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Synthesis of the first nickel borate nitrate

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Abstract: The novel potassium nickel borate nitrate $\text{K}_7\text{Ni}[\text{B}_{18}\text{O}_{24}(\text{OH})_9](\text{NO}_3)_6 \cdot (\text{H}_3\text{BO}_3)$ was obtained from a simple hydrothermal synthesis in a stainless-steel autoclave at $T = 513$ K starting with nickel dichloride hexahydrate, and boric and nitric acid with the pH adjusted to 8 by KOH. Single-crystal X-ray diffraction data provided the basis for the structure analysis and refinement. The compound crystallizes in the trigonal space group $R\bar{3}$ (no. 148) with the lattice parameters $a = 1222.29(8)$ and $c = 5478.4(4)$ pm. Generally, $\text{K}_7\text{Ni}[\text{B}_{18}\text{O}_{24}(\text{OH})_9](\text{NO}_3)_6 \cdot (\text{H}_3\text{BO}_3)$ is comprised of nitrate layers and complex nickel borate layers surrounded by boric acid, nitrate anions, and potassium cations.

Keywords: borate; borate-nitrate; crystal structure; nickel; nitrate; potassium.

1 Introduction

Borates incorporating cations from the transition metal group have long been of interest in our working group. This is especially true for high-pressure/high-temperature conditions as shown by several publications in the last decade. Borates allow for unique structural motifs incorporating not only $[\text{BO}_3]^{3-}$, but also $[\text{BO}_4]^{5-}$ units and even edge-sharing $[\text{BO}_4]^{5-}$ tetrahedra [1]. Transition metal borates offer a large variety of compounds like $\text{Co}_7\text{B}_{24}\text{O}_{42}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ [2], and $M_6\text{B}_{22}\text{O}_{39} \cdot \text{H}_2\text{O}$ ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cd}$) [3–5]. Further intensive focus has been directed to the synthesis of novel nickel borates, as evidenced by the publications on $\gamma\text{-NiB}_4\text{O}_7$ [6], $\text{NiB}_3\text{O}_5(\text{OH})$ [7], and

$\text{Ni}_3\text{B}_{18}\text{O}_{28}(\text{OH})_4 \cdot \text{H}_2\text{O}$ [8]. Another area of interest of our group has been the combination of simple metal borates with additional anionic groups like in $\text{Sn}_3[\text{B}_3\text{O}_7]\text{X}$ ($\text{X} = \text{F}, \text{I}$) [9, 10] and $\text{Pb}[\text{B}_2(\text{SO}_4)_4]$ [11]. The synthesis conditions could thereby be shifted from high-pressure/high-temperature conditions to ambient pressure in simple stainless-steel autoclaves and glass ampoules.

Similar to these syntheses, our group has prepared several new compounds containing borate and nitrate groups like $\text{K}_3\text{Na}[\text{B}_6\text{O}_9(\text{OH})_3]\text{NO}_3$ [12], $\text{Na}_{3-x}\text{K}_x[\text{B}_6\text{O}_{10}]\text{NO}_3$ [13], $\text{Lu}_2\text{B}_2\text{O}_5(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [14], and $\text{RE}[\text{B}_5\text{O}_8(\text{OH})(\text{H}_2\text{O})_x]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ [$\text{RE} = \text{Pr}$ ($x = 0.87$), Nd ($x = 0.85$), Sm ($x = 0$)] [15, 16]. To the best of our knowledge, less than 20 compounds containing borate as well as nitrate functionalities are known to date.

An extension of these investigations, while focusing on the synthesis of new transition metal containing compounds, resulted in the hitherto unknown potassium nickel borate nitrate. A simple hydrothermal synthesis in a stainless-steel autoclave could be utilized to prepare the potassium nickel borate nitrate $\text{K}_7\text{Ni}[\text{B}_{18}\text{O}_{24}(\text{OH})_9](\text{NO}_3)_6 \cdot (\text{H}_3\text{BO}_3)$. As the title compound could only be synthesized as a side phase, the characterization in this work is only focused on a X-ray single-crystal structure determination.

