Predicting Nitrogen-Based Families of Compounds: Transition-Metal Guanidinates TCN$_3$ ($T$ = V, Nb, Ta) and Ortho-Nitrido Carbonates T$_2$CN$_4$ ($T'$ = Ti, Zr, Hf)

Dongbao Luo, Xianji Qiao, and Richard Dronskowski*

In memory of Dr. Bernhard Eck

Abstract: Due to its unsurpassed capability to engage in various sp hybridizations or orbital mixings, carbon may contribute in expanding solid-state nitrogen chemistry by allowing for different complex anions, such as the known NCN$^{2-}$ carbodiimide unit, the so far unknown CN$_3^{5-}$ guanidinate anion, and the likewise unknown CN$_4^{4-}$ ortho-nitrido carbonate (onc) entity. Because the latter two complex anions have never been observed before, we have chemically designed them using first-principles structural searches, and we here predict the first hydrogen-free guanidinates TCN$_3$ ($T$ = V, Nb, Ta) and ortho-nitrido carbonates T$_2$CN$_4$ ($T'$ = Ti, Zr, Hf) being mechanically stable at normal pressure; the latter should coexist as solid solutions with the stoichiometrically identical nitride carbi di imides and nitride guanidinates. We also suggest favorable exothermic reactions as useful signposts for eventual synthesis, and we trust that the decay of the novel compounds is unlikely due to presumably large kinetic activation barriers (C–N bond breaking) and quite substantial Madelung energies stabilizing the highly charged complex anions. While chemical-bonding analysis reveals the novel CN$_4^{4-}$ to be more covalent compared to NCN$^{2-}$ and CN$_3^{5-}$ within related compounds, further electronic-structure data of one phases hint at their physicochemical potential in terms of photoelectrochemical water splitting and nonlinear optics.

Introduction

The search for new solid-state nitrides or nitrogen-based materials in general remains intense due to the wide range of exciting and quite diverse applications, such as N-based fertilizers, explosives, high-performance steel coatings, superconductors, electrodes, UV-LED materials, and a lot more.[2] Despite enormous promise in their chemical and physical functionalities, the sheer amount of N-based materials is much smaller than those of the oxides, for reasons well known to chemists.[3] Somewhat simplified, the most fundamental N-based anions which we dub “first generation” only contain nitrogen coordinated to a metal atom, such as simple nitrides,[3] pernitrides,[4] azides,[5] diazenides,[6] and the recently predicted LiN$_5$.[7] The so-called “second generation” may then incorporate an additional nonmetal atom such as, for instance, in nitrido borates[8] or oxido nitrides.[9] Another prominent branch of the second generation is based, at least in principle, on C-centered complex anions by utilizing the carbon atom’s diverse hybridization (sp, sp$^2$, sp$^3$), thereby, for example, forming the linear carbodiimide or cyanamide NCN$^{2-}$ anion, see Figure 1. By doing so, the anionic dimensionality grows from zero (N$^{3-}$) to one (NCN$^{2-}$).

Clearly, N$^{3-}$ nitride and also NCN$^{2-}$ carbodiimide chemistries are well developed. Not only is GaN the fundamental material for blue light-emitting diodes (LED), its chemistry started in the 1930s already[10] and was then extended, by Juza and successors, to practically all kinds of metals, growing ever since, now also covering metastable compounds such as Sn$_3$N$_4$ and Na$_3$N$_4$.[11] As for carbodiimides, the earliest phase CaNCN served as a fertilizer in the 19th century and was structurally confirmed in 1962.[12] This field started to grow since the 1990s with better routes for main-group metal carbodiimides.[13] After the turn of the millenium, transition-metal carbodi-
imidates also became accessible,[14] thereby opening up applications in (photo)electrochemistry.[15]

