

Nitridoborates

Ba₁₂[BN₂]_{6.67}H₄: A Disordered Anti-Skutterudite filled with Nitridoborate Anions

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Abstract: Skutterudites are of high interest in current research due to their diversity of structures comprising empty, partially filled and filled variants, mostly based on metallic compounds. We herein present Ba₁₂[BN₂]_{6.67}H₄, forming a non-metallic filled anti-skutterudite. It is accessed in a solid-state ampoule reaction from barium subnitride, boron nitride and barium hydride at 750 °C. Single-crystal X-ray and neutron powder diffraction data allowed to elucidate the structure in the cubic space group *Im* $\bar{3}$ (no. 204). The barium and hydride atoms form a three-dimensional network consisting of corner-sharing HBa₆ octahedra and Ba₁₂ icosahedra. Slightly bent [BN₂]³⁻ units are located in the icosahedra and the voids in-between. ¹H and ¹¹B magic angle spinning (MAS) NMR experiments and vibrational spectroscopy further support the structure model. Quantum chemical calculations coincide well with experimental results and provide information about the electronic structure of Ba₁₂[BN₂]_{6.67}H₄.

The class of skutterudites are of high interest in research due to their convincing thermoelectric properties.^[1–3] Regular AB₃ skutterudites, such as the archetype CoAs₃, can be

derived from the ReO₃ structure and consist of tilted corner-sharing AB₆ octahedra.^[4] The tilting results in large B₁₂ icosahedra, which form a body-centered cubic package. In the partially filled variant of this structure type, the crystallographic position in the center of these icosahedra is occupied. With the general sum formula LM₄X₁₂, such compounds usually consist of a rare-earth metal *L*, a transition metal *M* and a pnictogen *X*, with LaFe₄P₁₂ or CeFe₄Sb₁₂ being just two examples.^[5–6] While phosphorus or antimony (*X*) form the base lattice, iron (*M*) is placed in the octahedral voids and lanthanum or cerium (*L*) inside the icosahedra. Such filled skutterudites are known as low-cost thermoelectrics.^[7] For high efficiency, these materials are desired to have low thermal and high electronic conductivity. The heavy atom inside the icosahedra of filled skutterudites acts as a source for lattice phonon scattering, which reduces the thermal conductivity.^[8] For example, the voids in CoSb₃ can be occupied to enhance its thermoelectric properties and possible n- or p-type doping of the cobalt or antimony sites allows further modification of the material.^[9–10] However, the icosahedra are mostly filled with metal atoms, resulting in metal compounds or mixed compounds with metallic regions. Taking a closer look on the structure of such partially filled skutterudites, another void between the octahedra and icosahedra is noticeable. While being empty in the majority of skutterudites, it can be occupied, e.g., by triatomic anions such as an allenylide or carbodiimide unit in Ba₁₂InC₁₈H₄, Ca₁₂InC_{13-x} and (Ba₆N_{5/6})₂[NbN₄][CN₂]₆.^[11–12] These compounds all crystallize in an anti-type of the skutterudite structure with barium or calcium as the base lattice and hydrides, carbides and nitrides, respectively, filling the octahedral voids. In the icosahedra, metallic indium atoms or niobium nitride tetrahedra are found. Although the nitridoborate anion is isoelectronic to [C₃]⁴⁻ and [CN₂]²⁻, has similar bond lengths and often forms related structures, no skutterudites containing [BN₂]³⁻ units are reported so far. Similarly, hydride skutterudites are also only little known, with metallic Ba₁₂InC₁₈H₄ being the solely representative. In general, skutterudite structures are widely dominated by metals or partially metallic compounds and variants without any metallic character are very sparsely explored yet.

We herein report on Ba₁₂[BN₂]_{6.67}H₄, the first barium nitridoborate hydride crystallizing as a non-metallic anti-skutterudite filled with [BN₂]³⁻ anions. The combination of single-crystal X-ray and neutron powder diffraction experiments together with MAS NMR and vibrational spectroscopy provides a comprehensive structural analysis and

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Table 1: Crystallographic data of refinements based on single-crystal X-ray and neutron powder diffraction data of $\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$ and $\text{Ba}_{12}[^{11}\text{BN}_2]_{6.67}\text{H}_4$, respectively.

