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 WAu_{12}. Its hydrogen analogues turned out to exist as stable minima but to have either a mixture of M−H and M(H-H) 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_{9}^{2−}. 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)_{12} with n = 24.

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 point energy calculations at the DFT-optimized geometries were performed to take into account relativistic effects.

To investigate the electronic structure of these species, some single-point energy calculations at the DFT-optimized geometries were repeated using the complete active space (CAS) SCF method with dynamic correlation added by second-order perturbation theory (CASPT2). The CASCC/CASPT2 calculations were performed with all electron basis sets of the ANO type for all atoms. The exponents were optimized using the Douglas−Kroll Hamiltonian. The contracted basis set was 6s5p3d2f for Cr, 7s6p4d2f for Mo, 7s6p4d2f for W, and 2s1p for H. The active space included 12 active electrons in 12 active orbitals, which are the bonding and antibonding linear combination of the metal d orbitals and hydrogen s orbitals. Note that the four orbitals, mainly bonding to M ap and ns AOs lie further down. The programs Gaussian03 and MOLCAS6.0 were employed.

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{\textsubscript{2}} moieties (see Figure 1), while MoH_{12} and WH_{12} have D_{2d} symmetry, with four H{\textsubscript{2}} moieties and four M–H σ-bonds (see Figure 2). The D_{2d} 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_{9}, ν_{10}), 1000 (ν_{11}, ν_{12}), and 1500 (ν_{13}, ν_{14}).
perhaps due to kinetic and entropy reasons.

Results for CrH$_{12}^{+}$ in compounds, in their singlet ground state, and 3H into the bonds are linear combinations of Cr 3d orbitals and H 1s orbitals.

The lowest triplet lies separated from the higher electronic states. The orbitals intervening in the H$_2$ moiety. M = H$^-$H$_2$(H$_2$) is the distance between M and H forming a H$_2$ molecule.

\[ \nu_{12} \] and 3000 cm$^{-1}$ ($\nu_{19}$, $\nu_{20}$, $\nu_{21}$), respectively, corresponding to some HMM bending, HMM asymmetric stretching, and HH stretching motions, respectively.

The $D_2$ B3LYP harmonic frequencies of MoH$_{12}$, WH$_{12}$, TiH$_{12}^{2-}$, and VH$_{12}$ are reported in Table 2 in Supporting Information. The modes with a sizable intensity occur at a frequency of ca. 500–600 ($\nu_{19}$, $\nu_{20}$), 1050 ($\nu_{20}$), 1700–1800 ($\nu_{19}$, $\nu_{20}$, $\nu_{21}$), and 3000 ($\nu_{23}$) cm$^{-1}$, respectively. They correspond to some HMM bending ($\nu_{19}$, $\nu_{20}$), HMM asymmetric stretching ($\nu_{19}$, $\nu_{20}$, $\nu_{21}$), and HH stretching ($\nu_{23}$) motions, respectively (recall the H–H stretch of 4401 cm$^{-1}$ for free H$_2$).

To investigate the stability and chance of formation of these species we considered the formation/dissociation reaction for the various species: $6H^+ + M \rightarrow MH_{12}$, with $M =$ Cr and Mo in their septet ground state and $M =$ W in its quintet ground state. This reaction is 15.8 kcal/mol endothermic for CrH$_{12}$, while it is 55.0 kcal/mol lower in energy, respectively, than the corresponding MH$_{12}$.

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 H$_2$ 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**

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**Table 1.** B3LYP Bond Distances (Å) for the MH$_{12}$ Species

<table>
<thead>
<tr>
<th></th>
<th>CrH$_{12}$</th>
<th>MoH$_{12}$</th>
<th>WH$_{12}$</th>
<th>TiH$_{12}^{2-}$</th>
<th>VH$_{12}$</th>
<th>MH$_{12}^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M+H(H$_2$)</td>
<td>1.713</td>
<td>1.738</td>
<td>1.877</td>
<td>1.686</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M=H2(H$_2$)</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>H=H(H$_2$)</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. H–H is the distance in the H$_2$ moiety. M = H$_2$(H$_2$) is the distance between M and a nonbound H atom. M=H$_2$(H$_2$) is the distance between M and H forming a H$_2$ molecule.

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 H$_2$ unit from the complex vary from 15 to 19 kcal/mol. The present values per H$_2$ 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 K.

The intramolecular dynamics and dissociation barriers of the MH$_{12}$ 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 TiH$_{12}^{2-}$ compound with a triplet ground state that essentially corresponds to a ThH$_{12}$ moiety and four H$_2$ moieties at a large distance, at almost the same energy as TiH$_{12}^{4+}$. Thus, there is no gain in energy in going from 4 to 12 hydrogen atoms. The UH$_{12}$ cluster is unstable and clearly dissociates to UH$_3$ and 3H$_2$.

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 H$_2$ 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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*CASSCF/CASPT2 calculations were performed at the optimized DFT geometries for several electronic states. We report the CASPT2 results for CrH$_{12}$ as a test case. The singlet ground state is well separated from the higher electronic states. The lowest triplet lies ca. 60 kcal/mol higher in energy vertically. The orbitals interwoven into the bonds are linear combinations of 3d orbitals and H 1s orbitals. Tests with larger active spaces indicate that the ground state has a clear single-configurational character and gave similar results to those obtained with the 12/12 active space.*

The isoelectronic ions VH$_{12}^{2-}$, TiH$_{12}^{2-}$, and MnH$_{12}^{2-}$ also turned out to be stable in their singlet ground state. The MnH$_{12}^{2-}$ cation has a structure similar to CrH$_{12}$ and all real harmonic frequencies in $D_2$ symmetry, while VH$_{12}^{2-}$ and TiH$_{12}^{2-}$ have structures similar to MoH$_{12}$ and WH$_{12}$ and all real $D_2$ harmonic frequencies.

The counterion stabilization in crystals precludes a molecular-level study of their energetics.