

Cite this: DOI: 10.1039/c1nj20560a

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PAPER

# Molecular models for $\text{WH}_6$ under pressure<sup>†‡</sup>

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Received (in Montpellier, France) 26th June 2011, Accepted 8th July 2011

DOI: 10.1039/c1nj20560a

At atmospheric pressure, some tungsten hydrides exist as discrete molecular complexes in low temperature matrices, but are very reactive and cannot be isolated in bulk at room temperature. Under pressure, one observes WH in experiment at room temperature, and calculations indicate several other stoichiometries are stable, all extended and not molecular. This work aims at constructing a bridge between discrete molecules and the pressurized extended structures, with the emblematic example of  $\text{WH}_6$ . The equilibrium structure, known as a distorted trigonal prismatic molecule, is likely to be a good acceptor. In numerical experiments, discrete  $\text{WH}_6$  molecular complexes are allowed to interact with each other in their ground states at  $T = 0$  K and  $P = 1$  atm. They spontaneously rearrange to form 1D-chains, with the W centers adopting a tricapped trigonal prismatic environment. The electronic structure of these chains is examined and related to that of the monomer and extended solids.

## Introduction

Because of the low solubility of hydrogen in tungsten,<sup>1</sup> the metal is often used as a gasket material to seal hydrogen in diamond anvil cells at high pressure. Under extreme conditions, chemistry has a way of intruding; thus Strobel *et al.* recently reported the formation of a tungsten hydride, WH, during their studies of silane and hydrogen mixtures under pressure.<sup>2,3</sup> WH is formed from elemental W and  $\text{H}_2$  above 25 GPa and crystallizes in the anti-NiAs structure, as do  $\text{CrH}^4$  and  $\text{MoH}^5$ .

In conjunction with experimental studies by Timothy Strobel and coworkers on this system, we have undertaken a theoretical exploration of the structure and reactivity of the extended tungsten–hydrogen phases.<sup>6</sup> These include  $\text{WH}_n$ ,  $n = 1$ –8, some of which are stable at elevated pressure. The computed (and complicated) structures for these systems feature multiple W–H–W bridges, and increased coordination of W by H as  $n$  gets larger, eventually leading to dihydrogen complexes in  $\text{WH}_8$ . In this contribution, we look at molecular models for the extended tungsten hydrides.

## Simple molecular tungsten hydrides in matrices

While no tungsten hydrides are kinetically persistent under ambient conditions, we know a good bit about these molecules (and analogous compounds of Cr and Mo) in low temperature matrices, and some in the gas phase. In matrices, much of our knowledge of tungsten hydrides derives from the spectroscopic studies of Wang and Andrews at 3.5–11 K in neon and argon matrices.<sup>7,8</sup> In those experiments, the tungsten hydrides are formed by laser ablation, presumably of W atoms. WH,  $\text{WH}_2$ ,  $\text{WH}_3$ ,  $\text{WH}_4$  and  $\text{WH}_6$  hydrides have been identified by isotopic substitution and comparison with computational modeling.<sup>9,10</sup>

Their characteristic properties (most obtained from calculations) are summarized in Table 1.

The laser ablation process and photolysis provide the energy required for a tungsten atom (ground state  $^7\text{S}$ ) to insert into  $\text{H}_2$ . The insertion reaction is calculated to be exothermic (see Table 2); nonetheless, the intensity of the  $\text{WH}_2$  band decreases upon annealing, indicating that while thermodynamically favored, the formation reaction has to overcome a large activation barrier.<sup>9</sup> Subsequent reactions to give higher hydrides are also calculated to be exothermic (see Table 2). However, the intensity of  $\text{WH}_4$  and  $\text{WH}_6$  bands increases upon annealing of the matrix, indicating that, contrary to the case of  $\text{WH}_2$ , the formation of  $\text{WH}_4$  and  $\text{WH}_6$  is spontaneous. There also appears to exist a reaction channel leading to WH, and subsequently to  $\text{WH}_3$  and  $\text{WH}_5$ , though the latter species has not been identified experimentally. These reactions, whose energetics have been computed by others [at the DFT level (BPW91/6-311++G(d,p)/SDD)], are indicated below in Table 2.<sup>7</sup> We mention them because they may be relevant to chemistry seen in the solid under pressure.

The neon matrix in which these studies are carried out can be maintained up to  $\sim 12$  K. Above that temperature these simple

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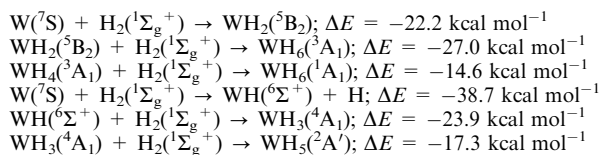
<sup>†</sup> Dedicated to our friend Didier Astruc.

