Supporting Information

The First High-Pressure Chromium Oxonitridoborate CrB₄O₆N—an Unexpected Link to Nitridosilicate-Chemistry

Birgit Fuchs, Dirk Johrendt, Lkhamsuren Bayarjargal, and Hubert Huppertz*

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Experimental Procedures

High-pressure synthesis

The title compound CrB₄O₆N was obtained through a high-pressure/high-temperature experiment in a 1000 t downstroke press with a modified Walker-type module (both Max Voggenreiter GmbH, Germany) at 7 GPa and 1623 K.

The starting materials Cr(NO₃)₃·9H₂O and B₂O₃ (Strem Chemicals, Inc., Newburyport, USA, >99.9%) were ground together in the stoichiometric ratio 1:2 in an agate mortar at ambient conditions. Subsequently, the mixture was filled into an h-BN-crucible, closed with a lid of the same material (both Henze Boron Nitride Products AG, Germany) and put into an 18/11 assembly. Eight tungsten carbide cubes were used to achieve quasi-hydrostatic pressure on the sample. For a more detailed description on the experimental setup, the reader is referred to the literature.[1]

A pressure of 7 GPa was built up in 175 minutes, before the reactant mixture was heated up to 1623 K within ten minutes. This temperature was kept constant for the following ten minutes before the heating was switched off to quench the sample to room temperature. After the 525-minute decompression process, the red microcrystalline CrB₄O₆N was mechanically separated from the surrounding crucible and the dark green side phase CrBO₃.

Slightly bigger crystals of CrB₄O₆N could be synthesized if the sample was not quenched to room temperature but was slowly cooled down in 30 or 80 minutes instead. These attempts also led to a larger amount of unwanted green CrBO₃, more with increasing cooling time, which could not be completely separated from the desired CrB₄O₆N.

Syntheses at the aforementioned conditions using the starting materials Cr₂O₃ (E. Merck AG, Darmstadt, Germany, 99%), B₂O₃ and h-BN (Strem Chemicals, Inc., Newburyport, USA, >99.9%) in the stoichiometric ratio 1:3:2 also led to the title compound CrB₄O₆N. However, in these experiments, the yield was significantly less than in the experiments using chromium nitrate as a starting material and the main product was the green CrBO₃.
**Powder X-ray diffraction**

A Stoe Stadi P powder diffractometer (STOE & Cie GmbH, Darmstadt, Germany) equipped with a Mythen 1K microstrip detector (Dectris) was used to characterize a flat sample of CrB$_4$O$_6$N which was mechanically separated from the crucible and side phase as thoroughly as possible. The measurement was performed in transmission geometry with Ge(111)-monochromatized Mo-$K_{\alpha_1}$ radiation ($\lambda = 0.7093$ Å) and a 2$\theta$ range of 2-52° was analysed with a step size of 0.015°. Additionally, a Rietveld refinement employing the TOPAS 4.2 software$^2$ was performed in comparison with the values derived from the single-crystal structure analysis.

**Single-crystal X-ray analysis**

For the single-crystal structure determination, a Bruker D8 Quest Kappa diffractometer with monochromatized Mo-$K_{\alpha}$ radiation ($\lambda = 0.7107$ Å) was employed, equipped with an Incoatec microfocus X-ray tube and a Photon 100 CMOS detector. The structure solution and parameter refinement was performed with Direct Methods using SHELXS$^3$ and the refinement against $|F_o|^2$ was done with SHELXL, both implemented in the WINGX software.$^4$ All atoms were refined with anisotropic displacement parameters and the atomic coordinates standardized with the software STRUCTURE TIDY$^5$ as implemented in PLATON.$^6$

**Second-harmonic generation measurements**

Second-harmonic generation (SHG) measurements were performed on a CrB$_4$O$_6$N powder-sample. The fundamental pump wave was created with a Q-switched Nd:YAG laser (1064 nm, 5–6 ns, 2 kHz). The generated SHG signal was collected on ten different areas of the sample to check its homogeneity and averaged afterwards. A background correction of the measured intensities was carried out using signals collected between the laser pulses. $\alpha$-Al$_2$O$_3$ and quartz were used as reference materials.

