

High-Pressure Chemistry

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The First High-Pressure Chromium Oxonitridoborate $\text{CrB}_4\text{O}_6\text{N}$ —an Unexpected Link to Nitridosilicate Chemistry

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

Abstract: $\text{CrB}_4\text{O}_6\text{N}$ crystallizes in the non-centrosymmetric space group $P6_3mc$ (no. 186) with the lattice parameters $a = 5.1036(1)$, $c = 8.3519(3)$ Å, and a volume of $188.40(1)$ Å³. It was synthesized in a high-pressure/high-temperature experiment at 7 GPa and 1673 K and represents the first high-pressure oxonitridoborate. It is built up of starlike-shaped entities of four BO_3N tetrahedra, connected via one common nitrogen atom that resembles the fourfold-coordinated nitrogen atoms in the homeotypic nitridosilicates MYbSi_4N_7 ($M = \text{Sr, Ba}$). Building up a network with channels that contain the Cr^{3+} ions, $\text{CrB}_4\text{O}_6\text{N}$ contains for the first time a tetrahedral building unit in contrast to trigonal planar $\text{B}(\text{O}/\text{N})_3$ entities in all other known oxonitridoborates. The structural relations as well as the results of spectroscopic measurements and calculations on the chromium oxonitridoborate are discussed.

Introduction

Through the application of high-pressure conditions during the syntheses of solid state materials, it is possible to accomplish new crystal structures and structural motifs that are often unknown and in most cases not accessible under ambient pressure conditions. Over the past two decades, a main aspect of our research has been the high-pressure synthesis of new borate materials. Astounding results in this field could be discovered, for example, the structural motive of edge-sharing BO_4 tetrahedra in centrosymmetric $\text{Dy}_4\text{B}_6\text{O}_{15}$ ^[1] and non-centrosymmetric $\text{La}_3\text{B}_6\text{O}_{13}(\text{OH})$,^[2] the discovery of an synthetic access to the substance class of

ammine borates ($\text{Cd}(\text{NH}_3)_2[\text{B}_3\text{O}_5(\text{NH}_3)]_2$)^[3] or unexpected Mo_4 -clusters in the borate framework of $\text{Mo}_2\text{B}_4\text{O}_9$.^[4]

Especially in the field of transition metal borates, a broad variety of new structures could be achieved. An excellent review of the newest developments with a special view on optical properties can be found in ref. [5]. Concerning the transition metal borates of the fourth period of the periodic table, there is only one element, from which no high-pressure borate is known up to now: chromium. There exist two ambient pressure chromium borates, the orthoborate CrBO_3 ^[6] with calcite type structure and Cr_3BO_6 ^[7] with norbergite structure. Herein, we report the synthesis of the new chromium oxonitridoborate $\text{CrB}_4\text{O}_6\text{N}$, which represents only the fourth existing oxonitridoborate and the first one synthesized under high pressure. The other known oxonitridoborates to date are $\text{Sr}_3(\text{B}_3\text{O}_3\text{N}_3)$,^[8] $\text{Eu}_5(\text{BO}_{2.51}\text{N}_{0.49})_4$,^[9] and $\text{La}_3(\text{OBN}_2)_2$,^[10] containing $[\text{B}_3\text{O}_3\text{N}_3]^{6-}$ rings, mixed O/N sites, and BON_2 units, respectively. All of these compounds require relatively complex starting materials such as imides and amides, and reaction times of several days. Additionally, an intricate setup is necessary, to ensure the exclusion of water or air during the syntheses of these oxonitridoborates. In contrast, the here presented chromium oxonitridoborate $\text{CrB}_4\text{O}_6\text{N}$ can be obtained by using simple starting materials, such as nitrates, nitrides, and oxides like $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, h-BN, and B_2O_3 that can be handled under ambient conditions. In combination with a high-pressure/high-temperature approach, this synthetic strategy enables the introduction of nitrogen into a boron oxygen network.