<sup>‡</sup> Electronic supplementary information (ESI) available: Histograms of the W–W, W–H and H–H distances in the  $\text{WH}_n$  ( $n = 1$ –6, 8) extended structures at  $P = 50$  GPa; experimental structures of  $\text{CaB}_6$ ,  $\text{CaC}_6$ ,  $\text{MoF}_6$ ,  $\text{WF}_6$ ,  $\text{WCl}_6$ . See DOI: 10.1039/c1nj20560a

**Table 1** Geometrical and spectroscopic characteristics of  $\text{WH}_n$  ( $n = 1-6$ ) molecular hydrides deduced from experimental and theoretical studies

$\text{WH}_n$	Symmetry <sup>a</sup>	Ground state <sup>a</sup>	W–H <sup>a</sup> /Å	HWH <sup>a</sup> /°	Frequencies <sup>b</sup> /cm <sup>-1</sup>
WH	$C_{\infty v}$	$^6\Sigma^{+c}$	1.72	—	1860.2 ( <i>str.</i> )
WH <sub>2</sub>	$C_{2v}$ (bent)	$^3B_2$	1.72	113	1831.9 ( <i>antisym. str.</i> )
WH <sub>3</sub>	$C_{3v}$ (pyramidal)	$^4A_1$	1.72	113	1894.6 ( <i>deg. antisym. str.</i> )
WH <sub>4</sub>	$T_d$ (tetrahedral)	$^3A_1$	1.71		1920.1 ( <i>deg. antisym. str.</i> ) 525.2 ( <i>deg. antisym. deform.</i> )
WH <sub>5</sub>	$C_s$	$^2A'$	1.73 1.71 1.68	115 116	Not identified
WH <sub>6</sub>	$C_{3v}$ (distorted trigonal prismatic)	$^1A_1$	1.72 1.67	115 62	2021.2 ( <i>sym. str.</i> ) 2004.4 ( <i>deg. antisym. str.</i> ) 1953.8 ( <i>sym. str.</i> ) 1927.5 ( <i>deg. antisym. str.</i> ) 1080.3 ( <i>sym. deform.</i> ) 840.7 ( <i>deg. antisym. deform.</i> )

<sup>a</sup> From DFT calculations at the BPW91/6-311++G(d,p)/SDD level.<sup>7</sup> <sup>b</sup> From experiments in neon matrices; for agreement with theory, see the original papers.<sup>7</sup> <sup>c</sup> See also ref. 11.

**Table 2** Chain of reactions for the formation of WH, WH<sub>2</sub>, WH<sub>3</sub>, WH<sub>4</sub>, WH<sub>5</sub> and WH<sub>6</sub> tungsten hydrides from W atoms and H<sub>2</sub> molecules. The energies of reaction given are computed by Wang and Andrews at  $T = 0$  K at the BPW91/6-311++G(d,p)/SDD level<sup>7</sup>

hydrides go away, in reactions to products that are not known. All of the above-mentioned hydrides are highly unstable with respect to molecular hydrogen and bulk W. The atomization energy of metallic W is +203.4 kcal mol<sup>-1</sup> at  $T = 298.15$  K. Thus even the most stable of the hydrides, WH<sub>6</sub>, has a heat of formation around +140 kcal mol<sup>-1</sup>. That's a lot of driving force for decomposition.

### The particular case of WH<sub>6</sub>

The most interesting molecule among those simple hydrides is WH<sub>6</sub>, just because it is not octahedral. The hydride here connects to the fascinating story of the non-octahedral nature of the more stable Group-6 metal alkyls,  $\text{M}(\text{CH}_3)_6$ ,  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ .<sup>12,13</sup> In the early seventies, a risky prediction emerged from calculations by T. A. Albright, O. Eisenstein and their coworkers, before experiment, that  $\text{MR}_6$  molecules,  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ,  $\text{R} = \text{H}, \text{CH}_3$ , will definitely not be octahedral.<sup>14,15</sup> Calculations<sup>16-20</sup> and experiments<sup>7,8</sup> agree on a distorted trigonal prism,  $C_{3v}$ , symmetry for WH<sub>6</sub>. This is in accord with Bayse and Hall's formulation of the symmetry-allowed geometries of simple transition metal polyhydride complexes.<sup>21</sup> The nonoctahedral nature of the d<sup>0</sup>  $\text{ML}_6$  geometry has been confirmed experimentally also for the more kinetically stable hexaalkyls.<sup>22-24</sup> An interesting review of bonding in d<sup>0</sup> systems can be found in the literature.<sup>25</sup>