Formula	$\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$	$\text{Ba}_{12}[^{11}\text{BN}_2]_{6.67}\text{H}_4$
space group	$Im\bar{3}$ (no. 204)	
lattice parameters/Å	$a = 11.065(3)$	$a = 11.0753(1)$
cell volume/Å ³	1354.7(11)	1358.54(2)
formula units/unit cell	2	
molecular weight/g mol ⁻¹	1910.98	1916.13
temperature/K	293(2)	298(1)
diffractometer	Bruker D8 Venture	WISH @ ISIS
radiation	Mo-K α ($\lambda = 0.71973$ Å)	neutrons, <i>time-of-flight</i>
refined parameters	22	45
goodness of fit	1.216	9.191
R indices	$R1[I \geq 2\sigma(I)] = 0.0230$ $\omega R2[I \geq 2\sigma(I)] = 0.0490$ $R1(\text{all data}) = 0.0248$ $\omega R2(\text{all data}) = 0.0494$	$R_p = 0.0211$ $R_{wp} = 0.0270$ $R_{exp} = 0.0029$ $R_{Bragg} = 0.0115$

allows to reliably determine light hydride ions next to heavy barium atoms. Moreover, $\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$ continues the series of reported calcium and strontium nitridoborate hydrides.

$\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$ was obtained in a solid-state ampoule reaction at 750 °C, which yielded block-like crystals up to 100 μm in length. The precursors Ba_3N , BaH_2 and h-BN were used in a 1:1:1 ratio, implying an excess of Ba_3N and BaH_2 . As Ba_3N readily reacts with the tantalum ampoule, the Ba surplus was necessary to achieve a high phase content of our compound. The synthesis temperature of 750 °C was chosen to compromise the low reactivity of BN at lower temperatures and the unwanted side reaction of Ba_3N at higher temperatures. With single-crystal X-ray diffraction (XRD) data, the structure was partially solved (Table 1). As hydrogen is a very weak X-ray scatterer, the crystallographic positions of only barium, nitrogen and boron could be determined reliably. Time-of-flight neutron powder diffraction data of the isotope modified compound $\text{Ba}_{12}[^{11}\text{BN}_2]_{6.67}\text{H}_4$ were acquired to corroborate the crystal structure (Table 1) with the hydride ions on a fully occupied 8c position. To avoid neutron absorption from ^{10}B , the synthesis was performed with ^{11}B -enriched reactants. The crystallographic data of both compounds can be found in Table S1 and S2.^[13] Rietveld refinement based on X-ray and neutron diffraction data of the bulk sample shows BaH_2 as a side phase (Figure S1 and S2 in the Supporting Information).

The crystal structure of $\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$ can be described as a stuffed anti-skutterudite with HBa_6 octahedra and Ba_{12} icosahedra, which are partially filled with disordered $[\text{BN}_2]^{3-}$ units (Figure 1a). In the voids between the icosahedra, additional nitridoborate units are found. The barium atoms are irregularly coordinated by two hydrogen, three boron and six nitrogen atoms (Figure 1b). The Ba–N and Ba–H distances are with 2.714(9)–3.100(7) and 2.930(1) Å in good agreement with comparable compounds reported in literature, which show bond lengths of 2.78–2.92 and 2.77–2.99 Å, respectively.^[14–16] The nitridoborate unit outside the icosahedra is coordinated in a bicapped trigonal prism, as