A detailed description of the experimental setup for the powder SHG measurement is given by Bayarjargal et al.$^7$
**Vibrational Spectroscopy**

The FTIR-ATR (Attenuated Total Reflection) spectrum of a CrB₄O₆N powder sample with CrBO₃ as a side phase was measured in the spectral range of 400-4000 cm⁻¹ using a Bruker ALPHA Platinum-ATR spectrometer. It is equipped with a 2×2 mm diamond ATR-crystal and a DTGS detector. 320 scans of the sample were recorded, and afterwards corrected for atmospheric effects employing the OPUS 7.2 software.[⁸]

**DFT calculations**

First-principles electronic structure calculations were performed using the Vienna ab initio simulation package (VASP 5.4.4)[⁹] based on density functional theory (DFT) and plane wave basis sets. Projector-augmented waves (PAW)[¹⁰] were used and contributions of correlation and exchange were treated within the generalized gradient approximation (GGA) using the PBE,[¹¹] PBEsol,[¹²] and SCAN[¹³] functionals. The $k$-space was sampled with the Monkhorst-Pack[¹⁴] scheme using a 17×17×9 grid. Convergence criteria were $10^{-8}$ eV for the total energy and $10^{-4}$ eV/Å for the structural relaxations regarding ion positions, respectively, with a plane wave cut-off energy of 500 eV. Phonon dispersions were calculated from interatomic force constants of a 2×2×2 supercell using the PHONOPY[¹⁵] code. Electronic and phonon band dispersions were plotted with the SUMO package,[¹⁶] Infrared spectra were calculated from force constants via the dipole approach with the program IR.[¹⁷]
Results and Discussion

Crystal Structure

A close relationship of the six-membered rings in the \textit{ab}-plane of CrB$_4$O$_6$N could be found to the rings of BO$_4$ tetrahedra in other borate structures, for example in Cd$_2$B$_2$O$_4$,\textsuperscript{[18]} $\alpha$-FeB$_2$O$_4$,\textsuperscript{[19]} and MB$_6$O$_9$(OH)$_3$ ($M =$ Sc, In).\textsuperscript{[20]} In these compounds, the six-membered rings can be characterized through the orientation of the BO$_4$ tetrahedra in the layer – downwards D or upwards U. The aforementioned borates for example show the sequences UDUDUD and UUDDDD in the cadmium-compound, UUDDDD in the iron-compound, and DDDDDD and UUUUUU in the scandium- and indium-compound. Applying this concept to the six-membered rings of BO$_3$N tetrahedra in the presented chromium oxonitridoborate, the sequence UUUUUU is obtained, similar to half of the six-membered rings in MB$_6$O$_9$(OH)$_3$ ($M =$ Sc, In). Looking only at the anions, an alternating arrangement of three oxygen and three nitrogen atoms is observed in the six-membered rings with the nitrogen anions positioned at the corners of the rings. These layers in the \textit{ab}-plane are interconnected via the B$_2$O$_3$N tetrahedra to form a network in which all tetrahedra point towards the direction [00\text{-}1], leading to the formation of channels of six-membered rings alongside [100] (Figure S1). Here, there are only two nitrogen atoms involved in the direct formation of one six-membered ring, with one of the corners being occupied by oxygen.

