For all metal atoms, energy-adjusted Stuttgart ECPs were used in perturbation theory, MP2. For H, the 6-31g* basis set was used.

Equilibrium geometries and harmonic frequencies were computed with all electron basis sets of the ANO type 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.

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. 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 used 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 method with dynamic correlation added by second-order perturbation theory (CASPT2). 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 n and ns AOs lie further down. The programs Gaussian03 and MOLCAS6.0 were employed.

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 MHn, 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 VH12+, TiH122-, and MnH12+ 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 WAu12. Its hydrogen analogues turned out to exist as stable minima but to have either a mixture of M–H and M(σ2-H2) bonds or only dihydrogen bonds. The literature on such bonds has been reviewed by Kubas and Maseras.

The previous M–Hn+ species had n values up to 9, occurring in ReH12+. 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)3(H2)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. For all metal atoms, energy-adjusted Stuttgart ECPs were used in order to take into account relativistic effects. 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 used 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 method with dynamic correlation added by second-order perturbation theory (CASPT2). 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 n 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 MH12 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 CrH12 species has D3 symmetry with six H moieties (see Figure 1), while MoH12 and WH12 have D4d symmetry, with four H moieties and four M–H σ bonds (see Figure 2). The D4d structure of CrH12 is only 3 kcal/mol higher in energy than the D3 structure, but it has three imaginary frequencies.

In Table 1, the B3LYP bond distances for the neutral and ionic MH12 local minima are reported. We do not report the MP2 bond 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 D3 B3LYP harmonic frequencies of CrH12 and MnH12+ are reported in Table 1 in Supporting Information. Some modes have a sizable intensity at a frequency of ca. 750 (νs, νg), 1000 (ν11, ν24).
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 K.

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 H4 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 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.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>CrH2</th>
<th>MoH2</th>
<th>WH4</th>
<th>TiH4</th>
<th>VH2</th>
<th>MH12</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–H1(α)</td>
<td>1.713</td>
<td>1.738</td>
<td>1.877</td>
<td>1.868</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M–H2(H2)</td>
<td>1.703</td>
<td>1.853</td>
<td>1.861</td>
<td>1.989</td>
<td>1.760</td>
<td>1.756</td>
</tr>
<tr>
<td>H–H1(H2)</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 H2 moiety. M–H1(α) is the distance between M and a nonbound H atom. M–H2(H2) is the distance between M and H forming a H2 molecule.

v12), and 3000 cm−1 (v19, v20, v21), respectively, corresponding to some HMH bending, HMM asymmetric stretching, and HH stretching motions, respectively.

The D2g B3LYP harmonic frequencies of MoH12, WH12, TiH4, and VH2 are reported in Table 2 in Supporting Information. The modes with a sizable intensity occur at a frequency of 500–600 (v9, v10), 1050 (v17), 1700–1800 (v19, v20, v21), and 3000 (v22) cm−1, respectively. They correspond to some HMH bending (v9, v10), HMM asymmetric stretching (v17, v19, v20, v21), and HH stretching (v22) 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: 6H + 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 CrH2, while it is 55.0 kcal/mol lower in energy than the corresponding MH12.

The molecules CrH12, MoH12, and WH4 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 WH4 are also 15, 32, and 35 kcal/mol lower in energy, respectively, than the corresponding MH6 compounds, in their triplet ground state, and 4H2 molecules, including ZPE. No WH4 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 CrH2 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 involving 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 VH2, TiH2, and MnH2 also turned out to be stable in their singlet ground state. The MnH2 cation has a structure similar to CrH2 and all real harmonic frequencies in D1h symmetry, while VH2 and TiH2 have structures similar to MoH12 and WH4 and all real D2h harmonic frequencies.

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

References

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

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