Stabilization of W\textsuperscript{VI} in Nitride Environment via Acid/Base Reactions, and General Route to Layered Transition Metal Nitrides\textsuperscript{*}

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DFT calculations for two hypothetical ternary nitrides of hexavalent tungsten: LaWN\textsubscript{3} and La\textsubscript{2}WN\textsubscript{4} (in perovskite and K\textsubscript{2}NiF\textsubscript{4} structures, respectively) show that these compounds should spontaneously form from WN\textsubscript{2} (acid) and LaN (base) reagents, or simply from (WN + 1/2 N\textsubscript{2} or W + N\textsubscript{2}) and LaN, at ambient or elevated temperature and high N\textsubscript{2} pressure to speed up the reactions. This concept may be utilized to stabilize other efemeric nitrides, like these of Re\textsuperscript{VII}, Os\textsuperscript{VIII}, and possibly even of unprecedented Ir\textsuperscript{IX}.

La\textsubscript{2}WN\textsubscript{4} is example of rare two-dimensional nitride materials. Band structure calculations confirm that LaWN\textsubscript{3}, La\textsubscript{2}WN\textsubscript{4} and several related compounds should exhibit metallic conductivity, and they show good prospect for 2D superconductivity via self-doping.

Key words: crystal structures, nitrides, polymorphism, transition metals, superconductivity

Nitrides of transition metals and of main group elements constitute a fascinating and fast-growing family of inorganic compounds. Some (BN, Si\textsubscript{3}N\textsubscript{4}) find use as superhard coatings and refractory materials [1], others (like NbN, Li\textsubscript{3}HfNCl) as superconductors [2] or (like GaN, InN) in optoelectronics [3], some – like Pt\textsubscript{3}N\textsubscript{5} – are simply a curiosity [4]. Interestingly, many stoichiometric binary nitrides cease to exist at ambient conditions; their list includes inter alia compounds at the highest available (or close to them) oxidation states of transition elements (W\textsuperscript{VI}N\textsubscript{2}, Re\textsuperscript{VII}N\textsubscript{7}, Os\textsuperscript{VIII}N\textsubscript{8}, Ir\textsuperscript{VII}N\textsubscript{2}, Pt\textsuperscript{IV}(N\textsuperscript{2}N\textsubscript{2}\textsuperscript{-2}), Au\textsuperscript{III}N, Au\textsuperscript{V}N\textsubscript{3}, etc. and their lighter congeners). However, it has recently been suggested that W\textsuperscript{VI}N\textsubscript{2} (a nitride analogue of well-known W\textsuperscript{VI}O\textsubscript{3}) is very close to thermodynamic stability at ambient conditions [5]. The computed \(\Delta H_{\text{form}}\) equals to \(-0.24\) eV for reaction

\[ \text{WN} + \frac{1}{2} \text{N}_2 \rightarrow \text{WN}_2^- \]  \hspace{1cm} (1)

which compares with entropy TS term for gaseous 1/2 N\textsubscript{2} at 298 K, \(\sim +0.30\) eV. In turn, the higher-density polymorph of WN\textsubscript{2}, WN\textsubscript{2}–II, should be achieved via high-pressure high-temperature synthesis at pretty harsh conditions (2800 K and 31–55 GPa), followed by rapid quenching [4]. Indeed, such strategy has been successful for platinum; synthesis has yielded unique semiconducting diazenide of Pt, Pt\textsuperscript{IV}(N\textsuperscript{2}N\textsuperscript{-}) [6,7].

\textsuperscript{*} Dedicated to Professor T.M. Krygowski on the occasion of his 70th birthday.

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Formation of WN$_2$ and of other above-mentioned nitrides are of redox type reactions. Here, N$_2$ oxidizes an element (or a lower nitride) to the highest oxidation state available. However, N$_2$ is not too good oxidant; the standard redox potential of the N$_2$/2N$^-3$ pair is only 0.25 V more positive than that of the Li$^+$/Li$^0$ couple at 400°C, as derived from the experiments on melted Li$_3$N [8]. No wonder that many nitrides of electronegative cations are not achievable via ambient-pressure routes.