2 Experimental section

2.1 Synthesis

The compound $\text{K}_7\text{Ni}[\text{B}_{18}\text{O}_{24}(\text{OH})_9](\text{NO}_3)_6 \cdot (\text{H}_3\text{BO}_3)$ was synthesized under simple hydrothermal conditions in a stainless-steel autoclave (volume: 8 mL) fitted with a Teflon inlet. A mixture of 135.4 mg (0.57 mmol) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98%, abcr GmbH, Karlsruhe, Germany) and 64.6 mg (1.04 mmol) H_3BO_3 ($\geq 99.8\%$, Roth GmbH + Co. KG, Karlsruhe, Germany) was thoroughly ground together in an agate mortar. To the mixture, 1 mL of water and 10 drops of nitric acid (65%, Roth GmbH + Co. KG, Karlsruhe, Germany) were added and the pH value was set to approximately 8 by addition of 2.8 mL KOH

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(1 mol L⁻¹) solution. The reaction vessel was then placed in a furnace, heated up to a temperature of 513 K and kept there for 2 d. Afterwards, the reaction mixture was cooled down to room temperature with a cooling rate of 5 K h⁻¹. A green product was obtained containing green, transparent crystals of $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$. Suitable crystals were isolated and analyzed by single-crystal X-ray diffraction.

2.2 X-ray structure determination

Under a polarisation microscope, a suitable single-crystal of $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ with a diameter of 60 µm was fixed on the tip of a MicroMount™ (MiTeGen, LLC, Ithaca, NY, USA) and immediately placed in the diffractometer. The intensity data was collected with a Bruker D8 Quest diffractometer (Bruker, Karlsruhe, Germany) equipped with a Photon 100 detector system and an Incoatec microfocus source generator (multi-layered optic, monochromatized MoK α radiation, $\lambda = 71.073$ pm). The collection strategy, concerning the ω and φ scans, was optimized using the APEX III [17] program package. Thus,

Table 1: Crystal data and structure refinement of $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ (standard deviations in parentheses).

Empirical formula	$K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$
Molar mass, gmol ⁻¹	1497.96
Crystal system	Trigonal
Space group	$R\bar{3}$ (no. 148)
Single-crystal diffractometer	Bruker D8 Quest Photon 100
Radiation; wavelength λ , pm	MoK α ; 71.073
a , pm	1222.29(8)
c , pm	5478.4(4)
V , nm ³	7.088(1)
Formula units per cell, Z	6
Calculated density, g cm ⁻³	2.11
Crystal size, mm ³	$0.14 \times 0.06 \times 0.04$
Temperature, K	297(2)
Absorption coefficient, mm ⁻¹	1.2
$F(000)$, e	4452
2θ range, deg	4.9–56.0
Range in hkl	$\pm 16, \pm 16, \pm 72$
Total no. of reflections	33867
Independent reflections/ R_{int}	3811/0.0634
Data/restraints/parameters	3811/4/283
Absorption correction	Multi-scan (Bruker SADABS 2016/2)
Final $R1/wR2$ [$I > 2 \sigma(I_p)$]	0.0677/0.1973
Final $R1/wR2$ (all data)	0.0850/0.2077
Goodness-of-fit on F_o^2	1.075
Largest diff. peak/hole, $e \text{ \AA}^{-3}$	1.74/–1.28

a complete data set up to high angles with high redundancies was received. For data processing and data reduction, the program SAINT [18] was employed. Thereafter, multi-scan absorption corrections were applied with the program SADABS [19].

The structure solution and parameter refinement with anisotropic displacement parameters for all non-hydrogen atoms, except the nitrogen atom N5 and the

Table 2: Atomic coordinates, Wyckoff positions, and equivalent isotropic displacement parameters U_{eq} (Å²) for $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ (space group $R\bar{3}$).

