High-Pressure Synthesis of Metal–Inorganic Frameworks Hf$_4$N$_{20}$·N$_2$, WN$_8$·N$_2$, and Os$_5$N$_{28}$·3N$_2$ with Polymeric Nitrogen Linkers

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Abstract: Polynitrides are intrinsically thermodynamically unstable at ambient conditions and require peculiar synthetic approaches. Now, a one-step synthesis of metal–inorganic frameworks Hf$_4$N$_{20}$·N$_2$, WN$_8$N$_2$, and Os$_5$N$_{28}$·3N$_2$ via direct reactions between elements in a diamond anvil cell at pressures exceeding 100 GPa is reported. The porous frameworks (Hf$_4$N$_{20}$, WN$_8$, and Os$_5$N$_{28}$) are built from transition-metal atoms linked either by polymeric polydiazenediy (polyacetylene-like) nitrogen chains or through dinitrogen units. Triply bound dinitrogen molecules occupy channels of these frameworks. Owing to conjugated polydiazenediyl chains, these compounds exhibit metallic properties. The high-pressure reaction between Hf and N$_2$ also leads to a non-centrosymmetric polynitride Hf$_4$N$_{17}$ that features double-helix catena-poly[tetraz-1-ene-1,4-diyl] nitrogen chains [−N=N=N=N−].

Homoatomic bonding, being a prominent feature of carbon chemistry, is also characteristic for nitrogens, which readily form extended polymers and homoatomic frameworks.[1,2] Contrary to carbon and phosphorus, the nitrogen–nitrogen single and double bonds possess much less than 1/3 and 2/3, respectively, of the energy of the triple bond. Therefore, the conversion of N–N single or double bonds to triple bonds results in a very large energy release and makes the polynitrides highly endothermic and thermodynamically unstable at atmospheric pressure. At high pressures, however, the decomposition of such phases with the evolution of nitrogen is efficiently suppressed that provides a playground for systematic studies of nitrogen-rich compounds, in which various nitrogen-containing polyanions can be stabilized by simple metal cations. Even if such compounds may appear to be unstable at ambient conditions, high-pressure experiments provide a proof of their existence and valuable information for further development of the ambient-pressure synthesis of nitrogen-rich phases. So, the first successful synthesis of alkali metal pentazolates (salts containing cyclo-N$_5^-$ anions) was performed at high pressure.[3] Later, unsubstituted cyclo-N$_5^-$ was stabilized at ambient conditions too.[4–8] Metal–pentazole frameworks (AgN$_5$, Cu(N$_5$)(N$_3$),[6,9] Na$_2$N$_{10}$, K$_2$N$_{10}$)[5] might not only have applications as energetic materials, but also be intrinsically interesting as direct inorganic structural analogues of azolate metal–organic frameworks and framework materials based on an aromatic inorganic linker.[9,10] Metal–azide frameworks based on transition metals linked through bridging azido ligands are important for the development of molecular magnets.[11,12]

Recent high-pressure studies have shown that various polynitrogen species may occur as a result of simple reaction between a metal and molecular nitrogen. Good examples of that are FeN$_5$ containing catena-poly[tetraz-1-ene-1,4-diyl]}
anions \([-N=N-N-N\]-)\(^{-}\)\(^{13,14}\), MgN\(_{4}\), and ReN\(_{8}\)N\(_{2}\) with polydiazenediyld (polyacetylene-like) nitrogen chains\(^{15,16}\). Thus, high-pressure synthesis conditions enable the exploration of numerous possible metal–nitrogen framework topologies.

Herein we studied chemical reactions between 5d transition metals Hf, W, Os, and nitrogen in laser-heated diamond anvil cells at pressures exceeding 1 Mbar. All metals were found to form metal–inorganic frameworks MIFs: Hf\(_{4}\)N\(_{2}\)N\(_{2}\) (1), WN\(_{7}\)N\(_{2}\) (2), Os\(_{5}\)N\(_{2}\)N\(_{2}\) (3) with polymeric nitrogen linkers and guest dinitrogen molecules that are arranged in one-dimensional arrays. In all experiments discussed herein, a piece of metal was placed inside a sample chamber in a BX90 diamond anvil cell\(^{17}\) loaded with nitrogen that served as a reagent and as a pressure-transmitting medium. Hf, W, and Os samples were compressed to a pressure of about 105 GPa and laser-heated to 1900(200), 2700(200), and 2800(150) K, respectively. The reaction products contained multiple good-quality single-crystalline domains of novel phases, which were studied using synchrotron single-crystal X-ray diffraction (SCXRD) at the beamlines P02.2 (PetraIII, DESY, Hf sample), GSECARS 13IDD (APS, W and Hf samples), ID15b (ESRF, W sample) and ID11 (ESRF, Os sample). More details on the experimental procedures are given in the Supporting Information.