The next topological step consists of the planar (hence, two-dimensional, see Figure 1) CN$_{3}$$^-$ guanidinate anion, and a similar class of guanidinate phases was firmly established through making RbCN$_{3}$H$_{4}$ in 2011[16] whose complex anion, descendant of the astonishingly basic guanidine molecule, still carries four N-bonded H atoms. Syntheses in liquid ammonia further led to singly deprotonated (Li, Na, K, Rb, Cs, Ba, Eu)[17] and also doubly deprotonated (Sr, Ca, Yb) guanidinates[18] but a hydrogen-free CN$_{3}$$^-$ guanidinate unit has not been accomplished up to the present day. And yet, there should be the tetrahedral CN$_{4}$$^-$ ortho-nitrido carbonate (onc), a three-dimensional complex anion (see Figure 1) which was never observed before, reminding us of the carbon atom’s sp$^{3}$ hybridization alluding to the diamond structure and a multitude of hydrocarbons or other CX$_{4}$ species, thereby also highlighting the huge challenge to find such “tetrahedral” C-based solid-state compounds.[19]

To path the way to their discoveries, we have performed an extensive structure search based on structural evolution through the Particle Swarm Optimization (PSO) algorithm.[20] Assuming that the terminal structures and compositions have been firmly determined, the corresponding synthetic routes can then be adjusted by chemical creativity. For the density-functional calculations, 3d-5d transition metals of the vanadate group were studied in detail whose well optimized structural parameters are shown in Table S1. Their stability was determined, the corresponding synthetic routes so successful synthesis should be tried. Other routes, better still, might be possible as well. Structurally, all TCN$_{3}$ are predicted to crystallize in the hexagonal system with space group P6$\overline{3}$c2 (see Figure 2) whereas, for T$_{5}$CN$_{4}$, three different types of compounds should be observable, trigonal P$\overline{3}$m1, tetragonal P$\overline{4}$2$_{c}$, and orthorhombic Cmc$_{2}$ (see Figure 3), all three differing in and indicative of their chemical characters.

**Results and Discussion**

**Stability**

The PSO structure predictions were performed by running CALYPSO[21] based on density-functional theory for unit cells containing up to four formula units TCN$_{3}$ and T$_{5}$CN$_{4}$, employing VASP together with projector augmented waves (PAW).[22] the generalized-gradient approximation (GGA) [23] and the Monkhorst-Pack scheme.[24] Twelve low-energy compounds were studied in detail whose well optimized structural parameters are shown in Table S1. Their stability was confirmed by three criteria, namely, phonon band structure by finite displacements (Phonopy)[25] elastic constants, and synthetic route. That is to say that, first, all twelve phases are dynamically stable with no imaginary modes in the phonon bands (Figure S1), even at zero pressure. Second, as regards mechanical stability, the calculated elastic constants all satisfy the corresponding Born elastic stability criteria[26] as shown in Table S2. With respect to chemistry, the selected metastatic pathway for the composition TCN$_{3}$ was chosen as [Eq. (1)]

$$TCl_{8} + Na_{2}NCN + Na_{3}N \rightarrow TCN_{3} + 5NaCl,$$

(1)

assuming convenient (i.e., high-energy Na$_{3}$N) starting materials. For the T$_{5}$CN$_{4}$ composition, the metathetic route was targeted as [Eq. (2)]

$$2TCl_{4} + Na_{2}NCN + 2Na_{3}N \rightarrow T_{5}CN_{4} + 8NaCl$$

(2)

Fortunately, the negative formation energies shown in Figure S2 indicate that all TCN$_{3}$ and T$_{5}$CN$_{4}$ are exothermic phases, so successful synthesis should be tried. Other routes, better still, might be possible as well. Structurally, all TCN$_{3}$ are predicted to crystallize in the hexagonal system with space group P6$\overline{3}$c2 (see Figure 2) whereas, for T$_{5}$CN$_{4}$, three different types of compounds should be observable, trigonal P$\overline{3}$m1, tetragonal P$\overline{4}$2$_{c}$, and orthorhombic Cmc$_{2}$ (see Figure 3), all three differing in and indicative of their chemical characters.
Structural Details

Starting with the TCN4 types crystallizing in P63c2, the compounds VCN4, NbCN5, and TaCN6 adopt the same structure as shown in Figure 2a), and we select the heavy TaCN6 for a detailed internal description, see Figure 2b).