In the past, the application of extreme synthetic conditions on borate systems already showed that new compositions homeotypic to silicate minerals could be enabled through the application of extreme high-pressure/high-temperature conditions in the sense of the boron/silicon diagonal relationship. E.g., the compounds $\text{M}_3\text{B}_5\text{O}_{12}$ ($M = \text{Sc, In, Er, Lu}$) crystallize in the structure type of the beryllosilicate semenovite,^[11] the compounds $\beta\text{-MB}_2\text{O}_5$ ($M = \text{Zr, Hf}$) exhibit structures analogous to the gadolinite-group,^[12] and $\text{Sc}_{1.67}\text{B}_3\text{O}_7$ represents the first ternary melilite-type compound.^[13] For the new oxonitridoborate $\text{CrB}_4\text{O}_6\text{N}$, we found that it is homeotypic to the ambient pressure nitridosilicates MYbSi_4N_7 ($M = \text{Ba, Sr, Eu}$),^[14] which crystallize in the $\text{NaBe}_4\text{SbO}_7$ (swendenborgite)^[15] structure type. In the literature, these nitridosilicates constitute the first representatives of a central fourfold coordinated nitrogen atom N^{4-} , bridging four silicon atoms. The Si-N-network forms six-membered rings along [100] in which the respective alkaline earth cations ($\text{Sr}^{2+}/\text{Ba}^{2+}$) and Yb^{3+} cations are located. In contrast to MYbSi_4N_7 ($M = \text{Sr, Ba, Eu}$), the new oxonitridoborate only features chromium

[*] B. Fuchs, Prof. Dr. H. Huppertz
Institut für Allgemeine, Anorganische und Theoretische Chemie,
Universität Innsbruck
Innrain 80–82, 6020 Innsbruck (Austria)
E-mail: Hubert.Huppertz@uibk.ac.at

Prof. Dr. D. Johrendt
Department Chemie, Ludwig-Maximilians-Universität München
Butenandtstr. 5–13 (Haus D), 81377 München (Germany)

Dr. L. Bayarjargal
Institut für Geowissenschaften, Goethe-Universität Frankfurt am
Main
Altenhöferallee 1, 60438 Frankfurt am Main (Germany)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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cations that occupy the ytterbium position, thus leaving the position of $\text{Sr}^{2+}/\text{Ba}^{2+}$ vacant. Later on, additional nitridosilicate representatives of this structure type were found.^[16] A fourfold connected carbon atom $\text{C}^{[4]}$, similar to the central nitrogen atom of the starlike-shaped entities, can be found in the isostructural phases $\text{RE}_2\text{Si}_4\text{N}_6\text{C}$ ($\text{RE} = \text{Y}, \text{La}, \text{Tb}, \text{Ho}$)^[17] and $\text{YScSi}_4\text{N}_6\text{C}$.^[18] Examples of oxonitridosilicates of this structure type could not be found up to now. Porob et al.^[19] claimed the existence of both oxygen and nitrogen in $\text{SrScSi}_4(\text{O},\text{N})_7$ due to the blue shift of the Eu^{2+} activated material in comparison to the isostructural nitride phosphor. However, the successful insertion of oxygen into this framework is possible with simultaneous substitution of silicon by aluminum, as presented for example in the sialons (oxonitridoalumosilicates) $\text{MLnSi}_{4-x}\text{Al}_x\text{O}_x\text{N}_{1-x}$ ($M = \text{Sr}, \text{Ba}, \text{Eu}; \text{Ln} = \text{Ho}-\text{Yb}$)^[20] and $\text{SrYSi}_{4-x}\text{Al}_x\text{O}_x\text{N}_{1-x}$.^[21] Within these compounds, the Al atoms are distributed statistically on the Si sites, while O atoms are only found on the twofold bridging sites, not on the fourfold connected position. In the following work, we will present a detailed structural description of the new chromium oxonitridoborate, also in comparison to the aforementioned nitridosilicates, and the results of vibrational spectroscopy, second-harmonic generation measurements as well as band structure calculations.

Results and Discussion

The title compound $\text{CrB}_4\text{O}_6\text{N}$ crystallizes in the hexagonal space group $P6_3mc$ (no. 186) with the lattice parameters $a = 5.1036(1)$ and $c = 8.3519(3)$ Å with two formula units per cell ($Z = 2$). All relevant data on the structure refinement is presented in Table 1, the positional and the displacement parameters can be seen in Tables S1 and S2, respectively.^[22]

The structure is built up of starlike-shaped entities of four BO_3N tetrahedra that are connected via the common nitrogen atom N1 (Figure 1a). In detail, the nitrogen atom links three tetrahedra with the central boron atom B1 and one tetrahedron with the central boron atom B2 (dark and light blue tetrahedra in Figures 1 to 4, respectively). Through the connection of these $[\text{N}(\text{BO}_3)_4]$ building blocks, the $\text{B1O}_3\text{N}$ tetrahedra form layers of three- and six-membered rings (Figure 1b,c) in the ab -plane.