The B–O distances in CrB$_4$O$_6$N lie in the narrow range of 1.465(2) to 1.478(3) Å. The average B–O distance of 1.471 Å fits to the average B–O bond length of 1.476(35) Å for BO$_4$ tetrahedra observed by Zobetz.\textsuperscript{[21]} The B–N bond lengths are 1.608(3) Å within the tetrahedra in the \textit{ab}-plane layers and 1.569(6) Å in the interconnecting tetrahedra. This is significantly longer than in the other known oxonitridoborates Sr$_3$(B$_3$O$_3$N)$_3$ (B–N: 1.438-1.491 Å),\textsuperscript{[22]} Eu$_5$(BO$_2.51$N$_{0.49}$)$_4$ (B–O/N: 1.360-1.411 Å for the mixed O/N positions)\textsuperscript{[23]}, and La$_3$(OBN)$_2$O$_2$ (B–N: 1.461 Å)\textsuperscript{[24]}. However, these three compounds only feature threefold coordinated boron atoms in trigonal planar entities. In Sr$_3$(B$_3$O$_3$N)$_3$, two neighboring boron atoms in the cyclic [B$_3$O$_3$N]$_3^-$ groups share one nitrogen atom, the oxygen atoms are on the outer corner of the three-membered rings. The europium oxonitridoborate consists of isolated trigonal planar units, where two of the nine crystallographically independent borate ions show a mixed oxygen/nitrogen occupancy of BO$_{1.38}$N$_{1.62}$ and BO$_{1.68}$N$_{1.32}$. Isolated BON$_2$ groups can be found in
La$_3$(OBN$_2$)O$_2$ in a staggered alignment. In contrast, our new chromium oxonitridoborate CrB$_4$O$_6$N features for the first time BO$_3$N tetrahedra, which also provide an explanation for the longer bonds, as a result of the increased coordination number of the boron atoms. A better comparison can be drawn to cubic BN, where every boron atom is tetrahedrally coordinated by nitrogen and vice versa. The B–N distance in c-BN is 1.565 Å,[25] which is around the bond lengths of 1.569 and 1.608 for the fourfold coordinated nitrogen atoms in CrB$_4$O$_6$N. This is also in good agreement with the B–N distance of 1.605 Å in the ammine borate Cd(NH$_3$)$_2$[B$_3$O$_5$(NH$_3$)$_2$].[26] The O–B–O and O–B–N angles range between 107.1(2) and 112.1(2)° with an average of 109.46°, which is in accordance with the expected ideal tetrahedral angle. Table S33 and S4 display all the bond lengths and angles.

Identifying the source of the nitrogen atoms in CrB$_4$O$_6$N posed a real challenge. From our experience, nitrate as in our educt Cr(NO$_3$)$_3$·9H$_2$O poses a good leaving group and does not participate in the reaction, when no platinum capsule is applied. In all successful experiments that led to the red CrB$_4$O$_6$N, the crucible material h-BN was always in contact to the educt mixture, leading to the conclusion that it plays a vital part in the formation of the title compound by providing the nitrogen atoms for the reaction. Moreover, the oxonitridoborate CrB$_4$O$_6$N was found almost exclusively on the side of the product mixture (the middle being mostly green CrBO$_3$), right next to the crucible material. Additionally, the mechanical separation of CrB$_4$O$_6$N from the crucible material was challenging, giving further proof of the essential role of h-BN for the formation of CrB$_4$O$_6$N.
Table S1: Atomic coordinates and equivalent isotropic displacement parameters $U_{eq}$ (Å$^2$) of CrB$_4$O$_6$N (standard deviations in parentheses).

| Atom | Wyckoff position | x    | y    | z    | $U_{eq}$ |
|------|------------------|------|------|------|----------|
| Cr1  | 2b               | ⅓   | ⅔   | 0.0720(5) | 0.0017(2) |
| B1   | 6c               | 0.8313(3) | 0.1687(3) | 0.2599(5) | 0.0031(3) |
| B2   | 2a               | 0   | 0   | 0   | 0.0025(7) |
| O1   | 6c               | 0.5113(2) | 0.4887(2) | 0.2095(5) | 0.0029(3) |
| O2   | 6c               | 0.8456(2) | 0.1544(2) | 0.4361(5) | 0.0038(3) |
| N1   | 2a               | 0   | 0   | 0.1879(7) | 0.0023(5) |

Table S2: Anisotropic displacement parameters $U_{ij}$ (Å$^2$) of CrB$_4$O$_6$N (standard deviations in parentheses).