First, and in perfect harmony with the sum of Shannon’s ionic radii for Ta5+ and N3−,[27] there are six equidistant Ta–N bonds of 2.10 Å inside a trans face-sharing TaN6 octahedron stacked along c, a bit similar to the wider SrN6 octahedron (Sr–N = 2.67 Å) in SrCN3 but more twisted.[18] As for the important CN4 core with D3h symmetry, there are no H atoms as in SrCN3, while C–N = 1.35 Å and N–C–N = 120° are practically identical.[18] As for the shortest N–N distance of 2.35 Å is nonbonding, and Ta–Ta = 2.8 Å is also far beyond the sum of the effective ionic radii for Ta5+ (0.64 Å), indicating essentially no N–N and Ta–Ta interactions. That being said, this first predicted transition-metal guanidinate without H atoms appears as showing a “layered” motif with guanidinate anions and metal cations alternately stacked on top of each other, Figure 2a).

As for the T,5CN4 formula, there are three different chemical motifs, corresponding to three different compound classes, and they are shown in Figures 3a) to 3c). For reasons of convenience, we select T = Hf to study their chemical and structural peculiarities, as depicted in Figures 3d) to 3f).

Similar to the previous discussion of TCN4, the shortest N–N distance of 2.32 Å and Hf–Hf distance of 2.97 Å are far beyond any significant interaction and will not be discussed any further. In contrast, the Hf–N and C–N bond lengths and connectivities help to separate the three different types of T,5CN4:

Figure 3a) depicts the first P3m1-type T,5CN4 representative which is predicted to crystallize with two spatially separated Hf–N and N–C–N layers, a nitride carbodiimide T,5N6(NCN). There are three shortest Hf–N = 2.09 Å bonds in a plane around each Hf4+ by nearest N3− neighbors to generate a heterographene-like Hf–N layer, and two such layers form a double layer. For comparison, the Hf–N distances in Hf(NCN)3 lie between 2.03 and 2.24 Å.[28] The second shortest Hf–N = 2.17 Å distance is the one connecting the upper and lower layers, see Figure 3a) and 3d). The third Hf–N = 2.52 Å distance is essentially nonbonding. For the isolated carbodiimide unit, see Figure 3d), there are two C–N = 1.24 Å double bonds and a linear N–C–N shape, just as expected. In a sense, this crystal structure is topologically reminiscent of the recently reported bismuth oxide carbodiimide, Bi2O6(NCN), consisting of layers of [Bi2O6]2+ and [N=N=C–N]2−.[29] In addition, Bi2O6(NCN) has been confirmed suitable as a photoanode for photochemical water oxidation, just like the predicted T,5N6(NCN) as will be discussed later.

The second Cmc2-type T,5CN4 candidate, depicted in Figure 3b), is easily identified as a nitride guanidinate T,5N6(CN4) but crystallizes with a lower symmetry than the previously predicted TCN4 guanidinates, mirrored by the irregular T,5N7 decahedron and the slightly distorted planar CN3− anion, see Figure 3c). The Hf–N distances in the HfN7 decahedron range from 2.09 to 2.34 Å, wider than before. As for the CN3− unit, the C–N bonds arrive at 2 × 1.35 Å and 1.40 Å, the angles being 115° and 128°, similar to Yb(CN,4H4),[18]

Third, there is the primarily sought T,5CN4 class of phases crystallizing in P42/c, given in Figure 3e), the one that has never been observed before. In that crystal structure, Hf is coordinated by six N with 2 × 2.11 Å and 4 × 2.23 Å to form a distorted edge- and corner-sharing HfN6 octahedron. The crucial CN4+ unit, corresponding to an ortho-nitrido carbonate (ONC) anion, contains four identical C–N bonds of 1.49 Å, slightly larger than those of the known carbodiimides and guanidinates. Judged by the N–C–N angles of 106° and 117°, the onc unit is almost tetrahedral and conforms to D2d symmetry, see Figure 3f). We will further analyze the different chemical behavior to be expected from those differing structures.