### Higher hydrides, involving H<sub>2</sub> ligands

Two years after the Wang and Andrews experiments in neon matrices, a tungsten hydride of WH<sub>12</sub> stoichiometry and  $D_{2d}$

symmetry, involving 4 formal H<sup>-</sup> and 4 H<sub>2</sub> ligands, was predicted to be thermodynamically stable with respect to H<sub>2</sub> dissociation.<sup>26</sup> The W–H(H<sub>-</sub>) distances are computed to be 1.74 Å, similar to the W–H distances in WH<sub>1-6</sub> (see Table 1); the W–H(H<sub>2</sub>) bonds are longer: 1.86 Å. The H–H bond of the coordinated H<sub>2</sub> ligands is elongated to 0.84 Å. We may describe these molecules as WH<sub>4</sub>(H<sub>2</sub>)<sub>4</sub>. The species was identified by Andrews *et al.* in new neon matrices experiments, with among others a broad band at 2500 cm<sup>-1</sup> assigned to the H–H stretching and a sharp band at 1782 cm<sup>-1</sup> assigned to the asymmetric W–H(H<sub>2</sub>) stretching.<sup>27</sup>

Three more complexes of WH<sub>8</sub> and WH<sub>10</sub> stoichiometry, and involving H<sub>2</sub> ligands, were computed to be thermodynamically stable with respect to H<sub>2</sub> dissociation<sup>27</sup> but have not been identified experimentally so far. Their computed geometrical parameters are given in Table 3. The bond between the metal center and the H<sub>2</sub> ligands is 0.1–0.3 Å longer than that between W and the H<sup>-</sup> ligands.

So far as we know, there is no information on other molecular tungsten hydrides. But there are a good number of polynuclear and cluster tungsten compounds with hydrogen bridges, to whose structures we now turn.

### Polynuclear tungsten compounds with hydrogen bridges

Some 85 polynuclear tungsten complexes with hydrogen bridges between at least two W centers are reported in the Cambridge Structural Database.<sup>28</sup> Among these, 70 involve a

**Table 3** Geometrical parameters for the  $\text{WH}_x(\text{H}_2)_y$  species and energies of the  $\text{WH}_x + y\text{H}_2 \rightarrow \text{WH}_x(\text{H}_2)_y$  reactions ( $T = 0$  K, zero-point energy included) computed by DFT at the BP86/TZVPP level of theory<sup>27</sup>

Complex	W–H/ Å	W–H(H <sub>2</sub> )/ Å	H(H <sub>2</sub> )–H(H <sub>2</sub> )/ Å	Energy of reaction/ kcal mol <sup>-1</sup>
WH <sub>8</sub> = WH <sub>6</sub> (H <sub>2</sub> )	1.69 1.72	1.99	0.80	-10
WH <sub>10</sub> =	1.70	1.95	0.82	-18
WH <sub>6</sub> (H <sub>2</sub> ) <sub>2</sub>	1.71	1.97	0.83	
WH <sub>10</sub> =	1.71	1.82	0.86	-31
WH <sub>4</sub> (H <sub>2</sub> ) <sub>3</sub>	1.71	1.83	0.89	

single bridging H atom between two W centers, 14 involve two bridging H atoms between two W centers, and 1 involves one bridging H between three W centers. Hydrogens are not well located in X-ray crystallographic studies, both because of the low scattering power of H, and because of the dominant scattering of W relative to H. So the coordinates of the bridging H are given for only 37 out of the 85 (28 with a single bridging H between two W, 9 with two bridging H between two W). The W–H bond lengths in those structures are shown in Fig. 1. Note that in the single reported case with a bridging H between three W centers, the hydrogen could not be located in diffraction experiments.<sup>29</sup> To our knowledge, there are very few neutron diffraction studies of W–H complexes, all those reported by Bau, Kirley, Koetzle and coworkers.<sup>30–32</sup>

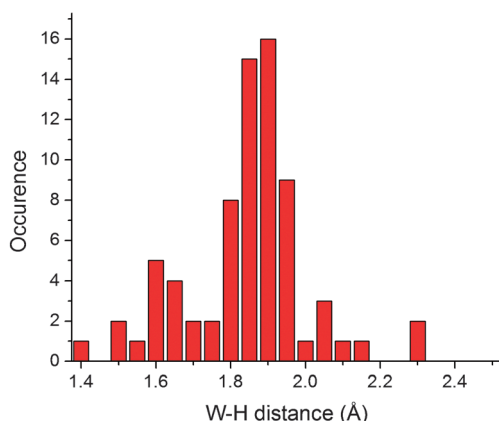
Keeping in mind that scattering limitations may distort the W–H distances obtained from crystallographic studies, the “normal” bond length between a tungsten metal center and a bridging hydrogen is about 1.85–1.90 Å and is comparable to the theoretically estimated bond length between a tungsten metal center and an H<sub>2</sub> ligand cited above.

### Tungsten hydrides in the solid state

For the extended tungsten hydrides, only the WH structure is known experimentally, under pressure, and that only recently.<sup>2,3</sup>

Above  $P = 25\text{--}30$  GPa, this molecule crystallizes in the *anti*-NiAs structure. The higher extended hydrides (WH<sub>2</sub> to WH<sub>8</sub>) are so far only theoretical constructs. We introduce the salient features of their structures here, as they motivate our calculations. Details may be found elsewhere,<sup>6</sup> but let us describe in a few sentences the computational methodology which led us to their structures.