The chromium cations Cr^{3+} are located in these six-membered rings being octahedrally coordinated by oxygen atoms (Figure 2). The Cr-O distances are 1.948(2) and 1.947(2) Å to the oxygen atoms O1 and O2, respectively, with an average value of 1.9475 Å. This is in good agreement with the other two known chromium borates CrBO_3 (Cr-O: 1.996 Å)^[6] and Cr_3BO_6 (Cr-O: 1.867–2.083 Å),^[7] where the chromium cations are also coordinated by six oxygen atoms. The mean octahedral angles of 90.0° and 179.5° are in agreement with the expected ideal values.

The B–N bond lengths are significantly longer (1.608(3) Å and 1.570(6) Å) than in the other known oxonitridoborates,^[8–10] but $\text{CrB}_4\text{O}_6\text{N}$ also has an increased coordination number of the boron atoms in comparison to these compounds. A better comparison of these BO_3N tetrahedra can be drawn to B–N distances for also tetrahedrally coordinated

Table 1: Crystal data and structure refinement of $\text{CrB}_4\text{O}_6\text{N}$.

Empirical formula	$\text{CrB}_4\text{O}_6\text{N}$
Molar mass, g mol^{-1}	205.25
Crystal system	hexagonal
Space group	$P6_3mc$ (no. 186)
Single-crystal data	
T , K	276(2)
Radiation	Mo- K_{α} ($\lambda = 0.7107$ Å)
a , Å	5.1036(1)
c , Å	8.3519(3)
V , Å ³	188.40(1)
Z	2
Calculated density, g cm^{-3}	3.618
Absorption coeff., mm^{-1}	2.995
$F(000)$, e	198
Crystal size, mm^3	0.030 × 0.030 × 0.020
θ range, deg	4.61–39.32
Index ranges	$-9 \leq h \leq 9, -9 \leq k \leq 9, -14 \leq l \leq 14$
Reflections collected	16 397
Independent reflections	470
$R_{\text{int}}/R_{\sigma}$	0.0502/ 0.0142
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	470/0/28
Goodness-of-fit on F^2	1.286
Final $R1/\omega R2$ indices [$I \geq 2\sigma(I)$]	0.0168/ 0.0479
Final $R1/\omega R2$ indices (all data)	0.0192/ 0.0488
Largest diff. peak/ hole, $e\text{Å}^{-3}$	0.37/ -0.61
Flack parameter	0.003(11)
Powder-diffraction data	
Radiation; wavelength λ , Å	Mo- $K_{\alpha 1}$; 0.7093
a , Å	5.1068(2)
c , Å	8.3575(5)
V , Å ³	188.76(2)
2θ range, deg	2.0–42.0
2θ step width, deg	0.015
R_{exp} , %	3.23
R_{wp} , %	7.93
R_p , %	4.83
Goodness-of-fit	2.46

boron in cubic BN (1.565 Å),^[23] and the ammine borate $\text{Cd}(\text{NH}_3)_2[\text{B}_3\text{O}_5(\text{NH}_3)]_2$ (1.605 Å).^[3]

To further verify the crystal structure solution and the oxidation states, BL/BS (bond-length/bond-strength; ΣV)^[24] and CHARDI (Charge distribution; ΣQ)^[25] calculations have been performed. The results are listed in Table 2 and correspond well with the expected values of +3 for chromium and boron, -2 for oxygen, and -3 for nitrogen. Especially the results of the CHARDI concept fit very well, with a deviation for the cations of only 0.2% and 0.5% for the anions. Furthermore, MAPLE calculations (Madelung Part of Lattice Energy)^[26] were performed on $\text{CrB}_4\text{O}_6\text{N}$, and compared to the result from the theoretical values of the binary starting materials CrN ^[27] and the high-pressure modification $\text{B}_2\text{O}_3\text{-II}$.^[28]

Due to the additive potential of MAPLE values, a hypothetical value for $\text{CrB}_4\text{O}_6\text{N}$ can be calculated. As a result, a lattice energy of 54701 kJ mol^{-1} was obtained for the product in comparison to the calculated value of 54362 kJ mol^{-1} starting from the binary components (CrN