In this contribution we propose to utilize old concept that high oxidation states are stabilized in basic environment. Specifically, we suggest that reactions:

\[ \text{LaN} + \text{WN} + 1/2 \text{N}_2 \rightarrow \text{LaWN}_3 \]  
\[ 2 \text{LaN} + \text{WN} + 1/2 \text{N}_2 \rightarrow \text{La}_2\text{WN}_4 \]

might help to shift significantly the W$^{III}$/W$^{VI}$ equilibrium to the right side of equations (2). Synthesis might thus be conducted at much milder conditions than formation reactions described in [4]. Computational test of validity of this assumption and the structure/property analysis for the resulting ternary nitrides are major goals of this paper.

**CALCULATIONS**

We have used CASTEP code for all calculations [9]. Our DFT optimization utilized the Perdew-Burke-Ernzerhof correlation-exchange functional, typical cut-off of 280 eV, k-point grid of 6×6×6 (LaWN$_3$) or 6×6×2 (La$_2$WN$_4$), and ultrasoft Vanderbilt pseudopotentials. Spin polarization was not enforced. The residual pressure on cells was no larger than ±0.01 GPa. The tetragonal I4/mmm cell was adopted for La$_2$WN$_4$, and the cubic P4/mmm perovskite cell for LaWN$_3$, as illustrated in Fig. 1. These structure types have been chosen because the structural condition of perovskite (ABX$_3$) structure is quite well fulfilled in these compounds, namely (R$_A$ + R$_X$)$^2$ = (R$_B$ + R$_X$), as judged from experimental ionic radii of La$^{3+}$, W$^{6+}$ and N$^{3-}$[10]. Use of structures with hexacoordinated W$^{VI}$ is also justified in view of WO$_3$ adopting similar coordination; in addition, increased coordination numbers (here, 6 instead of 4) are frequently encountered for high pressure phases [11].

For consistency, we have also recomputed WN$_2$–I (Fig. 1), WN$_2$–II, and its brookite polymorph [12] starting from optimized cells described in [4], and LaN in its NaCl structure [13] The unit cell vectors and fractional coordinates for optimized cells are given in ESI (supplementary information).

![Figure 1](image-url) View of the optimized unit cells of WN$_2$–I, LaWN$_3$ and La$_2$WN$_4$, i.e. [LaN]$_2$[WN$_2$] (W in bright blue, La – in green, N – in dark blue).
RESULTS AND DISCUSSION

We will start our analysis by discussion of enthalpies of formation reactions of ternary nitrides, and then we will proceed to description of properties of these as yet unknown materials, as predicted from the first principles.

**Enthalpies of formation reactions.** The calculated enthalpies of reactions:

\[
\text{LaN} + \text{WN}_2 \rightarrow \text{LaWN}_3 \quad (3a) \\
2 \text{LaN} + \text{WN}_2 \rightarrow \text{La}_2\text{WN}_4 
\]

are $-1.57 \text{ eV}$ (3a) and $-2.07 \text{ eV}$ (3b), respectively (see *ESI*). The appreciable and negative values of enthalpy of reactions (3a, 3b) clearly indicate that ternary compounds should form out of binaries, as far as kinetic obstacles can be overcome [14]. Since WN$_2$–I has been earlier predicted [5] to be only 0.06 eV per mole away from thermodynamic stability (Eq. 1), these values also imply that reactions (2a) and (2b) will be facilitated. This result is important, as pure stoichiometric WN$_2$ is not yet available as a starting reagent.

The substantial negative values of enthalpies of formation reactions of ternary nitrides indicate, that basic strategy, which has triggered our investigations, works well for the WN$_2$–LaN system. This approach is now new; it has been successfully applied in the past to synthesize huge range of inorganic compounds, including Cs$_2$Re$^\text{VII}$H$_9$, LiIn$^\text{III}$H$_4$, CsAg$^\text{III}$F$_4$, LiAu$^\text{V}$F$_6$, for which the related binaries are either now known (ReH$_7$, InH$_3$), or achievable only with the greatest difficulties (AgF$_3$, AuF$_5$). In the future, this strategy might be extended to many other compositions, such as for example BaCuI$_4$ (viz. efemeric Cu$^\text{II}$I$_2$), Cs$_5$YbH$_6$ (viz. Yb$^\text{III}$H$_3$) [15], CsTlS$_2$ (viz. Tl$^\text{III}$S$_3$) etc.