Atom	Wyckoff site	S.O.F.	x	y	z	U_{eq}
Ni1	6c	1/3	2/3	1/3	0.58391(2)	0.0142(2)
K1	18f	1	0.7591(2)	0.7066(2)	0.47596(2)	0.0490(4)
K2	18f	1	0.6100(2)	0.7147(2)	0.64007(2)	0.0654(5)
K3	6c	1/3	0	0	0.60614(6)	0.0760(8)
B1	18f	1	0.7519(4)	0.5518(4)	0.55053(9)	0.0240(9)
B2	18f	1	0.6145(5)	0.6118(4)	0.53164(8)	0.0232(9)
B3	18f	1	0.5186(4)	0.4305(4)	0.55894(9)	0.0232(9)
B4	18f	1	0.5154(4)	0.4265(4)	0.60923(9)	0.0233(9)
B5	18f	1	0.7531(5)	0.5542(5)	0.61676(9)	0.0253(9)
B6	18f	1	0.3396(5)	0.2933(5)	0.63597(8)	0.027(1)
B7	6c	1/3	1/3	2/3	0.5902(2)	0.035(2)
N1	18f	1	0.7359(5)	0.8849(5)	0.58030(9)	0.050(2)
N2	6c	1/3	0	0	0.6656(1)	0.023(2)
N3	6c	1/3	1/3	2/3	0.5003(1)	0.021(1)
N4	3b	1/6	0	0	1/2	0.053(3)
N5	6c	1/6	1/3	2/3	0.6703(2)	0.016(2)
O1	18f	1	0.7356(3)	0.6366(3)	0.53673(6)	0.0305(7)
O2	18f	1	0.5112(3)	0.5175(3)	0.54256(5)	0.0265(6)
O3	18f	1	0.6487(2)	0.4561(2)	0.56229(5)	0.0182(5)
O4	18f	1	0.8676(3)	0.5649(3)	0.55176(5)	0.0224(6)
O5	18f	1	0.6062(3)	0.6866(3)	0.51429(6)	0.0315(7)
O6	18f	1	0.4751(3)	0.4512(3)	0.58430(5)	0.0275(6)
O7	18f	1	0.4216(3)	0.4095(3)	0.62685(6)	0.0286(7)
O8	18f	1	0.2552(3)	0.2853(3)	0.65315(6)	0.0332(7)
O9	18f	1	0.3427(3)	0.1864(3)	0.62947(6)	0.0341(7)
O10	18f	1	0.6352(3)	0.5354(3)	0.61592(5)	0.0238(6)
O11	18f	1	0.7874(2)	0.4739(3)	0.60597(5)	0.0193(6)
O12	18f	1	0.4334(4)	0.6461(4)	0.59054(8)	0.047(1)
O13	18f	1	0.7376(6)	0.8639(5)	0.60225(8)	0.076(2)
O14	18f	1	0.6348(4)	0.8220(5)	0.56854(8)	0.060(2)
O15	18f	1	0.8299(5)	0.9684(5)	0.5696(1)	0.077(2)
O16	18f	1	0.1129(4)	0.0288(5)	0.6661(1)	0.067(2)
O17	18f	1	0.2217(4)	0.6436(4)	0.5006(1)	0.061(2)
O18	18f	1/2	0.9107(8)	0.8936(8)	0.5046(2)	0.055(2)
O19	18f	1/2	0.434(2)	0.683(2)	0.6737(3)	0.107(4)
H5	18f	1	0.534(3)	0.659(5)	0.509(1)	0.04(2)
H6	18f	1	0.440(7)	0.496(6)	0.585(2)	0.08(2)
H8	18f	1	0.209(5)	0.210(3)	0.657(1)	0.05(2)
H12	18f	1	0.508(3)	0.712(4)	0.590(2)	0.07(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses).

oxygen atom O19, was done utilising the SHELXS/L-2013 [20–21] software implemented in the program WINGX-2013.3 [22]. In the course of the refinement, the trigonal space group $R\bar{3}$ was found to be correct. The nitrogen and oxygen atoms N5 and O19 were refined isotropically. Furthermore, the hydrogen atoms H5, H6, H8, and H12 were refined isotropically, while employing a bond restraint of 84(2) pm using the DFIX command.

Relevant details of the data collection and evaluation are listed in Table 1, the atomic coordinates, Wyckoff positions, and the isotropic displacement parameters in Table 2, and the anisotropic displacement parameters in Table 3. Interatomic distances are shown in Table 4, bond angles in Table 5 and the hydrogen bond data in Table 6.

CCDC 1946591 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

3.1 Crystal structure

The structure consists of seven crystallographically independent boron atoms, whereby two are surrounded by four oxygen atoms forming tetrahedral $[BO_4]^{5-}$ units,