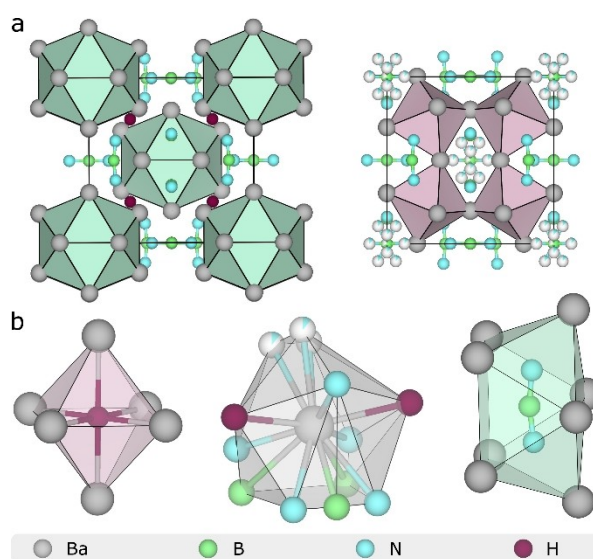


Figure 1. Depiction of the crystal structure of $\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$ (a) viewed along [100]. (b) HBa_6 octahedron, $\text{Ba}(\text{B}_3\text{N}_6\text{H}_2)$ polyhedron and $[\text{BN}_2]^{3-}$ unit coordinated by barium atoms in a bicapped trigonal prism. The Ba atoms and respective polyhedra are displayed in gray, B in green, N in blue and H in purple.

already found in several other nitridoborates (Figure 1b).^[17–18] They are slightly bent with a N–B–N angle of 169.9(2)° and a B–N bond length of 1.329(9) Å, agreeing with a typical B–N distance of 1.30–1.38 Å.^[19–20] $\text{Ba}_{12}\text{InC}_{18}\text{H}_4$ and $(\text{Ba}_6\text{N}_{5/6})_2[\text{NbN}_4][\text{CN}_2]_6$ are isotopic to $\text{Ba}_{12}[\text{BN}_2]_{6.67}\text{H}_4$ and feature the same anti-skutterudite structure with similar lattice parameters (11.145 and 11.258 Å).^[11–12] Rewriting their sum formulas as $\text{Ba}_{12}[\text{In}][\text{C}_3]_6\text{H}_4$, $\text{Ba}_{12}[\text{NbN}_4][\text{CN}_2]_6\text{N}_{1.67}$ and $\text{Ba}_{12}[\text{BN}_2]_{0.67}[\text{BN}_2]_6\text{H}_4$, the structural similarities become clearer. They all form similar ABA_6 octahedra ($A = \text{H}^-$ or N^{3-}) and Ba_{12} icosahedra with either indium atoms, NbN_4 tetrahedra or $[\text{BN}_2]^{3-}$ units in the center. The voids in-between are filled with allenylide ($[\text{C}_3]^{4-}$), carbodiimide ($[\text{CN}_2]^{2-}$) or nitridoborate ($[\text{BN}_2]^{3-}$) anions, respectively,

which are all isoelectronic and show similar bond lengths and angles.

Taking a closer look on the nitridoborate unit inside the Ba_{12} icosahedra (Figure 2), both X-ray and neutron data show large displacement ellipsoids for the nitrogen atom N2. When keeping this position unoccupied, the residual electron density forms a sphere around the boron atom in the center (Figure 2). The “B–e⁻” distance is 1.3 Å, which resembles a typical B–N bond length found in linear or slightly bent $[BN_2]^{3-}$ units.^[19] We therefore assume that inside this icosahedron, the nitridoborate unit is disordered. As low temperature powder XRD measurements (Figure S3) do not show any ordering or change of the structure, we anticipate a statistic, not a dynamic disorder.

