How Many Hydrogen Atoms Can Be Bound to a Metal? Predicted MH12 Species

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Abstract

Quantum chemical calculations predict the existence of new molecular species with general formula MH12, where M is a group 6 atom. The previous MHn species had n values up to 9. The new systems with n = 12 would be a new Record for metal hydrides.

Reference


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How Many Hydrogen Atoms Can Be Bound to a Metal? Predicted MH$_{12}$ Species

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Metal hydrides are of considerable current interest, among other reasons, as potential hydrogen storage systems. A design target of 6.5 wt % H has been regarded as adequate. We here report molecular-level calculations for a series of potential species of type MH$_{12}$, where M is a group 6 atom, Cr, Mo, and W. They turned out to be stable as single molecules. In a hypothetical solid Li-(VH)$_{12}$, the percentage would be 17, leaving plenty of room for adjustments. The isoelectronic ions VH$_{12}^-$, TiH$_{12}^{2-}$, and MnH$_{12}^{+}$ also turned out to be stable.

Our starting point was the Au/H chemical analogy and the recent discovery of the icosahedral, 18-valence-electron species W$_{18}$. Its hydrogen analogues turned out to exist as stable minima but to have either a mixture of M–H and M($\eta^3$-H)$_2$ bonds or only dihydrogen bonds. The literature on such bonds has been reviewed by Kubas and Maseras et al. The previous M–H$_n$ species had $n$ values up to 9, occurring in ReH$_{12}^-$. Thus, the new systems with $n = 12$ would be a new record for metal hydrides. A single hydride ion in solid hydrogen is reported to form ($H^-$)$_2$$_{12}$, where M is a group 6 atom, Cr, Mo, and W.

All species were studied using density functional theory, DFT, with the B3LYP exchange-correlation functional and second-order perturbation theory, MP2. For H, the 6-31g* basis set was used, with the B3LYP exchange-correlation functional and second-order dynamic correlation added by second-order perturbation theory.

Figure 1. Calculated structure of CrH$_{12}$. MnH$_{12}^+$ has a similar structure.

Figure 2. Calculated structure of WH$_{12}$, MoH$_{12}$, VH$_{12}^-$, and TiH$_{12}^{2-}$ have similar structures.

We shall discuss first the neutral molecules and then the ionic species. All the MH$_{12}$ species were found to be local minima, with all real harmonic frequencies in a singlet ground state. In all cases, the lowest triplet state lies ca. 35 kcal/mol adiabatically above the singlet ground state.

The CrH$_{12}$ species has $D_{3h}$ symmetry with six H$_2$ moieties (see Figure 1), while MoH$_{12}$ and WH$_{12}$ have $D_{3d}$ symmetry, with four H$_2$ moieties and four M–H 2σ-bonds (see Figure 2). The $D_{3d}$ structure of CrH$_{12}$ is only 3 kcal/mol higher in energy than the $D_{3h}$ structure, but it has three imaginary frequencies.

In Table 1, the B3LYP bond distances for the neutral and ionic MH$_{12}$ local minima are reported. We do not report the MP2 distances. The H–H MP2 bond distances are essentially identical to the B3LYP values, while the M–H MP2 bond distances are overall shorter than the B3LYP corresponding bond distances.

The $D_{3h}$ B3LYP harmonic frequencies of CrH$_{12}$ and MnH$_{12}^+$ are reported in Table 1 in Supporting Information. Some modes have a sizable intensity at a frequency of ca. 750 (ν$_3$, ν$_6$), 1000 (ν$_{11}$, ν$_{12}$),...
The H—H distances of the dihydrogen complexes in Table 1 are typical, compared to experimentally known complexes (see Table 4.2 in ref 10). The experimental dissociation energies of an H₂ unit from the complex vary from 15 to 19 kcal/mol. The present values per H₂ are slightly lower. For hydrogen storage applications they could be much lower: a value of only 1.6 kcal/mol would result in a 1 bar equilibrium pressure at 300 K².

The intramolecular dynamics and dissociation barriers of the MH₁₂ systems are not discussed here.

The possibility of forming analogous compounds with heavier atoms such as Th and U was also investigated. Th atom gives a stable ThH₂₂ compound with a triplet ground state that essentially corresponds to a ThH₄ moiety and four H₂ moieties at a large distance, at almost the same energy as ThH₄ + 4H₂. Thus, there is no gain in energy in going from 4 to 12 hydrogen atoms. The UH₂₂ cluster is unstable and clearly dissociates to UH₂ and 3H₂.

In conclusion, the present results suggest that the number of hydrogen atoms, bound to one metal atom, could be increased from the previously known n = 9 to n = 12. The four side-on bonded H₂ units can be detached more easily than the remaining four classical M—H hydrides. The suggested neutral molecules could be observed spectroscopically in solid hydrogen matrices. The ionic species, or their derivatives, could form crystalline compounds.

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Supporting Information Available: Tables with the harmonic frequencies for all the species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(14) ECPs and Corresponding Valence Basis Sets; Institut für Theoretische Chemie, Universität Stuttgart; Stuttgart, Germany. http://www.theochem.uni-stuttgart.de/.

Table 1. B3LYP Bond Distances (Å) for the MH₁₂ Species

<table>
<thead>
<tr>
<th>Species</th>
<th>CbH₂</th>
<th>MoH₁₂</th>
<th>WbH₂</th>
<th>TiH₁₂</th>
<th>VbH₁₂</th>
<th>NbH₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>M—H₁₁(α)</td>
<td>1.712</td>
<td>1.738</td>
<td>1.877</td>
<td>1.686</td>
<td>1.760</td>
<td>1.756</td>
</tr>
<tr>
<td>M—H₁₂(H₂)</td>
<td>1.703</td>
<td>1.853</td>
<td>1.861</td>
<td>1.898</td>
<td>1.760</td>
<td>1.756</td>
</tr>
<tr>
<td>M—H₁₁(H)</td>
<td>0.841</td>
<td>0.828</td>
<td>0.838</td>
<td>0.825</td>
<td>0.836</td>
<td>0.791</td>
</tr>
</tbody>
</table>

*For the numbering of the H atoms, see Figures 1 and 2. The H—H is the distance in the H₂ moiety. M—H₁₁(α) is the distance between M and a nonbound H atom. M—H₁₂(H₂) is the distance between M and H forming a H₂ molecule.