**Other related compounds.** In line with the reasoning presented above, one might anticipate reaction schemes analogous to those described earlier, which involve Re, N$_2$ and Ba$_3$N$_2$, or Os, N$_2$, K and N$_2$:

\[
\text{Re} + 7/3 \text{N}_2 \rightarrow 1/3 \text{Re}_3\text{N}_7 \quad (4a) \\
\text{Re} + 7/3 \text{N}_2 + 1/3 \text{Ba}_3\text{N}_2 \rightarrow \text{BaReN}_3 \quad (4b) \\
\text{Os} + 8/3 \text{N}_2 \rightarrow 1/3 \text{Os}_3\text{N}_8 \quad (5a) \\
\text{Os} + 3/2 \text{N}_2 + \text{K} \rightarrow \text{KO}_3\text{N}_3 \text{etc.} 
\]

It may be reasoned that Re$_3$N$_7$ and Os$_3$N$_8$ are not stable thermodynamically, judging from redox chemistry of the highest oxidation states of the 6$^\text{th}$ row transition elements [16]. However, their ternary derivatives, BaReN$_3$, KO$_3$N$_3$, or Ba$_2$OsN$_4$, might form at ambient, or possibly at elevated pressure of N$_2$. Preliminary estimate of unit cell dimensions for these and related compounds is given in *ESI*.

In conclusion, simplistic chemical concept utilized in this work to stabilize the W$^\text{VI}$–N$^\text{3–}$ system, may be easily extended to other, as yet unknown, transition metal nitrides [17].
Electronic structure and the 5d/2p mixing (‘hybridization’ ‘covalence’). Provided that LaWN$_3$ and La$_2$WN$_4$ could be synthesized, it is of immediate interest what their electronic structure would be. The calculated band structure of LaWN$_3$ is shown in Fig. 2, that of La$_2$WN$_4$ is presented in ESI.

The 2s band of N is seen centered at about $-13$ eV with respect to the Fermi level of LaWN$_3$. The 2p manifold, however, is firmly mixed with the 5d set of W (and with its virtual 6s), within the $-6$ eV to $+10$ eV energy window.

Three bands cross the Fermi level close to X and to $\Gamma$, and the electron density integrated over these bands is shown in Fig. 3. One of these bands (No. 18) extends from $-1.24$ eV and its uppermost part reaches $+0.17$ eV; this is clearly the W–N $\pi^*$ band. Another band of similar origin (No. 17) is seen from $-0.56$ eV to $+3.67$ eV.

Figure 2. Electronic band structure and electronic density of states (DOS [electrons/eV]) for hypothetical LaWN$_3$ ternary nitride in the perovskite structure. Partial DOS from s, p and d electrons is also shown.

Figure 3. Electron density (dark blue) integrated over three bands, which cross the Fermi level of LaWN$_3$. An isovalue of 0.02 e/$\text{Å}^3$ is shown. Number of each band is indicated, along with its dispersion. Note substantial participation of N(2p) states in the $\pi^*$ and lone pair fashion.
Apparently, there is much $\pi$-back bonding in LaWN$_3$, and only in approximation this compound can be ascribed as $\{La^{III}W^{VI}(N^{-3})_3\}$. Finally, the last band is from $-0.02$ eV to $+3.67$ eV; this is the N-centered (lone pair) band, with a vanishing contribution from the 5d set of W. Thus, according to the GGA calculation, LaWN$_3$ (and also possibly La$_2$WN$_4$, see ESI) have null band gap at the Fermi level, i.e. they are metals, the charge carriers being mainly holes delocalized within the N sublattice. Even considering deficiencies of the present DFT treatments of the low-band gap systems (persistent ’negative’ band gap), now resolved via a screened-exchange approach [18], we feel that it is unlikely that the band gap will open for LaWN$_3$ (mainly due to significant span of the band No. 17). It remains an open question if La$_2$WN$_4$ will semiconductor, or if it stays metallic, but certainly it will be a strongly correlated electronic material.

An interesting problem arises of the ionic/covalent nature of the W$^{VI}$–N$^{3-}$ bonding in LaWN$_3$ and La$_2$WN$_4$.

Table 1 shows the results of the Mulliken population analysis of s, p and d electrons and the net atomic charges for LaN, WN$_2$, LaWN$_3$ and La$_2$WN$_4$. The results for the related phases of Ru$^{VII}$, Os$^{VIII}$ and Ir$^{IX}$ are shown in the ESI.

Table 1. Population analysis for s, p and d electrons, and net atomic charges for LaN, WN$_2$, and for hypothetical LaWN$_3$ and La$_2$WN$_4$ ternary systems.