Due to the rather large and symmetric coordination sphere formed by the twelve barium atoms, the $[BN_2]^{3-}$ unit cannot be fixated at one position and several different orientations are energetically equivalent. For the refinements, we constrained N2 on a 24g position, whereas the multiplicity renders 12 possible N2 positions and therefore 6 orientations of the $[BN_2]^{3-}$ unit inside the icosahedron. In the diffraction patterns are no additional reflections at small angles visible, which renders a possible ordered variant with a superstructure as unlikely. Moreover, the isotopic compound $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ forms the same Ba_{12} icosahedron

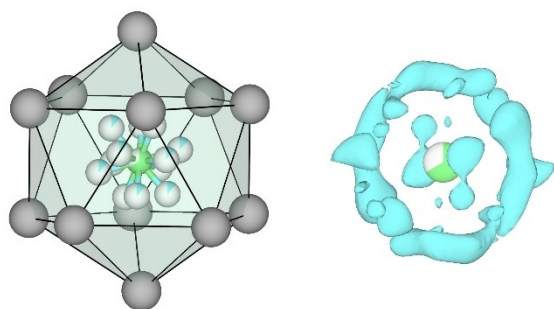


Figure 2. Disordered $[BN_2]^{3-}$ unit inside the Ba_{12} icosahedron (left) and residual electron density (blue) around the boron atom (green) in the center, when the nitrogen position is unoccupied. For this depiction, the crystal structure was refined in $P\bar{1}$ to reduce symmetry effects.

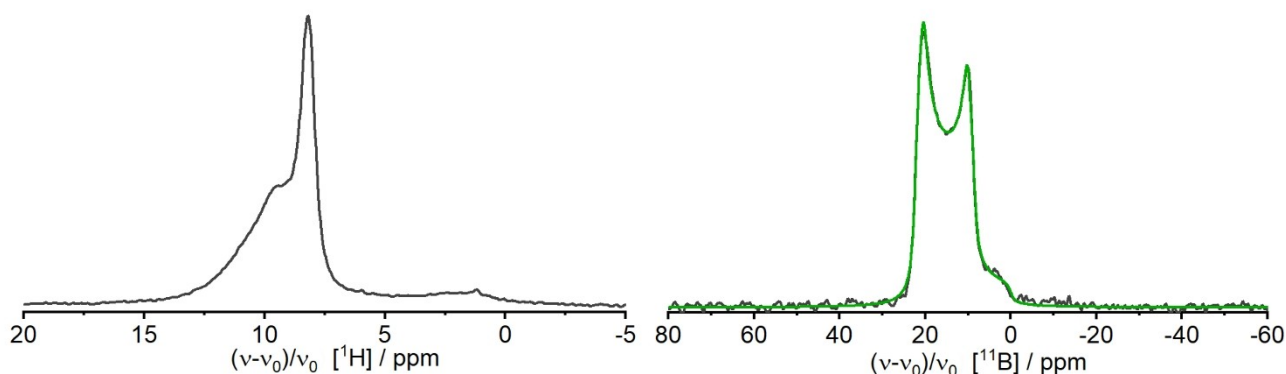


Figure 3. ¹H and ¹¹B MAS NMR spectra of $Ba_{12}[BN_2]_{6.67}H_4$ at 20 kHz spinning frequency, showing the experimental data in black and the fit of the ¹¹B signal in green.

with a disordered NbN_4 tetrahedron in the center.^[12] However, to achieve charge neutrality, the whole nitridoborate unit in our salt-like compound is only to two thirds occupied. This results in 67% occupancy for B2 and 11% occupancy for N2. Due to the disorder, these site occupation factors were constrained on the respective values for both XRD and neutron refinements.

For further validation of the proposed structure model, MAS NMR measurements were performed. The ¹H spectrum (Figure 3, left) shows a main signal at 8.2 ppm, which agrees with a single crystallographic site of hydrogen, and a broad shoulder which will be discussed below. A shift of the resonance line towards positive values of δ_{iso} is usually expected for protonic hydrogen, but it has been reported that such a chemical shift can also be observed for anionic species, depending on the metal-hydride distance.^[17,21–22] We also calculated the δ_{iso} with Density Functional Theory (DFT-PBE method, GIPAW method, see Supporting Information for full computational details). An ordered structural model was derived for the quantum chemical calculations (further description in the SI). The calculated ¹H isotropic chemical shift for this structure model is 7.6 ppm, very close to the experimental value. The broad shoulder at around 9.5 ppm belongs to the side phase BaH_2 and an unknown impurity causes the small signal at around 1.2 ppm. Due to the quadrupolar moment of ¹¹B ($I=3/2$) and the strong anisotropy of its electronic environment, the central transition resonance in the ¹¹B spectrum (Figure 3, right) shows a significant second-order broadening. In principle, the structure contains two boron sites with B1 sitting on a fully occupied Wyckoff 12e position and B2 on 2a with only 67% occupancy, anticipating two signals in the NMR spectrum with a 9:1 intensity ratio. However, since the immediate chemical environment of the two crystallographic sites of boron is almost identical, we expect the positions and shape of these two signals to be very similar, resulting in only one detectable resonance for both positions, which is indeed the case. The experimental spectrum was thus fitted with a single line shape, using the program DMFIT.^[23] This provided values for the isotropic chemical shift δ_{iso} and the quadrupolar coupling constant C_Q of