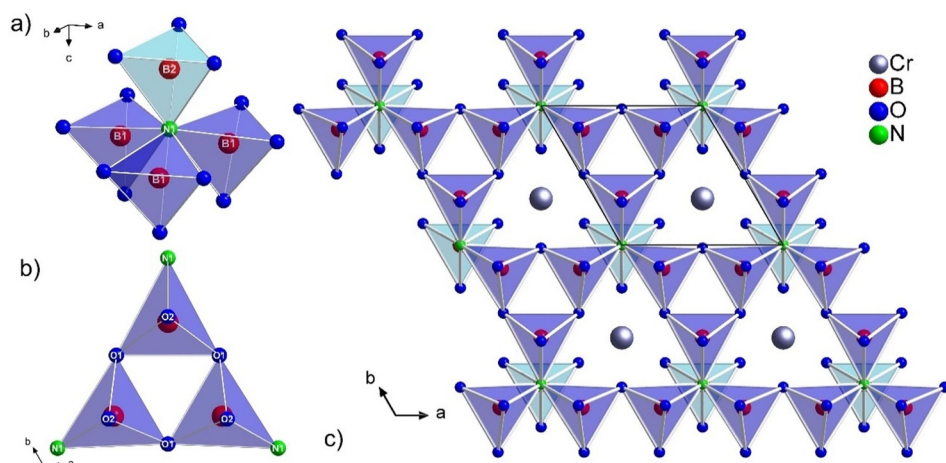


Figure 1. a) Fourfold connection of the N1 atoms. b) Three-membered ring of BO₃N tetrahedra, all pointing towards the direction [001]. c) The anionic oxonitridoborate structure of CrB₄O₆N consists of layers of three- and six-membered rings, that are formed by three [N(BO₃)₄] building blocks each. One layer is pictured here onto the *ab*-plane.

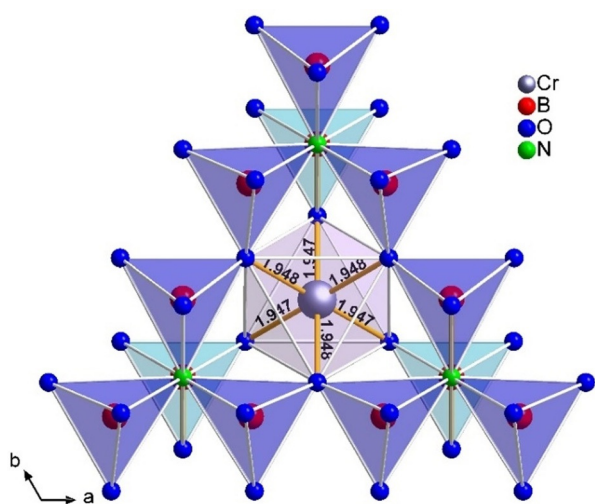


Figure 2. Octahedrally coordinated chromium cation Cr³⁺ in the middle of a six-membered ring of BO₃N tetrahedra. Cr-O distances in Å.

Table 2: Bond valence sums and charge distribution according to the bond-length/bond-strength (ΣV) as well as the CHARDI (ΣQ) concept, respectively.

	Cr1	B1	B2	O1	O2	N1
ΣV	+3.28	+2.94	+3.09	-2.06	-2.08	-2.83
ΣQ	+3.00	+3.00	+3.01	-2.01	-1.99	-3.00

(10486 kJ mol⁻¹) + 2 B₂O₃-II (2 × 21938 kJ mol⁻¹); deviation: 0.62 %).

The elucidation of the source of the nitrogen atoms in CrB₄O₆N was a real challenge. The first option is the chromium nitrate used as starting material, the second option is the crucible material h-BN. Up to this point, all contributions in the literature and our own work shows that the application of nitrates in combination with boron exclusively leads to borate nitrates in which isolated NO₃

groups exist next to a varying borate framework.^[29] Most of these compounds were synthesized in autoclaves under slightly increased pressure conditions. In this context, a new borate nitrate was recently synthesized at a reasonably low pressure of 3 GPa.^[30] Thus, from our experimental evidence the reaction of nitrates and borates results exclusively in borate nitrates. Further experiments showed that it was not possible to reproduce CrB₄O₆N by only using Cr(NO₃)₃·9H₂O and B₂O₃ in a platinum capsule, where no contact to h-BN was given. The initial experiment and seven reproduction experiments were only successful by

using Cr(NO₃)₃·9H₂O and B₂O₃ as starting materials inside a crucible made of h-BN. This leads to the conclusion that the contact to the crucible material h-BN is crucial for the formation of the title compound CrB₄O₆N, so the nitrogen atoms definitely stem from the h-BN. Self-evidently, experiments were performed in which h-BN was added to the educt mixture inside of a platinum capsule. Interestingly, these experiments led to a completely different product mixture consisting of CrO₂ and a yet unidentified new byproduct.