Table 3: Anisotropic displacement parameters ($\text{\AA}^2$) of $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ (space group $R\bar{3}$) with standard deviations in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	0.0147(3)	U_{11}	0.0132(4)	0	0	0.00733(14)
K1	0.046(7)	0.0899(10)	0.0315(6)	−0.0091(6)	−0.004(5)	0.0492(7)
K2	0.1249(14)	0.041(7)	0.0436(7)	0.0111(5)	0.035(8)	0.0515(8)
K3	0.0803(12)	U_{11}	0.0674(17)	0	0	0.0401(6)
B1	0.022(2)	0.019(2)	0.028(2)	0.0059(17)	0.0034(17)	0.0087(18)
B2	0.031(2)	0.02(2)	0.021(2)	0.0031(16)	0.001(17)	0.014(19)
B3	0.018(2)	0.022(2)	0.028(2)	0.0054(17)	−0.003(17)	0.0086(17)
B4	0.022(2)	0.021(2)	0.028(2)	0.0007(17)	0.0066(17)	0.0114(18)
B5	0.024(2)	0.026(2)	0.027(2)	−0.0069(18)	−0.0018(18)	0.0136(19)
B6	0.024(2)	0.037(3)	0.023(2)	0.0045(19)	0.0054(17)	0.018(2)
B7	0.032(3)	U_{11}	0.041(5)	0	0	0.0158(14)
N1	0.054(3)	0.05(3)	0.047(3)	0.012(2)	0.008(2)	0.027(3)
N2	0.0258(18)	U_{11}	0.017(3)	0	0	0.0129(9)
N3	0.0192(16)	U_{11}	0.024(3)	0	0	0.0096(8)
N4	0.032(3)	U_{11}	0.095(10)	0	0	0.0162(17)
O1	0.025(15)	0.0255(15)	0.0399(17)	0.015(13)	0.0054(13)	0.0119(13)
O2	0.0266(15)	0.027(15)	0.029(15)	0.0093(12)	0.0005(12)	0.0157(13)
O3	0.017(13)	0.0175(12)	0.0208(13)	0.0034(10)	0.0022(10)	0.0092(11)
O4	0.0188(13)	0.0181(13)	0.0294(14)	0.0043(11)	0.0049(11)	0.0086(11)
O5	0.0319(17)	0.031(16)	0.0308(16)	0.0134(13)	0.0008(13)	0.0152(14)
O6	0.0314(16)	0.03(16)	0.0285(15)	0.0044(12)	0.004(12)	0.021(14)
O7	0.0288(16)	0.0313(16)	0.0293(15)	0.0017(12)	0.0104(12)	0.0176(13)
O8	0.0337(17)	0.0405(19)	0.0299(16)	0.0084(14)	0.0154(13)	0.0219(16)
O9	0.0307(16)	0.0302(16)	0.0422(18)	0.01(14)	0.0181(14)	0.0159(14)
O10	0.022(14)	0.0217(14)	0.0299(15)	−0.0056(11)	−0.0007(11)	0.0126(12)
O11	0.0157(12)	0.0198(13)	0.0212(13)	−0.0043(10)	−0.0028(10)	0.0079(10)
O12	0.037(2)	0.038(2)	0.071(3)	0.0082(19)	0.0066(19)	0.0218(18)
O13	0.095(4)	0.08(4)	0.04(2)	0.02(2)	0.01(2)	0.034(3)
O14	0.051(3)	0.057(3)	0.057(3)	0.01(2)	0.005(2)	0.015(2)
O15	0.053(3)	0.09(4)	0.07(3)	0.038(3)	0.009(2)	0.023(3)
O16	0.045(2)	0.055(3)	0.102(4)	0.013(3)	0.009(2)	0.026(2)
O17	0.041(2)	0.05(2)	0.091(3)	0.007(2)	−0.001(2)	0.023(2)
O18	0.044(5)	0.034(4)	0.072(6)	−0.008(4)	−0.003(4)	0.008(3)

The hydrogen atoms and the N5 nitrate (N5 and O19) have not been refined anisotropically.

Table 4: Selected interatomic distances (pm) in $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ (standard deviations in parentheses).