25.0 ppm and 3.21 MHz, respectively. As the $[\text{BN}_2]^{3-}$ units are with an N–B–N angle of 170° only slightly bent, the asymmetry parameter η_Q obtained by the fitting routine is close to zero (0.13). These results are in good agreement with the NMR parameters for other linear or slightly bent $[\text{BN}_2]^{3-}$ units.^[17,24] The isotropic ^{11}B shift calculated with the DFT-PBE method is 20.7 ppm, in reasonable agreement with the experimental δ_{iso} value.

IR and Raman spectra of the title compounds were measured and compared to the respective theoretical spectrum, obtained from quantum chemical calculations with DFT-PBE0 method. The FTIR spectrum (Figure 4, top) is in good agreement with the simulated one, showing the expected N–B–N and Ba–H vibrations. Due to the larger coordination sphere and lower multiplicity of the nitridoborate unit in the icosahedra ($[\text{N–B–N}]_i$), its vibrations appear at smaller wavenumbers and with less intensity compared to the ones of the nitridoborate unit outside the icosahedra ($[\text{N–B–N}]_o$). Their strong antisymmetrical stretching vibrations (ν_2) are visible at 1645 and 1550 cm^{-1} . The weaker symmetrical stretching (ν_1) and bending (ν_3) arise at 1025, 590 and 565 cm^{-1} , respectively. Between 790

and 660 cm^{-1} , the Ba–H vibrations are observable. Furthermore, the full FTIR spectrum (Figure S4) does not show any N–H or O–H vibrations, excluding the presence of such species.

The Raman spectrum (Figure 4, bottom) shows the intense symmetrical stretching vibrations (ν_1) at 995 and 1050 cm^{-1} and the N–B–N bending (ν_3) between 580 and 630 cm^{-1} . The Ba–H vibrations appear rather broad at around 520 cm^{-1} . All N–B–N vibrations are in the expected range for linear or slightly bent $[\text{BN}_2]^{3-}$ units.^[17,19,25] The assignment of the vibrations can be found in Tables S3 and S4. As allenylide and carbodiimide anions are also IR and Raman active, the spectra of the isotopic compounds $\text{Ba}_{12}\text{InC}_{18}\text{H}_4$ and $(\text{Ba}_6\text{N}_{5/6})_2[\text{NbN}_4][\text{CN}_2]_6$, show the same symmetrical and antisymmetrical stretching and bending vibrations.^[11–12] Due to their different bond lengths, the vibrational bands are shifted toward higher or lower energies, respectively.

To investigate the electronic structure of $\text{Ba}_{12}[\text{BN}_2]_{6,67}\text{H}_4$, quantum chemical calculations with DFT-PBE0 method were performed. To remove the disorder of the nitridoborate unit in the icosahedra, the symmetry was lowered to space group $P\bar{3}$ (no. 147). After optimizing the crystal structure of the ordered model, no imaginary frequencies were detected and the structure was determined to be relaxed at a local energetic minimum. The electronic band structure (Figure S5 in the Supporting Information) shows an indirect band gap of 5.1 eV, agreeing with the colorless appearance of the compound, classifying it as an insulator. The projected density of states shows nitrogen at the top of the valence band, similar to other known nitridoborate hydrides.^[17,26]