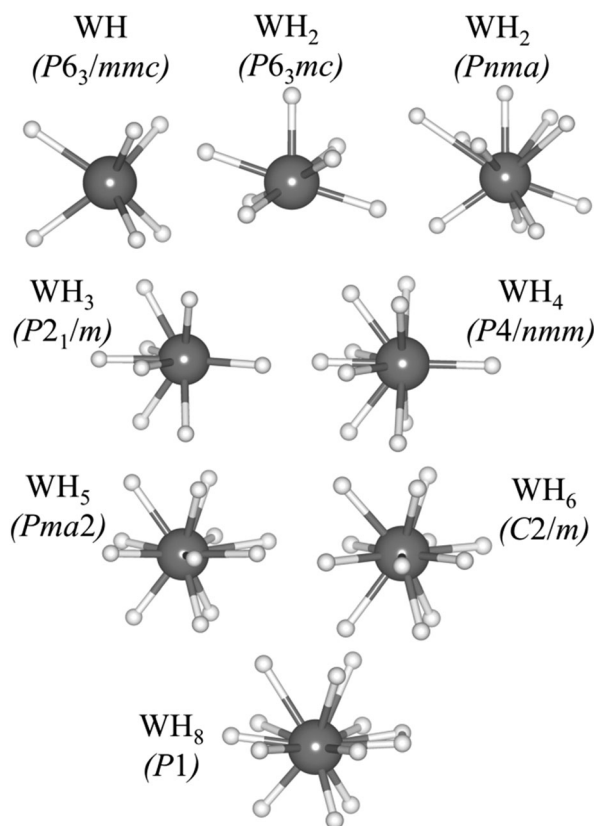
We considered seven WH<sub>*n*</sub> stoichiometries from WH to WH<sub>8</sub>. For each of them we performed an extensive computational search for the ground state structures and two given pressures,  $-25$  GPa and 150 GPa. The search combined complementary approaches: a purely random search, two using evolutionary algorithms<sup>33</sup> (USPEX,<sup>34</sup> Xtalopt<sup>35</sup>) and the examination of prototypical structures, using up to  $Z = 4$  formula units per unit cell. This composite structure-searching methodology was coupled with DFT calculations, details of



**Fig. 1** W–H distance in polynuclear tungsten complexes reported in the Cambridge Structural Database involving hydrogen bridges.

which can be found in the Computational methods section at the end of this paper. The geometry of the resulting WH<sub>*n*</sub> phases was then optimized for several pressures from 1 atm to 150 GPa, at the same level of theory.

Fig. 2 shows the hydrogen environment of the W atoms in these WH<sub>*n*</sub> phases at  $P = 50$  GPa and  $T = 0$  K.<sup>2,3,6</sup> It is worth mentioning that the crystal structure search described above resulted in the experimental *anti*-NiAs structure for the WH stoichiometry. Note the progressive increase in coordination of W, from 6 in WH, to 12 in WH<sub>6</sub>. Coordination number is not an unambiguous concept; the W–H distances vary, with histograms of W–H separations given in the ESI.† Of course, the coordination number will also depend on pressure. Because of the PV term in the Gibbs free energy  $G$ , higher  $P$  favors denser structures; this is usually achieved by increasing coordination for all atoms.<sup>36</sup> Fig. 2 shows the coordination sphere of W in the computationally preferred WH<sub>*n*</sub> structures at  $P = 50$  GPa. The hydrogens in the extended structures, of course, all bridge W atoms. The actual bonding patterns are quite complex, and a function of the pressure. No particular effect of the hydrogen richness can be observed on the W–H bond length. At  $P = 50$  GPa, it extends approximately from 1.7 to 2.0 Å for each stoichiometry, except WH where all W–H bonds are about 2.0 Å. Only in WH<sub>8</sub> does



**Fig. 2** Local environments of W atoms in the WH<sub>*n*</sub> structures ( $n = 1\text{--}6, 8$ ) at  $P = 50$  GPa.<sup>6</sup> Note that there is no molecular tungsten complex involved in the structures; in reality the hydrogen atoms (small spheres, white) are shared between several W atoms (large spheres, grey), resulting in 3D extended structures whose space groups are indicated between parentheses.

one have H–H bonds; note the formal resemblance here to molecular  $\text{WH}_4(\text{H}_2)_n$ .

It is worthwhile to show a couple of the 3D-extended structures; these are presented for WH and  $\text{WH}_6$  at  $P = 50$  GPa in Fig. 3. It should be noted that at  $P = 1$  atm none of the extended hydrides are thermodynamically stable with respect to the elements; it is only at elevated pressures that they are stabilized. Nor are they likely to be kinetically stable at  $P = 1$  atm; our calculations at ambient pressure move away from compounds and toward segregated elements.