Chemical Bonding and Electronic Structure

Because we are mostly interested in the behavior of the complex CN4-based anions of the T,5CN4 formula, let us focus on them first. For the nearest intraionic C–N bonds (dubbed C–N1) listed in Figure 4a), the bond lengths slightly increase as we go from nitride carbodiimides T,5N6(NCN) to nitride guanidinates T,5N6(CN4) to onc T,5N6(CN4), a trivial function of the increasing coordination number of the central C atom; a similar course is not found for the T–N distances. That is to say that the C–N1 bond slightly weakens but the larger number of C–N bonds upon going from carbodiimide (2) to guanidinate (3) to onc (4) must increase covalency as a whole.

On the other side, there is a changing and likewise trivial trend of the T–N distances, consistent with the changing ionic radii. If we take the onc structure, for example, in which T is sixfold coordinated, Shannon’s ionic radii for such coordination are 0.61 Å for Ti4+, 0.72 Å for Zr4+, and 0.71 Å for Hf4+,[23] and the course runs parallel to what is found theoretically. In fact, the situation is a bit more complex because one finds two types of a T–N bond, the slightly longer T–N1 and slightly shorter T–N2, Figure 3f). For T,5N6(NCN) and T,5N6(CN4), the T–N1 distance is significantly longer than the T–N2 distance, so the existence of the isolated N3− anion in T,5N6(NCN) and T,5N6(CN4) is quite obvious even from geometry.
The strengths of the chemical bonds are directly quantified by the Integrated Crystal Orbital Population (ICOHP) as projected by LOBSTER,[30] plotted in Figure 4b. For \( T^7N_2\) (NCN) and \( T^7N\) (NCN), the covalent part of the \( T^7-N\) bonding is not too large, as expected for a metal-nitrogen bond. As for the much more covalent and stronger intraionic C–N1 bond, the corresponding strength in the entire complex anions increases from carbodiimide to guanidinate to one, see Figure 4b), as a function of increasing condensation. This can also be illustrated in color by the so-called electron localization function (ELF)[31] of the N=C=N\(^{-}\), \( \text{CN}_3\(^{2\text{-}}\) and \( \text{CN}_4\(^{8\text{-}}\) units (for \( T^7=\text{Hf} \)), as displayed in Figure 4b) using an isosurface level of 0.8. In the language of ELF, the clouds around the N atoms indicate “lone-pair” electrons while the “localized” ones are visible, at least in principle, between C and N. ICOHP directly and numerically quantifies the higher covalency of the \( \text{CN}_4\(^{8\text{-}}\) anion.

Questions of relative stability as a function of condensation (or volume) are most easily answered from energy-volume plots. In order to do so, Vinet equations-of-state were calculated for \( \text{Hf}_2\text{N}_2\) (NCN), \( \text{Hf}_2\text{N}\) (CNN), and \( \text{Hf}_2\text{CN} \) to directly provide that information, see Figure 5a).[32] It immediately turns out that, under standard conditions, the nitride carbodiimide \( \text{Hf}_2\text{N}_2\) (NCN) may be considered the most stable compound (see also convex-hull discussion below), the chemical ground state, while the nitride guanidinate \( \text{Hf}_2\text{N}-\) (CNN) and the ortho-nitrido carbonate \( \text{Hf}_2\text{CN} \) are the metastable ones. As the pressure increases, see Figure 5b), \( \text{Hf}_2\text{N}_2\) (NCN) will transform into \( \text{Hf}_2\text{N} \) (CNN) at about 26 GPa and, at about 168 GPa, into \( \text{Hf}_2\text{CN} \). On the other hand, it is puzzling that the spatial requirement of the different anions, as given at zero pressure, does not run parallel to the condensed nature of the complex anions. As seen from Figure 5a), a nitride guanidinate is more densely packed than the one, while one is still better packed than the nitride carbodiimide, so the mutual fit of the Hf–N bonds or the packing itself also must play a role. Given sufficient pressure, however, the nitride carbodiimide will condense into a nitride guanidinate, and a nitride guanidinate will condense into an ortho-nitrido carbonate, so the highly covalent bonds eventually determine the effective volume.