Summing up, we present the novel barium nitridoborate hydride $\text{Ba}_{12}[\text{BN}_2]_{6,67}\text{H}_4$ synthesized in a solid-state ampoule reaction. A combination of single-crystal X-ray and neutron powder diffraction data allowed elucidating the crystal structure. The title compound crystallizes as a non-metallic filled anti-skutterudite with HBa_6 octahedra and Ba_{12} icosahedra. Nitridoborate units are located in the icosahedra and the voids in-between, creating a three-dimensional network. MAS NMR measurements and vibrational spectroscopy helped to confirm the proposed structure model. The experimental results were supported by quantum chemical calculations, which also revealed the electronic structure. While most skutterudites are metallic species, $\text{Ba}_{12}[\text{BN}_2]_{6,67}\text{H}_4$ is one of very few compounds featuring non-metal atoms inside and outside the icosahedra. However, further substitution of the different motifs of such filled skutterudites opens up a large field of structurally intriguing compounds. To $[\text{BN}_2]^{3-}$ isoelectronic anions such as $[\text{C}_3]^{4-}$ and $[\text{CN}_2]^{2-}$ already formed similar structures, which can be further modified with other related building units such as $[\text{CBN}]^{4-}$ or $[\text{BO}_2]^-$. Moreover, $\text{Ba}_{12}[\text{BN}_2]_{6,67}\text{H}_4$ extends the series of nitridoborate hydrides, which have only been reported for calcium and strontium so far.

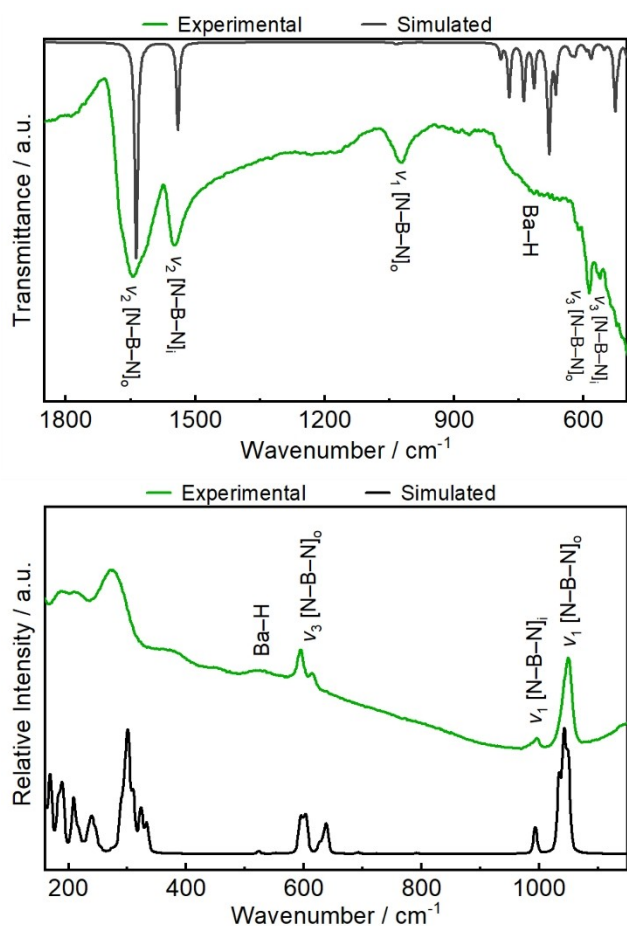


Figure 4. Experimental and simulated (obtained with DFT-PBE0 method) FTIR (top) and Raman (bottom) spectrum of $\text{Ba}_{12}[\text{BN}_2]_{6,67}\text{H}_4$, showing the Ba–H and N–B–N vibrations of the nitridoborate units inside ($[\text{N–B–N}]_i$) and outside the icosahedra ($[\text{N–B–N}]_o$).

Supporting Information

The authors have cited additional references within the Supporting Information.^[27–55]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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