<table>
<thead>
<tr>
<th>System/atom</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>total</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>2.23</td>
<td>6.35</td>
<td>1.58</td>
<td>10.16</td>
<td>+0.84</td>
</tr>
<tr>
<td>N</td>
<td>1.76</td>
<td>4.08</td>
<td>—</td>
<td>5.84</td>
<td>−0.84</td>
</tr>
<tr>
<td>WN$_2$–I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.63</td>
<td>0.10</td>
<td>4.15</td>
<td>4.88</td>
<td>+1.12</td>
</tr>
<tr>
<td>N1</td>
<td>1.72</td>
<td>3.90</td>
<td>—</td>
<td>5.62</td>
<td>−0.62</td>
</tr>
<tr>
<td>N2</td>
<td>1.71</td>
<td>3.79</td>
<td>—</td>
<td>5.50</td>
<td>−0.50</td>
</tr>
<tr>
<td>LaWN$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>1.54</td>
<td>5.93</td>
<td>1.26</td>
<td>8.73</td>
<td>+2.27</td>
</tr>
<tr>
<td>W</td>
<td>0.76</td>
<td>1.10</td>
<td>4.31</td>
<td>6.18</td>
<td>−0.18</td>
</tr>
<tr>
<td>N</td>
<td>1.70</td>
<td>4.00</td>
<td>—</td>
<td>5.70</td>
<td>−0.70</td>
</tr>
<tr>
<td>La$_2$WN$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>1.87</td>
<td>6.13</td>
<td>1.42</td>
<td>9.42</td>
<td>+1.58</td>
</tr>
<tr>
<td>W</td>
<td>0.83</td>
<td>1.07</td>
<td>4.28</td>
<td>6.18</td>
<td>−0.18</td>
</tr>
<tr>
<td>N1 (in-plane)</td>
<td>1.74</td>
<td>4.06</td>
<td>—</td>
<td>5.80</td>
<td>−0.80</td>
</tr>
<tr>
<td>N2 (apical)</td>
<td>1.69</td>
<td>4.01</td>
<td>—</td>
<td>5.70</td>
<td>−0.70</td>
</tr>
</tbody>
</table>

As it may be seen from Table 1, WN$_2$–I contains pretty covalent W–N bonds, the description of this compound being far from the $W^{6+}(N^{-3})_2$ formulation. This should also be the reason of moderate thermal stability of this compound, as the decomposition reaction would be facile even at room temperature (when entropy term of N$_{2(g)}$ takes over the beneficial enthalpy of formation term).
On the other hand, LaWN$_3$ and La$_2$WN$_4$ show more negative charges on N centers and more negative charge on W than in binary WN$_2$; this is due to electron density transfer from LaN layers to the WN$_2$ sheet. Each LaN layer is charged at +1.57 e in LaWN$_3$, and at +0.88 e in La$_2$WN$_4$. The associated negative charge (−1.57 e and −1.76 e, respectively) moves to [WN$_2$] layers, where it is distributed unequally between W and two N’s. Thus, more ionic LaN charge reservoir serves to ‘dilute’ the binary WN$_2$ and make the W–N bonding less covalent. The W–N bond also becomes more stable, i.e. less susceptible to N®W electron transfer, connected with decomposition of the compound.

The absolute occupation of s and p states on W (yielding negative charge on this center) is probably artifactual, and it originates from imprecise division of electron density within the [WN$_2$] sheets. Anyway, Mulliken population analysis testifies nice trend of stabilization of the oxidizing center (W$^{VI}$) via an acid/base reaction; recollect, this fundamental assumption has triggered our investigations.

**Doping, self-doping and superconductivity?** The negatively charged [WN$_2$] sheets, present in LaWN$_3$ and in La$_2$WN$_4$ are reminder of the analogous [CuO$_2$] layers seen for all oxocuprate superconductors. La$_2$WN$_4$ could thus be seen as a structural analogue of the first oxocuprate superconductor, La$_{2−x}$Ba$_x$CuO$_4$ [19], and of certain fluorides of Ag$^{II}$ [20]. The question arises: could La$_2$WN$_4$ become superconducting, if cooled to sufficiently low temperature?