Before discussing other physical properties, two additional chemical questions must be answered, at least tentatively, as regards absolute thermochemical stability and chemical inertness under laboratory conditions. With respect to the first question, we have calculated possible decomposition pathways and theoretical phase diagrams (Figure S3). Confirming the prior arguments, \( \text{Hf}_2\text{N}_2\) (NCN) is the true ground state by \(-0.24\) eV per Hf atom, thermodynamically stable against the convex hull, and should be straightforward to make. Surprisingly enough, \( \text{Hf}_2\text{N}_3\) (CNN), previously made by the Meyer group, turns out as being unstable by \(+0.08\) eV. Its existence and strong inertness, even against water and air, points towards large activation barriers, a common phenomenon involving complex C/N-containing anions (see below).

As regards \( \text{Hf}_2\text{N}(\text{CN})_3 \) and \( \text{Hf}_2\text{N}(\text{CN})_4 \), they are prone to decay by \(+0.55\) and \(+0.62\) eV per Hf atom, whereas TaCN \(_3\) is unstable by \(+1.41\) eV per Ta atom. That being said, the Ta phase is indeed less likely (but not impossible) whereas the two Hf phases would just need substantial kinetic barriers, larger than in the case of the known \( \text{Hf}(\text{CN})_2\). While we have been unable to carry out the necessary activation-barrier calculations, partly due to the sheer complexity (far more complex than, say, the graphite-diamond problem), partly due to our restricted computational facilities, other semiquantitative arguments are very much in favor of such large kinetic barriers. First, any decomposition of a carbodiimide, guanidinate, or ortho-nitrido carbonate will involve C–N or C=N covalent bond breaking, on the order of 305–615 kJ mol\(^{-1}\) (3.2–6.4 eV).[33] and this is unlikely to begin with: this is also what makes diamond being inert for eternities. Second, electrostatic reasoning points into the same direction, as the LOBSTER-calculated Madelung energies (per Hf atom) arrive at \(-31.9\) eV for \( \text{Hf}_2\text{N}_2\) (NCN), \(-28.1\) eV for \( \text{Hf}_2\text{N}(\text{CN})_3\), and \(-32.0\) eV for \( \text{Hf}_2\text{(CN)}_4 \). Not only must these impressive energies be overcome for decomposition, they go back to the highly charged \( \text{CN}_3\(^{-}\) \) and \( \text{CN}_4\(^{8\text{-}}\) anions and favor such densely packed high-pressure phases. As a side note, we reiterate that the (even smaller) Madelung energy of \( \text{Cr}_2\) (NCN), makes this unstable carbodiimide inert even at high temperatures as well as in acidic to alkaline media between pH 1–14.[46]

This brings us to the second question targeting chemical stability which can only be answered experimentally. For example, some carbodimides such as \( \text{Hf}(\text{CN})_2\) (CN) \(_3\), PbN-CN, etc. are perfectly inert in water,[28, 14b, 34] sometimes simply due to surface passivation, others such as Li\(_3\)C-CN, Na\(_3\)N-CN, or Ca-CN are not.[15, 16] Hence, we truly need the experiment to corroborate the aforementioned signposts as regards activation barriers and to test the surface stability against a typical laboratory atmosphere.

Coming back to physical properties, the metal-nonmetal interactions (i.e., covalent part of the Hf–N bonds) mirror what goes on between conduction and valence band, so they determine the band gap, as shown in the calculated densities of states (DOS) for \( \text{Hf}_2\text{N}_2\) (NCN), \( \text{Hf}_2\text{N} \) (CNN), and \( \text{Hf}_2\text{CN} \) given in Figure 6. Clearly, the nitrogen DOS spreads over the entire energy window through interaction with Hf and C, and the difference between an isolated N\(^{2\text{-}}\) nitride and a C-bonded nitrogen is easy to spot. As regards the band centers (shown as arrows on the right), the energetic proximity of Hf and N also indicates some covalent interactions in general, as already seen from COHP analysis, and the DOS shapes clearly broaden upon going from a) to b) to c), so the C–N

![Figure 5.](image-url)
covalency also strengthens and becomes maximized for the most condensed ortho-nitrodo carbonate, as expected.