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| Cr1  | 0.0017(2) | 0.0017(2) | 0.0014(2) | 0.0000(4) | 0.0000(4) | 0.00084(6) |
| B1   | 0.0035(6) | 0.0035(6) | 0.0024(7) | 0.0000(4) | 0.0000(4) | 0.0019(7) |
| B2   | 0.0018(9) | 0.0018(9) | 0.004(2)  | 0.0000(4) | 0.0000(4) | 0.0009(5) |
| O1   | 0.0018(4) | 0.0018(4) | 0.0044(5) | 0.0007(3) | –0.0007(3) | 0.0005(4) |
| O2   | 0.0061(5) | 0.0061(5) | 0.0016(6) | –0.0001(3) | 0.0001(3) | 0.0049(5) |
| N1   | 0.0030(7) | 0.0030(8) | 0.0006(2) | 0.0000(4) | 0.0000(4) | 0.0015(4) |

Table S3: Interatomic B–O/B–N and Cr–O distances /Å for CrB$_4$O$_6$N (standard deviations in parentheses).

|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| B1   | –O1  | 1.477(2) | 2×   | B2   | –O2  | 1.465(2) | 3×   | Cr1  | –O2  | 1.947(2) | 3×   |
| –O2  | 1.478(3) |      |      | –N1  | 1.569(6) |      |      | –O1  | 1.948(2) | 3×   |
| –N1  | 1.608(3) |      |      |      |      |      |      |      |      |      |      |
| $\bar{d}$ | 1.51 |      |      | $\bar{d}$ | 1.491 |      | $\bar{d}$ | 1.9475 |      |      |      |

Table S4: Bond angles /deg for CrB$_4$O$_6$N (standard deviations in parentheses).

|      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| O2–B1–N1 | 107.0(2) |      | O2–B2–O2 | 107.5(2) | 3×   | O1–Cr1–O1 | 88.8(1) | 3×   |
| O1–B1–O1 | 107.2(2) |      | O2–B2–N1 | 111.4(2) | 3×   | O2–Cr1–O2 | 89.5(1) | 3×   |
| O2–B1–O1 | 109.2(2) | 2×   | O1–B1–N1 | 112.1(2) | 2×   | O1–Cr1–O2 | 90.9(1) | 6×   |
| O1–B1–N1 | 112.1(2) | 2×   |      |      |      |      |      |      |      |
| $\emptyset$ | 109.47 | $\emptyset$ | 109.45 |      |      |      |      |      |      |
|      |      |      |      |      |      |      |
| O1–Cr1–O2 | 179.5(1) | 3×   |      |      |      |      |      |      |      |
Table S5: Comparison of the standardized atomic coordinates of CrB₄O₆N and BaYbSi₄N₇ (standard deviations in parentheses).

| Wyckoff position | Atom | x     | y     | z         | Wyckoff position | Atom | x     | y     | z         |
|------------------|------|-------|-------|-----------|------------------|------|-------|-------|-----------|
| 2b               | Cr1  | ⅓ ⅔  | 0.0720(5) |           | Yb1             | ⅓ ⅔  | 0.0776(1) |           |
| 2b               | Ba1  | ⅓ ⅔  | 0.4512(1) |           |                 |      |       |       |           |
| 6c               | B1   | 0.8313(3) | 0.1687(3) | 0.2599(5) | Si1             | 0.8257(1) | 0.1743(2) | 0.2667(2) |
| 6c               | Si2  | 0     | 0     | 0.0000(2) |                 |      |       |       |           |
| 2a               | B2   | 0     | 0     | 0         | N1              | 0.5113(5) | 0.4887(3) | 0.2144(3) |
| 6c               | Si2  | 0     | 0     | 0         | N2              | 0.8466(3) | 0.1534(5) | 0.4408(3) |
| 2a               | N1   | 0     | 0     | 0.1879(7) | N3              | 0     | 0     | 0.1922(4) |