We want to build a bridge between discrete molecular  $\text{WH}_6$ , a species that has aroused much interest among inorganic chemists during the last past twenty years,<sup>4,8,14,37</sup> and the extended  $\text{WH}_6$  structure shown above in Fig. 3. We do this by an Aufbau from the molecule, increasing dimensionality as we go along.

### Molecular $d^0$ $\text{WH}_6$ and its acceptor character

In  $\text{WL}_6$  molecular complexes, the tungsten atom is hexacoordinated and has a (+VI) formal oxidation state, *i.e.* is a  $d^0$  species. Experimentally, two main kinds of stereochemistry are encountered around the metal center in such cases: octahedral ( $O_h$ ) or trigonal prismatic (regular ( $D_{3h}$ ) or distorted ( $C_{3v}$ )).<sup>38</sup> The factors that might make a hexacoordinated transition metal complex assume that one or the other of these two geometries have fascinated inorganic chemists for several decades now (see for example ref. 39 and references therein). Ligand repulsion militates in favor of an octahedral arrangement. But in the case of  $d^0$ - $d^2$  complexes, a trigonal prismatic geometry can be favored on account of better bonding interactions between d orbitals of the metal fragment and MOs of ligands. An excellent review of bonding in  $d^0$  systems can be found as ref. 25.

In this context, the  $d^0$   $\text{WH}_6$  complex, with its small ligands, is the prototypical example of a hexa-coordinated complex whose geometry can differ significantly from  $O_h$ .

As already mentioned, in 2002 Wang and Andrews were able to synthesize molecular  $\text{WH}_6$  by reaction of laser-ablated tungsten atoms with  $\text{H}_2$  during condensation in excess neon.<sup>7,8</sup> The metastable molecule could be characterized by infrared

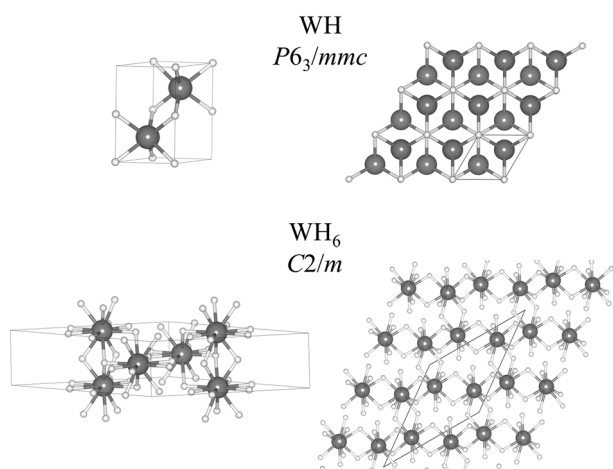


Fig. 3 The computed structures of WH and  $\text{WH}_6$  at 50 GPa.

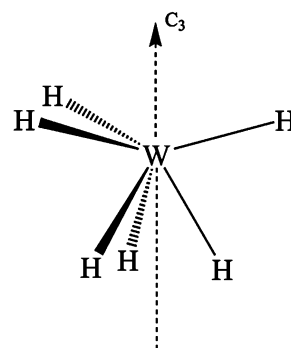


Fig. 4 Molecular  $\text{WH}_6$  in a distorted trigonal prismatic geometry.

spectroscopy, and comparison of its experimental spectrum with computed ones for several hypothetical geometries indeed indicated that the  $\text{WH}_6$  complex exhibits a distorted trigonal prismatic structure, as sketched in Fig. 4.

Starting from the optimal geometry of the  $\text{WH}_6$  complex given by DFT at the B3LYP<sup>40</sup>/6-311++G(d,p)/LANL2DZ<sup>41</sup> level using the Gaussian package,<sup>42</sup> and after having checked through a vibrational analysis that this geometry was indeed a minimum of the potential energy surface, we computed the orbitals of  $\text{WH}_6$  with the extended Hückel method,<sup>43</sup> as implemented in the YAeHMOP package<sup>44</sup> and with DFT calculations as well. These orbitals are schematically shown in Fig. 5. The molecule is a closed shell singlet. Note, however, the low-lying unfilled non-bonding  $3a_1$  and  $3e$  orbitals. These confer on the molecule very good electron-acceptor character. DFT also gives an energy gap between the highest occupied levels and the lowest unoccupied ones of 5.7 eV (the extended Hückel method gives 3.7 eV).  $\text{WH}_6$  is likely to react with almost any base present in its environment. And indeed it does react on heating of the neon matrix in which it was isolated, to unknown products.

The question then arises: if one has an aggregate of  $\text{WH}_6$  molecules, will the individual species persist, or will they polymerize? This is the question we approach next.

