

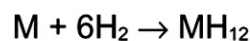
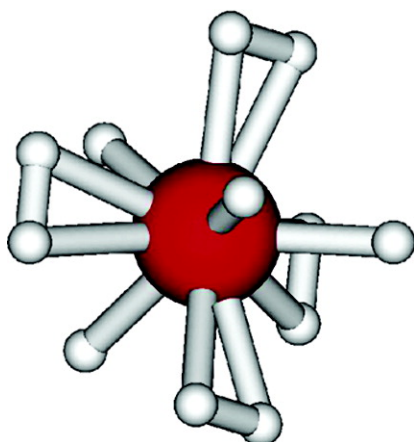
Communication

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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.^{1,2} 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^{3–6} and the recent discovery of the icosahedral, 18-valence-electron species WAu_{12} .^{7–9} Its hydrogen analogues turned out to exist as stable minima but to have either a mixture of $M-H$ and $M(\eta^2-H_2)$ bonds or only dihydrogen bonds. The literature on such bonds has been reviewed by Kubas¹⁰ and Maseras et al.¹¹ 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 $(H^-)(H_2)_{12}$ with $n = 24$.¹²

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. For all metal atoms, energy-adjusted Stuttgart ECPs were used in order to take into account relativistic effects.¹³ The number of valence electrons is 12 for Ti, 13 for V, 14 for Cr, Mo and W, and 15 for Mn. The 6s5p3d valence basis sets accompanying the ECPs were used¹⁴ for all atoms. The calculations were repeated also with larger basis sets, in which the metal valence basis set were increased with one f function 6s5p3d1f. The H basis used in this second set of calculations was of the 6-31g** type, contracted to 2s1p. We shall report only the results obtained with the larger basis set. Equilibrium geometries and harmonic frequencies were computed for all species at the DFT level of theory and MP2 level of theory. 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 method¹⁵ with dynamic correlation added by second-order perturbation theory (CASPT2).¹⁶ The CASSCF/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 np and ns AOs lie further down. The programs Gaussian03 and MOLCAS6.0¹⁷ were employed.

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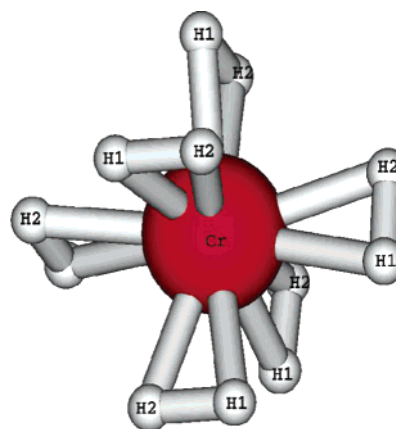


Figure 1. Calculated structure of CrH_{12} . MnH_{12}^+ has a similar structure.

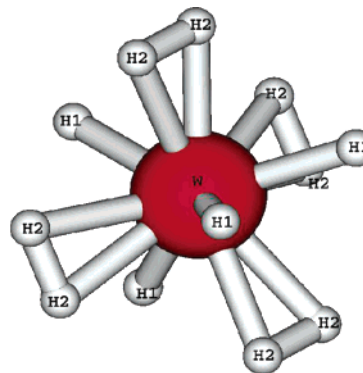


Figure 2. Calculated structure of WH_{12} . MoH_{12} , VH_{12}^- , and TiH_{12}^{2-} have similar structures.

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_3 symmetry with six H_2 moieties (see Figure 1), while MoH_{12} and WH_{12} have D_{2d} symmetry, with four H_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_3 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_3 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_8 , ν_9), 1000 (ν_{11} ,

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

	CrH ₁₂	MoH ₁₂	WH ₁₂	TiH ₁₂ ²⁻	VH ₁₂ ⁻	MnH ₁₂ ⁺
M–H1(σ)		1.713	1.738	1.877	1.686	
M–H2(H ₂)	1.707	1.853	1.861	1.898	1.760	1.756
	1.713					1.761
H–H(H ₂)	0.841	0.828	0.838	0.825	0.836	0.791

^a For the numbering of the H atoms, see Figures 1 and 2. H–H is the distance in the H₂ moiety. M–H1(σ) is the distance between M and a nonbound H atom. M–H2(H₂) is the distance between M and H forming a H₂ molecule.

ν_{12}), and 3000 cm⁻¹ (ν_{19} , ν_{20} , ν_{21}), respectively, corresponding to some HMH bending, HMH asymmetric stretching, and HH stretching motions, respectively.

The D_{2d} B3LYP harmonic frequencies of MoH₁₂, WH₁₂, TiH₁₂²⁻, and VH₁₂⁻ are reported in Table 2 in Supporting Information. The modes with a sizable intensity occur at a frequency of ca. 500–600 (ν_5 , ν_6), 1050 (ν_{14}), 1700–1800 (ν_{19} , ν_{20} , ν_{21}), and 3000 (ν_{23}) cm⁻¹, respectively. They correspond to some HMH bending (ν_5 , ν_6), HMH asymmetric stretching (ν_{14} , ν_{19} , ν_{20} , ν_{21}), and HH stretching (ν_{23}) motions, respectively (recall the H–H stretch of 4401 cm⁻¹ for free H₂).

To investigate the stability and chance of formation of these species we considered the formation/dissociation reaction for the various species: 6H₂ + M → MH₁₂, 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 CrH₁₂, while it is 55.0 and 89.0 kcal/mol exothermic for MoH₁₂ and WH₁₂, respectively (including the zero-point energy correction, ZPE).

We conclude that the Mo and W 12-hydrogen clusters would form exothermally, if the metal atom M is shot into solid hydrogen, for instance, while CrH₁₂ is slightly endothermic.

We also compared the stability of different clusters by considering reactions such as 3H₂ + MH₆ → MH₁₂ and 4H₂ + MH₄ → MH₁₂.

The molecules CrH₁₂, MoH₁₂, and WH₁₂ are, respectively, 42, 29, and 23 kcal/mol lower in energy than the corresponding MH₆ compounds, in their singlet ground state, and 3H₂ molecules, including ZPE. CrH₁₂, MoH₁₂, and WH₁₂ are also 15, 32, and 35 kcal/mol lower in energy, respectively, than the corresponding MH₄ compounds, in their triplet ground state, and 4H₂ molecules, including ZPE. No WH₁₂ was observed in the WH₆ experiment,¹⁸ perhaps due to kinetic and entropy reasons.

CASSCF/CASPT2 calculations were performed at the optimized DFT geometries for several electronic states. We report the CASPT2 results for CrH₁₂ 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 intervening into the bonds are linear combinations of Cr 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 VH₁₂⁻, TiH₁₂²⁻, and MnH₁₂⁺ also turned out to be stable in their singlet ground state. The MnH₁₂⁺ cation has a structure similar to CrH₁₂ and all real harmonic frequencies in D_3 symmetry, while VH₁₂⁻ and TiH₁₂²⁻ have structures similar to MoH₁₂ and WH₁₂ and all real D_{2d} harmonic frequencies.

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

The H–H distances of the dihydrogen complexes in Table 1 are typical, compared to experimentally already 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 ThH₁₂ 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 UH₁₂ cluster is unstable and clearly dissociates to UH₆ 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 matrixes. 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>.

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