Figure S1: CrB₄O₆N is built up of three- and six-membered rings alongside the a-axis (tetrahedra with the central atom B1 in dark blue and with the central atom B2 in light blue).
Second-harmonic generation measurements

**Table S6:** SHG intensities of a CrB₄O₆N powder-sample compared to two reference materials.

| Sample (Size)          | SHG intensity /mV | \( I_{\text{SHG}}/I_{\text{quartz}} \times 100\% \) |
|------------------------|-------------------|-----------------------------------------------|
| Quartz (5-10 micrometer) | 50.2 (7.8)        | 100.0                                         |
| \( \alpha \)-Al₂O₃ (9 micrometer) | 0.2 (1.0)         | 0.4                                           |
| CrB₄O₆N (<5 micrometer) | 41.2 (20.1)       | 82.07                                         |

**Vibrational Spectroscopy**

In general, stretching vibrations of tetrahedral BO₄ groups can be found in the region of 800–1200 cm⁻¹.²⁷ This also seems to be the case for the BO₃N entities in CrB₄O₆N since the strongest absorption bands can be found in the same area and is also confirmed by theoretical calculations (see the red spectrum in Figure 5). In contrast to cubic boracites, that feature a fourfold coordinated oxygen atom similar to the fourfold coordinated nitrogen atom in CrB₄O₆N, the strongest band occurs at around 1000 cm⁻¹. In the boracites, the stretching vibration is shifted to higher wavenumbers due to the strong distortion of the BO₄ tetrahedra around the fourfold coordinated oxygen atom.²⁸

A drawing of the strongest A1-Mode in CrB₄O₆N, the B–N stretching vibration, can also be seen in the insert in Figure S2, the spectrum up to 3600 cm⁻¹ is shown in Figure S3. Signals at ~1200 cm⁻¹ can be assigned to the trigonal BO₃-groups of the by-product CrBO₃ (see the blue spectrum in Figure 5). Signals below ~800 cm⁻¹ can be assigned to O–B–O bending and Cr–O vibrations.
Figure S2: FTIR-ATR spectrum of a powder-sample containing CrB$_4$O$_6$N and CrBO$_3$. The insert shows a visual representation of the strongest A1-Mode (B in red, O in blue, N in green).

Figure S3: FTIR-ATR spectrum of a powder-sample containing CrB$_4$O$_6$N and CrBO$_3$ in the spectral range of 400–3600 cm$^{-1}$. 
DFT calculations

Table S7: Results of the structure relaxations with different functionals.

|       | Experiment | PBE    | PBEsol | SCAN     |
|-------|------------|--------|--------|----------|
| a, Å  | 5.1036(1)  | 5.1377 [+0.7%] | 5.1003 [-0.06%] | 5.0923 [-0.2%] |
| c, Å  | 8.3519(3)  | 8.4063 [+0.7%] | 8.3471 [-0.06%] | 8.3334 [-0.06%] |
| V, Å³ | 188.40(1)  | 192.16 [+2.0%] | 188.04 [-0.2%]  | 187.15 [-0.7%]  |
| B₀, GPa | -         | 256.6   | 271.9   | 279.8     |
| E, eV | -          | 1.96 i, 2.00 d | 1.97 i, 2.01 d | 1.65 i, 1.69 d |

Table S8: Magnetism calculated with different functionals.

|       | PBE    | PBEsol | SCAN |
|-------|--------|--------|------|
| ΔE (kJ/mol) | μ(μB) | ΔE (kJ/mol) | μ(μB) | ΔE (kJ/mol) | μ(μB) |
| NM    | +168.2 | 0      | +155.7 | 0      | +159.3 | 0      |
| FM    | +0.15  | 2.82   | +0.26  | 2.80   | +0.01  | 2.91   |
| AFM   | 0      | 2.81   | 0      | 2.80   | 0      | 2.91   |

Figure S4: Phonon dispersion and phonon-DOS of CrB₄O₆N (PBEsol).
References

[1] a) D. Walker, M. A. Carpenter, C. M. Hitch, *Am. Mineral.* **1990**, *75*, 1020-1028; b) D. Walker, *Am. Mineral.* **1991**, *76*, 1092-1100; c) H. Huppertz, *Z. Kristallogr.* **2004**, *219*, 330-338.