Atoms	Distance	Atoms	Distance
Ni1–O3	200.8(3)	B7–O12	136.6(4)
Ni1–O3 ^a	200.8(3)	B7–O12 ^c	136.7(4)
Ni1–O3 ^b	200.8(3)	B7–O12 ^d	136.7(4)
Ni1–O11 ^a	201.3(3)		$\emptyset = 136.7$
Ni1–O11 ^b	201.3(3)		
Ni1–O11	201.3(3)	N1–O13	123.2(6)
	$\emptyset = 201.1$	N1–O15	123.7(7)
		N1–O14	125.8(7)
			$\emptyset = 124.2$
B1–O4	134.4(5)		
B1–O1	137.5(5)		
B1–O3	137.8(5)	N2–O16	124.2(5)
	$\emptyset = 136.6$	N2–O16 ^e	124.2(5)
		N2–O16 ^f	124.2(5)
			$\emptyset = 124.2$
B2–O2	135.1(5)		
B2–O5	135.8(5)		
B2–O1	138.3(6)	N3–O17	124.8(4)
	$\emptyset = 136.4$	N3–O17 ^d	124.8(4)
		N3–O17 ^c	124.8(4)
			$\emptyset = 124.8$
B3–O4 ^b	142.8(5)		
B3–O2	142.9(5)		
B3–O3	147.1(5)	N4–O18 ^g	123.6(8)
B3–O6	155.3(6)	N4–O18 ^h	123.6(8)
	$\emptyset = 147.0$	N4–O18 ⁱ	123.6(8)
			$\emptyset = 123.6$
B4–O7	143.2(5)		
B4–O10	145.0(5)	N5A–O19A	116(2)
B4–O11 ^b	146.1(5)	N5A–O19A ^c	116(2)
B4–O6	153.2(6)	N5A–O19A ^d	116(2)
	$\emptyset = 146.9$		$\emptyset = 115.8$
B5–O10	134.2(5)	N5A–O19B ⁱ	128(2)
B5–O11	137.9(5)	N5A–O19B ^k	128(2)
B5–O9 ^a	138.0(6)	N5A–O19B ^l	128(2)
	$\emptyset = 136.7$		$\emptyset = 128.4$
B6–O7	135.9(6)		
B6–O8	136.3(5)		
B6–O9	137.3(6)		
	$\emptyset = 136.5$		

Symmetry operations: ^a1+y–x, 1–x, +z; ^b1–y, +x–y, +z; ^c1–y, 1+x–y, +z; ^d+y–x, 1–x, +z; ^e–y, +x–y, +z; ^f+y–x, –x, +z; ^g+y, 1–x+y, 1–z; ^h1–y+x, +x, 1–z; ⁱ2–x, 2–y, 1–z; ^j–1/3+y, 1/3–x+y, 4/3–z; ^k2/3–y+x, 1/3+x, 4/3–z; ^l2/3–x, 4/3–y, 4/3–z.

and four are surrounded by three oxygen atoms building up trigonal planar $[BO_3]^{3-}$ units. These six borate units are linked *via* common corners as shown in Fig. 1a. The smallest crystallographically independent $[B_6O_{10}(OH)_3]^{5-}$ unit can be subdivided into two *dreier* rings [23] consisting of two trigonal planar coordinated (B1, B2 and B5, B6, respectively) and one tetrahedrally coordinated (B3 and B4, respectively) borate unit interconnected *via* oxygen atoms (O1, O2, O3, and O7, O9, O11, respectively). The *dreier* rings are connected *via* the oxygen atom O8. This complete unit can

Table 5: Selected bond angles (deg) in $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ (standard deviations in parentheses).

Atoms	Bond angle	Atoms	Bond angle
O4–B1–O1	118.6(4)	O12–B7–O12 ^c	119.98(3)
O4–B1–O3	122.7(4)	O12–B7–O12 ^d	119.98(3)
O1–B1–O3	118.8(4)	O12 ^c –B7–O12 ^d	119.98(3)
	$\emptyset = 120.0$		$\emptyset = 119.98$
O2–B2–O5	122.1(4)	O13–N1–O15	121.8(6)
O2–B2–O1	122.7(4)	O13–N1–O14	119.1(5)
O5–B2–O1	115.2(4)	O15–N1–O14	119.1(5)
	$\emptyset = 120.0$		$\emptyset = 120.0$
O4 ^b –B3–O2	111.4(3)	O16–N2–O16 ^e	119.96(3)
O4 ^b –B3–O3	111.9(3)	O16–N2–O16 ^f	119.96(3)
O2–B3–O3	112.6(3)	O16 ^e –N2–O16 ^f	119.96(3)
O4 ^b –B3–O6	108.0(3)		$\emptyset = 120.0$
O2–B3–O6	106.6(3)		
O3–B3–O6	106.0(3)	O17–N3–O17 ^d	119.98(2)
	$\emptyset = 109.4$	O17–N3–O17 ^c	119.98(3)
		O17 ^d –N3–O17 ^c	119.98(3)
			$\emptyset = 120.0$
O7–B4–O10	109.3(3)		
O7–B4–O11 ^b	112.9(3)		
O10–B4–O11 ^b	111.8(3)	O18 ^g –N4–O18 ⁱ	116.0(3)
O7–B4–O6	108.5(3)	O18 ^g –N4–O18 ^h	116.0(3)
O10–B4–O6	108.7(3)	O18 ^h –N4–O18 ^h	116.0(3)
O11 ^b –B4–O6	105.5(3)		$\emptyset = 116.0$
	$\emptyset = 109.5$		
		O19A ^c –N5A–O19A ^d	117.5(5)
O10–B5–O11	123.1(4)	O19A ^c –N5A–O19A	117.5(5)
O10–B5–O9 ^a	118.5(4)	O19A ^d –N5A–O19A	117.5(5)
O11–B5–O9 ^a	118.4(4)		$\emptyset = 117.5$
	$\emptyset = 120.0$		
		O19B ⁱ –N5A–O19B ^k	101(2)
O7–B6–O8	117.7(4)	O19B ⁱ –N5A–O19B ^l	101(2)
O7–B6–O9	122.8(4)	O19B ^k –N5A–O19B ^l	101(2)
O8–B6–O9	119.4(4)		$\emptyset = 100.8$
	$\emptyset = 120.0$		