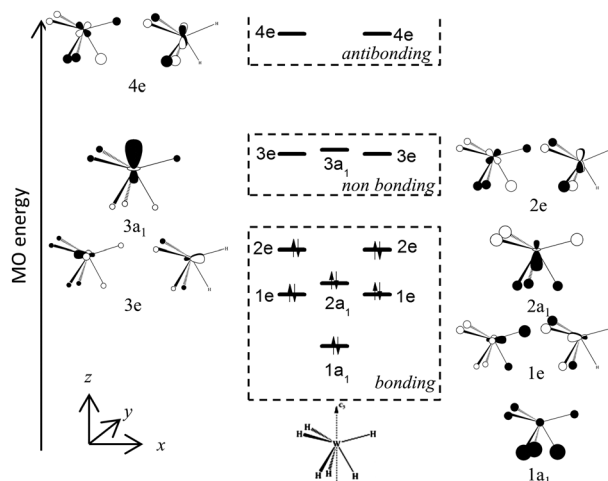


Fig. 5 Schematic MO diagram of the molecular  $\text{WH}_6$  complex in its  $C_{3v}$  distorted trigonal prismatic geometry.

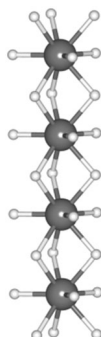
## At 1 atm, $\text{WH}_6$ wants to polymerize

Our extended structure studies<sup>6</sup> indicate that, at  $P = 1$  atm, segregation into the elements is favored thermodynamically. We have so far no information on the barriers for decomposition that might intervene. As we saw, all molecular compounds are also thermodynamically unstable with respect to the elements, very much so. The interesting question is whether a three dimensional molecular crystal of  $\text{WH}_6$  is kinetically persistent at  $P = 1$  atm.

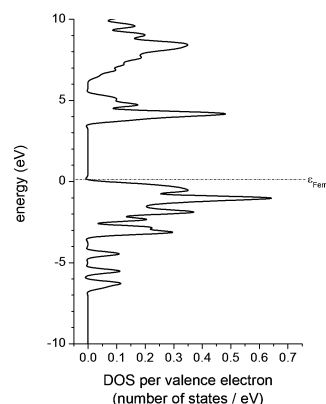
To address this problem, we optimized extended 3-dimensional structures of  $\text{WH}_6$  at  $P = 1$  atm starting from several  $\text{AX}_6$  structures known experimentally, such as that of  $\text{CaB}_6$ ,  $\text{CaC}_6$ ,  $\text{MoF}_6$ ,  $\text{WF}_6$  and  $\text{WCl}_6$  but without imposing any constraints (the unit cell shape and volume as well as atom positions were allowed to vary; see the Computational Methods section for more details about the methodology used). A picture of these structures can be found in the ESI.† Some of them are three-dimensional, some— $\text{MoF}_6$ ,  $\text{WF}_6$  and  $\text{WCl}_6$ —are molecular and locally octahedral.

The optimizations starting from the  $\text{WF}_6$  and  $\text{WCl}_6$  structures are those which lead to the most stable phases for the  $\text{WH}_6$  composition. Both involve molecules that are not 3D-networks, but 1D-chains as the one shown in Fig. 6. The two structures differ only by the relative arrangement of those chains, the typical distance between them (between 2 W atoms belonging to 2 different chains) being 5.7–5.9 Å. Getting polymeric chains through an optimization procedure that starts from an ensemble of molecular complexes is strong indication of lack of kinetic persistence of the  $\text{WH}_6$  molecular complex itself. The  $\text{WH}_6$  polymer is only metastable—it lies about 1.21 eV per formula unit higher in energy than the elements. The density of states is shown in Fig. 7. It is characterized by a band gap of 3.5 eV. Note however that DFT is known to underestimate band gaps. The local stereochemistry around the W atoms is tricapped trigonal prismatic, with W–H bonds of 1.69 Å between W atoms and capping H atoms, and longer W–H bonds (1.86 Å) between W atoms and bridging H atoms.

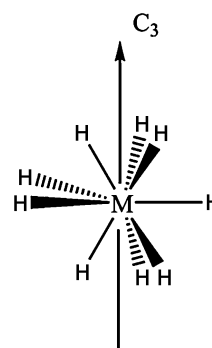
This tricapped trigonal prismatic (TTP) geometry, sketched in Fig. 8, is quite common for 18-electron 9-coordinated complexes, such as  $\text{IrH}_9$ ,  $\text{OsH}_9^{3-}$ , or  $\text{ReH}_9^{2-}$ . The tungsten equivalent would be  $\text{WH}_9^{3-}$ , experimentally unknown as far as we are aware, probably because of the high negative charge involved.



**Fig. 6** One-dimensional chain of  $\text{WH}_6$  stoichiometry, with a local tricapped trigonal prismatic arrangement around W atoms.

