and C_{60} , for example, is highly endothermic and requires about 100 kcal/mol of energy, allowing for both the zero point vibrational energy and the basis set superposition error corrections (less than 2 kcal/mol). An alternative and, probably more realistic route, would consist of inserting the metal and molecular hydrogen into a fullerene. The formation of the MH_n species might then occur directly inside C_{60} . The formation of $\text{ZrH}_4@\text{C}_{60}$ from a Zr atom, two H_2 molecules, and C_{60} , for example, is about 10 kcal/mol exothermic and thus energetically much more favorable than the above reaction. This energetic balance has been estimated as the difference between the electronic energy of $\text{ZrH}_4@\text{C}_{60}$ minus the electronic energy of one Zr atom in its triplet state and the energy of two H_2 molecules, allowing for both the zero point vibrational energy and the basis set superposition error corrections.

We also considered the possibility of forming metal–hydride clusters inside a nanotube, and we studied, as a model example, a system formed by two TiH_{16} clusters inside a single wall nanotube (9,0) which was closed with two partial fullerenes at the two extremities, C_{114} (Figure 4). The system turned out to be stable with all real harmonic frequencies. One of the TiH_{16} clusters inside the nanotube evolved to $\text{TiH}_{12} + 2\text{H}_2$, while the other one remained bound. A third TiH_{16} cluster, on the other hand, does not fit inside C_{114} , and some hydrogen atoms bind to the internal surface of C_{114} .

Conclusions

Quantum chemical calculations have shown that metal–hydride molecules are more compact when they are placed inside a fullerene cage than when they are isolated molecules. Species such as $\text{ZrH}_4@\text{C}_{60}$, $\text{ScH}_{15}@\text{C}_{60}$, and $\text{ZrH}_{16}@\text{C}_{60}$ exist and have very short metal–hydrogen bonding. These results pose several questions. First of all it is important to find a synthetic route to make hydrogen–metal clusters inside the fullerene. It might be possible to insert the metal and molecular hydrogen into a fullerene. The formation of the MH_n species might then occur directly inside C_{60} . This study indicates that the $\text{MH}_n@\text{C}_{60}$ supersystems require a large amount of energy to be made, but once they are synthesized, they may have a chance to be stable.

An alternative route, probably easier from the synthetic point of view, would be to synthesize the clusters inside nanotubes, instead of fullerenes. The calculations have shown that two TiH_{16} clusters are stable inside a (9,0) bicapped nanotube, C_{114} . A general question that we pose is the following: is it possible to make also other species inside a fullerene. Preliminary results indicate that also $\text{CH}_4@C_{60}$ is stable. Can we make clusters with a larger number of hydrogen atoms? It seems evident from the present study that metal–polyhydride clusters have indeed a chance to exist inside a fullerene cage and a nanotube, and this approach may represent a conceptually new way of synthesizing, stabilizing, and storing metal–polyhydrides.

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