Surprisingly, the structure of the new chromium oxonitridoborate CrB₄O₆N is closely related to the nitridosilicates MYbSi₄N₇ (M = Sr, Ba, Eu),^[14] which were synthesized at ambient pressure in a HF-furnace. These nitridosilicates are built up of [N(SiN₃)₄] building blocks, similar to the [N(BO₃)₄] entities in CrB₄O₆N and were the first compounds to feature nitrogen atoms coordinated to four silicon atoms. The linkage of these building blocks leads to a network of three- and six-membered rings where, in comparison to CrB₄O₆N, the silicon and nitrogen atoms occupy the positions of the boron and oxygen atoms, respectively. The ytterbium cations are octahedrally coordinated by nitrogen and located in the six-membered rings along [001] on the same positions as the chromium cations. As there is no analog to the alkaline earth cations Sr²⁺/Ba²⁺, these positions remain vacant in the oxonitridoborate (see Figure 3 and Table S5 for the comparison with BaYbSi₄N₇). The structure type of the nitridosilicates, NaBe₄SbO₇ (swendenborgite),^[15] also occurs as other substitution variants like BaLuAlZn₃O₇,^[31] where the silicon position is statistically occupied by Al³⁺ and Zn²⁺. In all these compounds, there are two metal cations incorporated into the anionic network. In contrast, there is only one species (Cr³⁺) inside the six-membered rings of the presented CrB₄O₆N, leaving the other 2*b* site vacant for the first time in this structure family.

Figure 4 shows the Rietveld refinement of a CrB₄O₆N sample. The experimental powder diffraction data is in good agreement with the values derived from the single-crystal structure refinement (see Table 1). Additional reflections

experimental parameters with deviations as small as 0.2% (Table S7). Calculated band gaps are ≈ 2 eV using PBE and ≈ 1.65 eV using SCAN functionals. Magnetism reduces the total energy significantly by about 160 kJ mol^{-1} , while the difference between the ferro- and antiferromagnetic magnetic models is very small. The magnetic moments integrated in the Wigner-Seitz sphere are $2.8\text{--}2.9 \mu_{\text{B}}/\text{Cr}$ in agreement with the expected $3 \mu_{\text{B}}$ for Cr^{3+} (Table S8). Figure 6 shows the electronic band structure and the atom-projected density-of-states. Direct and indirect band gaps are almost identical (Table S7) and occur between the occupied and unoccupied parts of the Cr 3d-bands (Figure 6) with small contributions of oxygen and boron states. The phonon dispersions (Figure S4) reveal neither anomalies nor any imaginary modes, which confirms the mechanical stability of $\text{CrB}_4\text{O}_6\text{N}$.

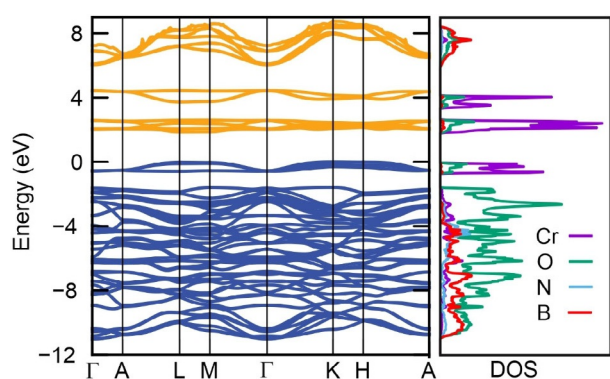


Figure 6. Electronic band structure of $\text{CrB}_4\text{O}_6\text{N}$ with atom-projected DOS.

Conclusion

$\text{CrB}_4\text{O}_6\text{N}$ represents the first high-pressure oxonitridoborate to date. Synthesized at 7 GPa and 1623 K, it comprises building blocks of four BO_3N tetrahedra that share one common corner, leading to a fourfold coordinated nitrogen atom. This structural unit is found in this class of compounds for the first time, the other three known oxonitridoborates only feature trigonal planar BON_2 groups that occur as isolated units or as $\text{B}_3\text{O}_3\text{N}_3$ rings. Additionally, $\text{CrB}_4\text{O}_6\text{N}$ is homeotypic to MYbSi_4N_7 ($M = \text{Sr}, \text{Ba}, \text{Eu}$), the first nitrido-silicates to feature fourfold coordinated nitrogen atoms.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: crystal structure · electronic band structure · high-pressure chemistry · oxonitridoborate · vibrational spectroscopy

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