Unfortunately, resemblances between La$_2$WN$_4$ and La$_{2−x}$Ba$_x$CuO$_4$ end at structural aspect. La$_2$CuO$_4$, a parent (undoped) compound of La$_{2−x}$Ba$_x$CuO$_4$, is an insulator, and it requires doping, while we predict La$_2$WN$_4$ to be metallic per se. Electronic configuration of Cu$^{II}$ is d$^9$, which enforces the half-occupation of the metal–ligand antibonding σ* band. On the other hand, electronic configuration of W$^{VI}$ is d$^0$, thus given some back-bonding, conducting electrons of La$_2$WN$_4$ would move mainly in the metal–ligand antibonding π* band. Vibrionic coupling is usually much weaker if it is based on π and not on σ manifold.

In any case, we think that hypothetical La$_2$WN$_4$, with its 2D electronic structure (see ESI), either self-doped or with an extra chemical doping, is interesting in context of superconductivity. One could reach this conclusion coming from various directions: (i) recognition of large potential for superconductivity of covalent compounds of strongly electronegative elements (here: nitrogen) [21], (ii) chance for electronic curve crossing in the W$^{VI}$/N$^{3−}$ system, by analogy to oxocuprates [22], (iii) from the particular importance of the steep band – flat band scenario for superconductivity [23], and last but not least by certain analogies between La$_2$WN$_4$ and layered Hf–N superconductor [2]. Therefore we think that it is worth to attempt synthesis of LaWN$_3$ and La$_2$WN$_4$, and verify their electric, magnetic and transport properties. Possibly, some of these phases would indeed superconduct.

With this hope, we look forward to the anticipated synthesis of the La–W–N compounds.
CONCLUSIONS

2D metals constitute a fascinating research field. In this contribution we have shown that acid/base reactions, such as those described by the equations (3), should enable for facile synthesis of selected layered transition metal nitrides, notably LaWN_3, La_2WN_4, BaReN_3, etc. Many of these have 3D (LaWN_3) or 2D (La_2WN_4) electronic structure, which is good prognostic for generation of superconductivity in these systems.

Supplementary information. Electronic supplementary information (ESI) accompanies this report, and is available on request from the author (Prof. W. Grochala, e-mail: wg22@cornell.edu).

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Note added in proof: When this manuscript was in proof, the theoretical work has appeared on the difficulties in synthesis of ‘CaN’ nitride [24].

REFERENCES AND NOTES

6. Gregoryanz E., Sanloup C., Somayazulu M., Badro J., Fiquet G., Mao H.K. and Hemley R.J., Nature Mater., 3, 294 (2004). In this work, the product of DAC synthesis has been erroneously described as Pt^III N.
11. If, say, La_N_3 turns out to crystallize in other structure type with, say, 4-coordinated W (for example, in the K_2CrO_4 type structure), its formation would be even easier than for the phases described in this work (the enthalpies of the formation reactions would be even more negative). In such instance, the K_3NiF_4 type might possibly be achieved at high pressures.
12. In our calculations, similarly as in Ref. 5, baddeleyite type (WN_2—I) is preferred over WN_2—I (cotunnite) by +1.20 eV.
13. LaN has been predicted to transform to the CsCl structure type only at 27 GPa: Vaitheeswaran G., Kaneshina V. and Rajagopalan M., Solid State Commun., 124, 97 (2002).
14. Increased external pressure should make synthesis even more feasible (thermodynamically at least, via the pV term), because LaWN_3 and La_2WN_4 have unit cell volumes smaller than those of starting binary reagents by 4.2% and 1.9%, respectively.
16. In the isoelectronic series, La$^{III}$, Hf$^{IV}$, Ta$^{V}$, W$^{VI}$, Re$^{VII}$, Os$^{VIII}$, the oxidizing power obviously increases. Therefore, LaN, Hf(N$_3$)$_4$ and Ta(N$_3$)$_5$ are known, WN$_2$ is on the verge of stability at ambient temperature and pressure, while Re(N$_3$)$_7$ and Os(N$_3$)$_8$ have not been synthesized so far.
17. As improbable as it may seem at the first sight, one may also address the issue of stability of Ir$^{IX}$N$_3$, a nitride of unprecedented nonavalent iridium, and of its quaternary salts, e.g. (KBr)IrN$_4$ etc. In ESI we list the predicted unit cell vector of cubic Ir$^{IX}$N$_3$ (in the RuO$_3$ structure). Considerations of kinetic stability of this fascinating phase require demanding phonon calculations for a large supercell, with particular attention to the presumed N–N pairing. Studies of unbelievable Ir$^{IX}$, Pt$^{X}$ and Au$^{XI}$ molecular and extended species are now conducted in our laboratory.