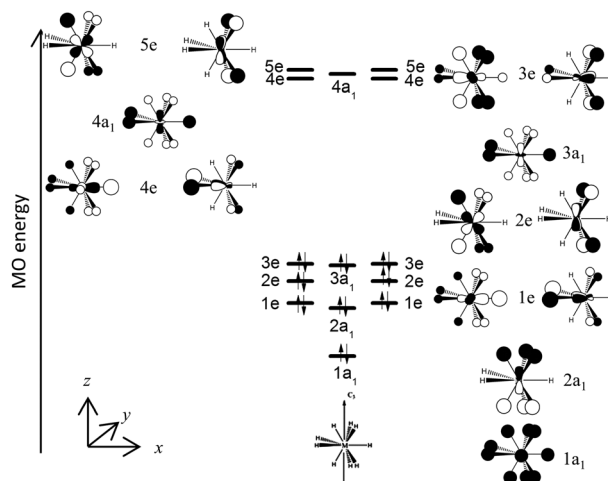


**Fig. 7** Density of states per valence electron of the  $\text{WH}_6$  solid state structure shown in Fig. 6. The Fermi energy level has been set to zero.



**Fig. 8** Molecular  $\text{MH}_9$  complex in a tricapped trigonal prismatic geometry.

A schematic orbital diagram for a  $d^0$   $\text{MH}_9$  complex is shown in Fig. 9, computed by the extended Hückel method.<sup>43</sup> Although the tricapped trigonal prismatic geometry is of  $D_{3h}$  symmetry, the label given for the MOs is that of the  $C_{3v}$  symmetry, to highlight possible symmetry-allowed orbital interactions between  $C_{3v}$ - $\text{WH}_6$  and the hypothetical  $D_{3h}$ - $\text{WH}_9^{3-}$ . The particular stability of 18-electron  $d^0$  complexes in the



**Fig. 9** Schematic MO diagram of the molecular  $\text{MH}_9$  complex in its  $C_{3v}$  tricapped trigonal prismatic geometry.

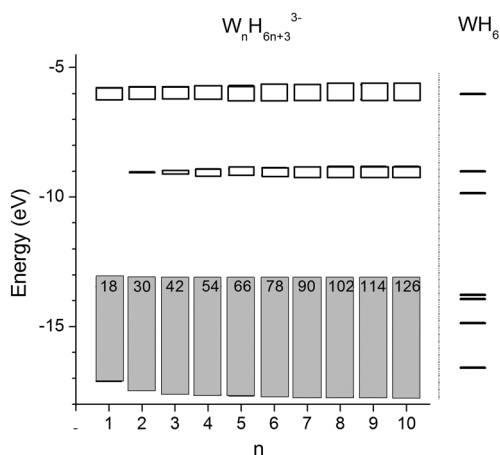
tricapped trigonal prismatic geometry is apparent in the gap between filled and unfilled orbitals. For  $\text{WH}_6$  computed in its optimal geometry (as given by DFT/B3LYP/6-311++G(d,p)/LANL2DZ), the extended Hückel method, which is insensitive to charge, gives an energy gap of 7.3 eV, *i.e.* 3.6 eV more than for  $C_{3v}\text{-WH}_6$ .

## 12 $e^-$ —a good electron count for 1D-chains of metals in a tricapped trigonal prismatic environment

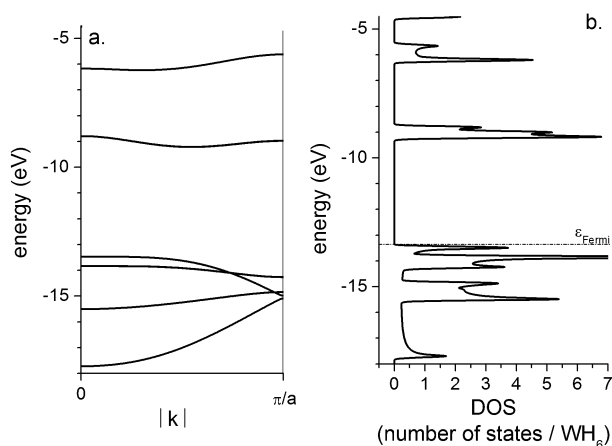
How can we understand the formation of the  $\text{WH}_6$  infinite chains from discrete  $\text{WH}_6$  molecular complexes? Let us consider as a first step the linear oligomer of  $n$  W atoms, a cluster of general formula  $[(\text{W}_n\text{H}_{6n+3})^{3-}]$ , that can also be written  $[(\text{WH}_{6+3/n})^{(3/n)-}]_n$ . The  $\text{WH}_9^{3-}$  anionic complex mentioned previously simply corresponds to the particular case  $n = 1$ , whereas the  $\text{WH}_6$  infinite chains correspond to the case  $n$  tending to  $\infty$ .