The hybrid functional HSE06 was chosen to arrive at the most reliable band-gap values that are depicted in Figure 7. For each composition and crystal structure, the band gap (grey and orange patterns) obviously increases with an increasing atomic number of the metal atom. It is straightforward to correlate this behavior with the course of the lowering Pauling electronegativities (Ti > Zr > Hf, and V > Nb > Ta), so the metal–N interactions become more ionic (larger band gap) upon going down each group of transition metals. What is puzzling, however, is the fact that the band-gap character generally differs between the different classes of compounds. Clearly, the pure guanidinates $T'N_{2}(CN_{2})$, and ortho-nitrido carbonates $T'_{2}CN_{4}$, orange, black and green lines represent Hf, C and N, respectively. Arrows on the right axis represent the atomic band centers below the Fermi level.

Figure 7. Calculated HSE06 band gaps for stable compounds of the composition TCN$_3$ (T = V, Nb, Ta) and $T'_{2}CN_{4}$ (T = Ti, Zr, Hf), the latter grouped into nitride carbodiimides, nitride guanidinates, and ortho-nitrido carbonates. The band-edge potentials are referenced to the reversible hydrogen electrode. Grey and orange colors indicate the band gap itself whereas green and blue colors represent the conduction band minimum (CBM) and valence band maximum (VBM), respectively.

**Photochemical Water Splitting**

Likewise, the band-edge potentials were calculated with respect to the reversible hydrogen electrode (RHE), including the conduction band minimum (CBM) and the valence band maximum (VBM) estimated by the semiconductor electronegativity concept (Supporting Information), see again Figure 7. The VBM and CBM of the nitride carbodiimides $T'_{2}N_{2}(NCN)$ and the ortho-nitrido carbonates $T'_{2}CN_{4}$ bracket the water redox energy range for $T = Zr$ and Hf, and for these elemental combinations they would achieve water splitting without any external bias voltage (EBV). The CBM of the other materials, however, locate under the H$^+/H_2$ energy level, indicating the necessary EBV for water splitting. On the other hand, the band-gap value limits the type of light being harvested. As for $T = Zr$ and Hf, $T'_{2}N_{2}(NCN)$ and $T'_{2}CN_{4}$ are the near ultraviolet (from 305 to 367 nm) light-harvesting materials. As for the materials with a slightly too narrow band gap, thereby requiring a small EBV, that is, nitride carbodiimide Ti$_2$N$_2$(NCN) and one Ti$_2$CN$_4$, they are capable to harvest the red (689 nm) and green light (502 nm), respectively. As such, the nitride carbodiimides $T'_{2}N_{2}(NCN)$ and ortho-nitrido carbonates $T'_{2}CN_{4}$ have been identified as potential candidates for water splitting. Especially for the first ones, the layered structures should turn out as particularly useful for making almost 2D-like crystals, which would provide additional potential as multifunctional compounds.

**Nonlinear Optics**

Within the ortho-nitrido carbonates of the $T'_{2}CN_{4}$ compounds, the complex CN$_4^-$ anion itself comprises a large number of valence electrons (32) that may be shifted around the anion itself comprises a large lattice, giving rise to a high birefringence. In addition, the calculated birefringence shown in Table 1 is larger than 0.1, as derived from their refractive index (Figure S4).
Mechanical Properties

For practical fabrication and device applications, the mechanical properties of the $T'_2CN_4$ composition which are computationally accessible by VASPkit[42] must be studied (Table 2). For being brief, we here focus on the Hf compounds. Despite the sp$^3$-like carbon within ortho-nitrido carbonate Hf$_2$CN$_4$, the calculated bulk modulus $K = 212$ GPa and Young’s modulus $Y = 250$ GPa, indicating its resistant ability to compression and stiffness, are much smaller than diamond’s sp$^3$-carbon ($K = 435$, $Y = 1120$ GPa), simply due to the much softer Hf–N bonds. The compound’s universal elastic anisotropy $A_u = 0.30$, however, is close to that of diamond (0.27). In addition, the “softness” of the Hf–N interaction differs, as a function of the different chemical functionality, between the three types of compounds. For example, the negative Cauchy pressure or $K/G < 1.75$ indicate the brittleness of the nitride guanidinate Hf$_2$N(CN)$_3$.[43] The nitride carbodiimide Hf$_2$N$_2$(NCN) and the ortho-nitrido carbonate Hf$_2$CN$_4$, however, are expected to show a more ductile behavior. Finally, the values of the minimum lattice thermal conductivity as derived from the elastic constants indicate the potential of all three compounds in terms of good thermal conductivity.