The crystal-structure solution and refinement revealed the chemical formulas of new compounds as Hf\(_{4}\)N\(_{2}\)N\(_{2}\), WN\(_{7}\)N\(_{2}\) and Os\(_{5}\)N\(_{2}\)N\(_{2}\) (Figure 1). The refinement against SCXRD data resulted in very good agreement factors (Supporting Information, Table S1). For a cross-validation of the crystal structures we performed theoretical calculations based on density functional theory. We carried out the full structure optimization for all of the compounds from ambient to the synthesis pressure and found that optimized crystal structures are in a very good agreement with the experimental ones (Supporting Information, Table S2).

The structure of WN\(_{7}\)N\(_{2}\) has the orthorhombic space group \(Immm\) with one W and two N atomic positions. WN\(_{7}\)N\(_{2}\) is isosctructural to previously reported inclusion compound ReN\(_{5}\)N\(_{2}\)\(^{15}\). W atoms are eightfold coordinated by four planar polydiazenediyld nitrogen chains with conjugated \(\pi\)-systems (Figure 1g, Scheme 1). The 3D framework WN\(_{7}\) possesses rectangular-shaped channels that are occupied by dinitrogen molecules (Figure 1d). In the ionic consideration, each W atom gives four of its six valence electrons to four N\(_{2}\) units. Thus, each N\(_{2}\) unit accommodates 2 electrons and has 22 valence electrons in total: four N–N σ bond pairs (8e), four dative N–W bonds (8e), and six π-delocalized electrons with an effective N–N bond order of 1.25. Tungsten, therefore, should have a formal oxidation state +4 and the formula of the framework can be written as W\(^{4+}\)(N\(_{2}\))\(_{2}\). The framework topology can be described by a point symbol \(5^{2}6^{7}(5^{2},6^{12},9^{3})\) as determined by the software ToposPro\(^{19}\).
The structure of Os₅N₂₈·3N₂ has the orthorhombic space group Pnmm with 3 Os and 9 N atomic positions. It exhibits two types of nitrogen units: N–N dumbbells and polydiazenediyl chains, so that the chemical formula of the framework may be rewritten as Os₅(N₂)₁₂(N)₉. The nitrogen–nitrogen distances within the dumbbells vary in a range 1.22–1.33 Å, which is characteristic for a double bond of the [N=N]²⁻ unit. This is in a good agreement with the common oxidation state of osmium + IV and the formula of the framework can be written as (Os⁴⁺)₁₂(N₂)₁₂(N)₉. All Os atoms possess distorted cubic coordination by nitrogen atoms. Os₁ atoms are coordinated only by nitrogen atoms that form dumbbells, while Os₂ and Os₃ atoms are coordinated by both type of units in the proportion 1:1 (Figure 1h). The framework contains rectangular and octagonal-shaped channels occupied by dinitrogen molecules. The framework topology can be described by a point symbol [4.6.1]₁₂[4².5.6.8².9²]₁₂[4.6.8²]₁₂-{5².6}₁₂. The structure of Hf₄N₂₀·N₂ has the orthorhombic space group Cmcm with 2 Hf and 5 N atomic positions. Among all reported compounds, Hf₄N₂₀·N₂ has the highest number of various nitrogen units: polydiazenediyl nitrogen chains, N–N dumbbells, and discrete N atoms. Nitrogen–nitrogen distances within the dumbbells are 1.32 Å and, therefore, the formula can be written as (Hf⁴⁺)₁₂(N₂)₁₂(N)₉ with Hf⁴⁺ in good agreement with the most common oxidation state of Hf (+ IV). The framework contains rhombus-shaped channels occupied by dinitrogen molecules. The framework topology can be described by the point symbol [3.4.5.7.9.10²][4.5.7.9²][4.5.7.9²]₁₂-{5²}₁₂. The frameworks of all of the compounds 1–3 and Re₅N₇₂[13] are built of a set of standard units: N–N dumbbells, discrete N⁺ anions and polydiazenediyl chains. An important factor for the stability of the polydiazenediyl chains is a resonance, which imparts partial double-bond character for nitrogen–nitrogen bonds. The stabilization through the resonance is well-known, with the classic examples of azides and pentazolates.[19] Recently synthesized MgN₆ featuring polydiazenediyl chains could be even recovered at ambient conditions.[34] Polydiazenediyl chains are also theoretically predicted to exist in Cu₅N₆, Re₅N₇₆ and Hf₅N₇₂.[20–24] Along with a pentazole anion, the polydiazenediyl chain may be one of the most stable structural units to be preserved at ambient pressures.