[2] *Bruker TOPAS*, v4.2, Bruker AXS Inc., Madison, WI, USA, *2009*.

[3] a) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122; b) G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.

[4] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849-854.

[5] L. M. Gelato, E. Parthé, *J. Appl. Crystallogr.* **1987**, *20*, 139-143.

[6] A. L. Spek, *Acta Crystallogr.* **2009**, *D65*, 148-155.

[7] L. Bayarjargal, C. J. Fruhner, N. Schrodt, B. Winkler, *Phys. Earth Planet. Inter.* **2018**, *281*, 31-45.

[8] *Bruker OPUS*, v7.2, Bruker, Billerica, MA, USA, *2012*.

[9] a) G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251-14269; b) G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15-50.

[10] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953-17979.

[11] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

[12] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, K. Burke, *Phys. Rev. Lett.* **2008**, *100*, 136406.

[13] J. Sun, A. Ruzsinszky, J. P. Perdew, *Phys. Rev. Lett.* **2015**, *115*, 036402.

[14] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188-5192.

[15] A. Togo, I. Tanaka, *Scripta Materialia* **2015**, *108*, 1-5.

[16] A. M. Ganose, A. J. Jackson, D. O. Scanlon, *Journal of Open Source Software* **2018**, *3*, 717.

[17] a) J. George, R. Dronskowski, *JaGeo/IR: IR (Version 1.0.4).* Zenodo, *2019*, [http://doi.org/10.5281/zenodo.3241592](http://doi.org/10.5281/zenodo.3241592); b) A. L. Görne, J. George, J. Van Leusen, R. Dronskowski, *Inorganics* **2017**, *5*, 10.

[18] J. S. Knyrim, H. Emme, M. Doblinger, O. Oeckler, M. Weil, H. Huppertz, *Chem. – Eur. J.* **2008**, *14*, 6149-6154.

[19] J. S. Knyrim, H. Huppertz, *J. Solid State Chem.* **2008**, *181*, 2092-2098.

[20] a) B. Fuchs, H. Huppertz, *Z. Naturforsch.* **2020**, *75b*, 597-603; b) D. Vitzthum, L. Bayarjargal, B. Winkler, H. Huppertz, *Inorg. Chem.* **2018**, *57*, 5554-5559.

[21] E. Zobetz, *Z. Kristallogr.* **1990**, *191*, 45-57.

[22] S. Schmid, W. Schnick, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1192-1195.

[23] H. A. Höppe, K. Kazmierczak, C. Grumbt, L. Schindler, I. Schellenberg, R. Pöttgen, *Eur. J. Inorg. Chem.* **2013**, *2013*, 5443-5449.

[24] T. Dierkes, M. Ströbele, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2014**, *640*, 1275-1279.

[25] R. H. Wentorf Jr., *J. Chem. Phys.* **1957**, *26*, 956-956.

[26] G. Sohr, N. Ciaghi, M. Schauperl, K. Wurst, K. R. Liedl, H. Huppertz, *Angew. Chem. Int. Ed.* **2015**, *54*, 6360-6363.

[27] R. Kaindl, G. Sohr, H. Huppertz, *Spectrochim. Acta A* **2013**, *116*, 408-417.

[28] S. C. Neumair, J. S. Knyrim, O. Oeckler, R. Kaindl, H. Huppertz, *Z. Naturforsch.* **2011**, *66b*, 107-114.