| $T'_2CN_4$ | $\lambda$ (nm) | SHG coefficients (pm V$^{-1}$) | $\Delta\lambda$ (nm) |
|------------|----------------|-------------------------------|---------------------|
| Ti$_2$CN$_4$ | 502 | $d_{33} = -10.35$ | 0.123 |
| Zr$_2$CN$_4$ | 390 | $d_{33} = -3.96$ | 0.160 |
| Hf$_2$CN$_4$ | 367 | $d_{33} = 2.62$ | 0.127 |

| $T'_2CN_4$ | $K$ (GPa) | $Y$ (GPa) | $A_u$ | $C$ | $G/K$ | $\kappa_{\text{min}}$ (W m$^{-1}$ K$^{-1}$) |
|------------|----------|---------|------|-----|-------|--------------|
| Hf$_2$N$_2$(NCN) | 168 | 111 | 0.6 | 130 | 4.2 | 1.0 |
| Hf$_2$N(CN)$_3$ | 182 | 133 | 0.6 | 130 | 4.2 | 1.4 |
| Hf$_2$(CN)$_4$ | 212 | 133 | 0.6 | 130 | 4.2 | 1.4 |

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbodiimide · guanidinate · non-linear optics · ortho-nitrido carbonate · water splitting

Acknowledgements

D.L. gratefully acknowledges expert help by the late Dr. Bernhard Eck for the technical support of the high-performance cluster. Dr. Bernhard Eck passed away, aged 52, tragically and unexpectedly on August 14, so this work is meant in memoriam. We would also like to thank Peter Müller for help in the Madelung calculations. The simulation work is well-supported by the IT center of RWTH Aachen University under grant JARA-HPC (JARA0179). Open access funding enabled and organized by Projekt DEAL.

References

[1] a) A. F. Holleman, N. Wiberg, E. Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, New York, 2007; b) N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, Second Edition, Butterworth-Heinemann, Oxford, 1997; c) J. L. Doss, G. E. Totten, ASM Handbook: Steel Heat Treating Fundamentals and Processes, ASM International, Maerlins Park, 2013; d) S. Yamanaka, K.-I. Hotehama, H. Kawai, Nature 1998, 392, 580–582; e) K. Lee, S. W. Kim, Y. Toda, S. Matsuishi, H. Hosono, Nature 2013, 494, 336–340; f) J. T. Falk, B. N. Pushpakanar, S. B. Bayne, J. Electron. Mater. 2016, 45, 2673–2682.
[2] T. Scholz, A. L. Gorne, R. Dronkowski, Prog. Solid State Chem. 2018, 51, 1–18.
[3] a) K. H. Jack, Proc. R. Soc. London Ser. A 1951, 208, 200–215; b) A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, R. Boehler, Nature 1999, 400, 340–342; c) W. H. Sun, C. J. Bartel, E. Arca, S. R. Baurers, B. Matthews, B. Orvananos, B. R. Chen, M. F. Toney, L. T. Schelhas, W. Tumas, J. Tate, A. Zakutayev, S. Lany, A. M. Holder, G. Ceder, Nat. Mater. 2019, 18, 732–739.
[4] a) M. Wessel, R. Dronkowski, J. Am. Chem. Soc. 2010, 132, 2421–2429; b) R. Yu, O. Zhan, L. C. De Jonghe, Angew. Chem. Int. Ed. 2007, 46, 1136–1140; Angew. Chem. 2007, 119, 1154–1158.