The compounds 1–3 can be rationalized based on the Mooser–Pearson extended (8–N) rule.[24] For the polynitride compound MNₓ, the number of nitrogen–nitrogen bonds per one nitrogen atom, b(NN), can be calculated as b(NN) = (8–[n(M)+x(N)]/x), where n(M) and n(N) are the numbers of valence electrons of metal and nitrogen, respectively. The results of the calculations applied to polynitrides are presented in the Table 1. It should be noted that b(NN) is fully consistent with the assignments of the bond orders from the crystal-chemical analysis and with the calculated charge density maps (discussed below).

To gain a deeper insight into the electronic properties of the compounds, we calculated the electronic density of states (DOS) and the electron localization function (ELF). At high pressure, all the considered materials are metallic and the main contribution to the DOS at the Fermi level comes from nitrogen chains (Figure 2) forming delocalized π-bonds, as demonstrated by the spatial distribution of electronic density in the range –0.1:0 eV (the inset in Figure 2b shows an example of WN₅N₂).

The ELF demonstrates strong covalent bonding between nitrogen atoms: the attractor associated with the N–N bond is located halfway between the atomic spheres (Figure 3a,c,e). The attractor thickness along the N–N bonds decreases from the nitrogen chains to dumbbells, and to nitrogen molecules. This demonstrates the increase of the bond order (from about 1.25 to 2, and to 3, respectively) that is in a good agreement with the crystal-chemical analysis.

Metal–nitrogen bonds reveal a different type of the ELF maxima. Separated attractors shifted toward the nitrogen atoms are found on the Me–N bond lines suggesting formation of two-center polar covalent bonds. Both discrete nitrogen atoms and those of the dumbbell form three-center Me–N–Me bonds with Os and Hf atoms with slight delocalization. According to the calculated charge density maps (Figure 3b,d,f), the electron density is nearly similar between all of the atoms of the nitrogen chains with only a slight increase on the bonds parallel to the line connecting the metal atoms compared to the side bonds. This leads to a small difference in the lengths of N–N bonds in polydiazenediyl chains.

Although the synthesis of some porous materials may require high pressure (for example, ZIF-8,[25] hydrothermal synthesis of zeolites[26]), the formation of porous structures at megabar pressures seems to be counterintuitive, as these conditions are expected to destabilize less dense framework structures. However, the pressures of about 110 GPa and temperatures of 2000 K are the conditions of the thermodynamic equilibrium between molecular and polymeric nitrogen, thus the volume gain of polymeric nitrogen is balanced by the energy of the triple nitrogen–nitrogen bond.[27] Furthermore, the polar covalent character of M–N bonds means that polydiazenediyl chains act as classical ligands (as donors for N–Me bonding). This imposes additional restrictions on the geometry of the system, namely, because of the sp³ hybridization of nitrogen atoms, a metal must be in the same plane as the coordinating nitrogen chain. It is indeed the case for the compounds 1–3 studied in the current work and

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<th>Table 1: Application of the Mooser–Pearson extended (8–N) rule for the description of polynitrides.</th>
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<tr>
<td>Unit</td>
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<tr>
<td>N=N</td>
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<tr>
<td>[N=N]⁺⁻</td>
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<tr>
<td>Polydiazenediyl</td>
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<tr>
<td>[N–N]+</td>
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<td>Av. no. of covalent N–N bonds per N atom (crystal-chemical analysis)</td>
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<td>Av. no. of covalent N–N bonds per N atom (the (8–N) rule)</td>
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ReN₈N₂,[15] which enables us to suggest that the covalent character of the transition metal–nitrogen bonds is one of the important factors for the framework architecture: the imposed geometry constraints lead to the formation of framework structures, rather than to the densest packing of atoms even at ultrahigh pressures. Another factor stabilizing the compounds 1–3 is the inclusion of nitrogen molecules into the pores. Entrapment of a pressure-transmitting medium by metal–organic frameworks upon compression is a well-known phenomenon, which significantly affects their properties, such as compressibility, amorphization pressures, and the sequence of phase transitions.[28–30]