Formally, the formation of the  $\text{WH}_6$  infinite chains can be seen as the successive additions of  $\text{WH}_6$  fragments starting from the  $\text{WH}_9^{3-}$  anionic complex. The energy of reaction of those  $\text{WH}_6$  additions was calculated by the extended Hückel theory<sup>43</sup>—which again is insensitive to charge-cutting each fragment from an isolated  $\text{WH}_6$  infinite chain optimized at  $P = 1$  atm and  $T = 0$  K with VASP (see the Computational Methods section for details).<sup>45</sup> Within the limits of this method, whatever the value of  $n$ , the  $[(\text{W}_n\text{H}_{6n+3})^{3-}] + \text{WH}_6 \rightarrow [(\text{W}_{n+1}\text{H}_{6(n+1)+3})^{3-}]$  reaction leads to a stabilization of 2.4 eV per  $\text{WH}_6$ . This is a clear indication of an energetic drive for polymerization of molecular  $\text{WH}_6$ .

The evolution with  $n$  of the energy levels of the  $[(\text{W}_n\text{H}_{6n+3})^{3-}]$  clusters computed by the extended Hückel method in their frozen geometry cut from the DFT-optimized 1D chain is shown in Fig. 10. They have to be compared to the band structure and density of states of the isolated  $\text{WH}_6$  infinite chain shown in Fig. 11. Note the rapid development of the bands of the polymer. Because of the 4-electron interactions between occupied levels of the  $\text{WH}_6$  complex and occupied



**Fig. 10** Bands in  $\text{W}_n\text{H}_{6n+3}^{3-}$  complexes, shown in block format.  $\text{W}_n\text{H}_{6n+3}^{3-}$  and  $\text{WH}_6$  have been cut from the optimized  $\text{WH}_6$  1D-chain. Grey bands correspond to bands fully occupied whereas white ones correspond to empty bands. The numbers at the top of the grey bands indicate the total number of electrons occupying them.



**Fig. 11** Band structure (a) and density of states (b) computed by the extended Hückel method for an isolated  $\text{WH}_6$  chain in its optimal geometry determined by DFT (structure shown in Fig. 6).

levels of the  $[(\text{W}_n\text{H}_{6n+3})^{3-}]$  polymer to form  $[(\text{W}_{n+1}\text{H}_{6n+9})^{3-}]$ , the occupied band widens upon polymerization. Nonetheless, whatever  $n$ , the lowest unoccupied MO of the  $\text{WH}_6$  complex interacts with the occupied MO of  $[(\text{W}_n\text{H}_{6n+3})^{3-}]$  of same symmetry. The polymerization thus results in a widening of the occupied band, keeping the highest occupied level remarkably constant and thus the band gap wide. Polymerization is then favored until the eventual formation of an infinite chain, characterized, in its isolated form, by an extended Hückel energy band gap of 4.0 eV, *i.e.* 3.3 eV narrower than that of the hypothetical  $D_{3h}\text{-WH}_9^{3-}$  computed at the same level of theory and 0.3 eV wider than that of  $C_{3v}\text{-WH}_6$ .

## Concluding comments

After a review of what is known experimentally about the matrix-isolated (but very unstable with respect to the elements) molecular  $\text{WH}_n$  species,  $n = 1\text{--}12$ , we have outlined the hydrogen coordination patterns observed in calculations on extended  $\text{WH}_n$  structures. We then broached the question of what molecular  $\text{WH}_6$  might do under conditions where other  $\text{WH}_6$  molecules are nearby. Interestingly, arrays of  $\text{WH}_6$  transform without activation energy neither into the elements themselves nor into the  $\text{WH}_6$  structure stabilized at higher pressures. Instead they form polymeric one-dimensional chains, with 9-coordinated tungsten and triply bridging hydrogens. The enthalpics underlying this polymerization are examined, along with the build-up of the polymer's electronic structure.

## Computational methods

All of the solid-state calculations were performed using density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE)<sup>46</sup> parameterizations of the generalized gradient approximation (GGA), as implemented in the VASP code (ver. 4.6).<sup>45</sup> The projector-augmented wave (PAW) method<sup>47</sup> was applied with the PAW pseudo-potentials taken from the VASP archive. The  $1s^1$  and  $5d^46s^2$  electrons were included in the valence space for H and W atoms, respectively. For the plane-wave basis-set

expansion, an energy cutoff of 750 eV was used. The accuracy of sampling the first Brillouin zone (FBZ) is assured by using dense  $k$ -point grids resulting from a series of convergence tests.

The same methodology was used to optimize the geometry, at  $T = 0$  K and  $P = 1$  atm, of a 1D-chain of  $\text{WH}_6$  stoichiometry, whose interaction with other  $\text{WH}_6$  chains was ensured by imposing large unit cell dimensions in the two directions perpendicular to the chain ( $> 10$  Å).

## Acknowledgements

This work was supported by the National Science Foundation through grants CHE-0910623 and DMR-0907425. VL would like to thank the Franco-American Commission for Educational Exchange for its financial support. Calculations were performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant ECS-0335765).

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