The synthesis of nitrogen-rich MIFs requires a substantial excess of nitrogen over metal. Owing to the design of the DAC experiment, in which the reagents are initially in different states of aggregation (metal is solid, and nitrogen is gaseous), it is not possible to make a homogeneous mixture with a definite M:N ratio. Therefore, the formation of MIFs happens at the interface between a metal piece and nitrogen (Figure 4), whereas the bulk of the metal sample either remains intact or partially transforms to other nitrides. For example, a considerable part of the Os sample (Figure 4c) turned into osmium pernitride OsN₂ with the marcasite structure type.[31]

In the Hf–N system, the reaction product, along with Hf₄N₂₀·N₂, contains a novel compound with a chemical formula Hf₂N₁₁ (4) (Figure 5; Supporting Information, Tables S3, S4). The structure of Hf₂N₁₁ is built of Hf atoms coordinated by discrete nitrogen atoms, N=N dumbbells and catena-poly[trans-tetraz-1-ene-1,4-diyl] chains [–N=–N–N–] (Figure 5e) similar to those previously observed in FeN₇.[36–39] Discrete nitrogen atoms and dumbbells are within Hf₄ tetrahedra (Figure 5d), while polymeric nitrogen chains form double-helix structure (Figure 5e). Inorganic double
same reasoning could also explain why Os does not form a 20e OsN₄ complex. Second, Hf metal has much lower electronegativity and readily forms bonds of more ionic character that explains N₃⁻ and N₂⁺⁺ ions in the crystal structure of Hf₂N₁₀·N₂ and Hf₂N₁₁.

Phonon dispersion relations calculated for compounds 2–4 show their dynamic stability at high pressure, as evidenced by the absence of any imaginary phonon modes (Supporting Information, Figures S1–S3). At the same time, the phonon dispersion curves of WN₄N₂ (compound 2) and Hf₂N₁₁ (4) do have imaginary modes at atmospheric pressure that suggests their instability at ambient pressure and T = 0 K. Indeed, WN₄N₂ produced good diffraction patterns down to about 25 GPa. Further pressure release resulted in an unknown compound with the following lattice parameters: \( a = 5.431(5), b = 6.36(7), c = 7.236(9) \text{ Å}, \alpha = \gamma = 90{^\circ}, \beta = 95.3(1)^{\circ} \). Unfortunately, the quality of its diffraction pattern did not allow a reliable structure solution. We would like to note that small magnitude of the imaginary frequencies seen in Hf₂N₁₁ and WN₄N₂ at ambient pressure is expected to be removed at finite temperature by anharmonic effects (renormalization). Similar argument supports the stabilization of Hf₂N₁₀·N₂ at finite temperature even though phonon calculations in the harmonic approximation at T = 0 K resulted in small imaginary frequencies for some optical modes (Supporting Information, Figure S4).

The decompressed Os–N sample contained only Os and OsN₂ (Supporting Information, Figure S5). The crystal quality of both Hf₂N₁₄ and Hf₂N₁₆·N₂ deteriorated rapidly on decompression and the diffraction from these compounds was almost undetectable below 80 GPa. In the search of the predicted Hf₂N₁₂ compound at lower pressures, we reheated the sample at 73 GPa. Another compound with the following lattice parameters: \( a = 6.2946(13) \text{ Å}, \alpha = \gamma = 90{^\circ}, \beta = 95.3(1)^{\circ} \). The resulting material was cubic Hf₂N₁₂ (\( \text{I} \bar{4} \text{3d}, \text{No. 220}, a = 6.2946(13) \text{ Å} \)), as evident from the SCXRD analysis (Supporting Information, Table S5).

In conclusion, at extremely high pressures we have discovered three novel inclusion compounds, Hf₂N₁₆·N₂, WN₄N₂, and Os₅N₂₈·3N₂, which are built from host metal–inorganic frameworks and guest dinitrogen molecules. The one-step synthesis of these materials is achieved via a reaction between elemental metal and nitrogen. Their common characteristic structural units, the resonance-stabilized polydiazenediyl (polyacetylene-like) chains, may appear to be appropriate building blocks of other nitrogen-rich compounds that offer an elegant approach to the purposed synthesis of various metal–inorganic frameworks and enables further exploration of the remarkable chemistry of polynitriles.

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Conflict of interest

The authors declare no conflict of interest.

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