Symmetry operations as in Table 4.

be described *via* the descriptor $4\Delta 2\Box:(2\Delta 1\Box)(2\Delta 1\Box)$ [24, 25] including all crystallographically independent boron and oxygen atoms. For the trigonal planar $[BO_3]^{3-}$ units, the B–O distances range from 134.2(5) to 138.3(6) pm with an average B–O distance of 136.5 pm, which is in good agreement with other borates known from literature like $NiB_3O_5(OH)$ ($\emptyset = 137.8$ pm) [7] and $NiB_{12}O_{14}(OH)_{10}$ ($\emptyset = 136.7$ pm) [26]. The O–B–O angles range from 115.2(4) to 123.1(4)° with average values of 120.0°, exactly matching the theoretical value. Additionally, these findings are in good concordance with the mean values obtained by Zobetz (137.0(19) pm and 120.0(29)°) [27].

In the tetrahedrally coordinated $[BO_4]^{5-}$ units, the B–O distances range from 142.8(5) to 155.3(6) pm with an average B–O distance of 147.0 pm, which is also in good agreement with values known from literature [5, 8].

Fig. 1: The $[B_6O_{10}(OH)_3]^{5-}$ anion forms the largest crystallographically independent structural unit (a). Three of those anions surround the central nickel atom forming an octahedral coordination sphere of the Ni atom by oxygen atoms (b). The central motif in $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ is the $Ni[B_{18}O_{24}(OH)_9]^{3-}$ complex (c), which incorporates two *sechser* rings built up by three *dreier* rings (blue, orange, purple).

The O–B–O angles range from $105.5(3)$ to $112.9(3)^\circ$ with average values close to the theoretical value of 109.47° (B3: 109.4° , B4: 109.5°). For $[BO_4]^{5-}$ units, a broader range of B–O distances is given by Zobetz (144.4 – 153.4 pm) [28]. The mean values for the B–O distances of $147.6(35)$ pm, as well as the O–B–O angles of $109.44(278)^\circ$ are in good agreement with our findings.

Three of these polyborate units enclose a Ni(II) ion forming two *sechser* rings that are interconnected *via* the borate tetrahedra. The central $Ni[B_{18}O_{24}(OH)_9]^{3-}$ complex is depicted with the nickel coordination sphere in Fig. 1b, c. The nickel ion is six-fold coordinated forming an octahedron with Ni–O distances ranging from $200.8(3)$ to $201.3(3)$ pm ($\bar{\varnothing} = 201.1$ pm), which is in good agreement with nickel borates known from literature like $Ni_3B_{18}O_{28}(OH)_4 \cdot H_2O$ ($\bar{\varnothing} = 210.3$ pm) [8], $NiB_3O_5(OH)$ ($\bar{\varnothing} = 206.2$ pm) [7], and γ - NiB_4O_7 ($\bar{\varnothing} = 208.2$ pm) [6].

The seventh crystallographically independent boron atom forms a trigonal planar H_3BO_3 unit isolated from the central $[B_{18}O_{24}(OH)_9]^{3-}$ complex. The B–O distances are $136.7(4)$ pm, which is similar to the values encountered in $[BO_3]^{3-}$ units of the central complex. The O–B–O angles are 120° , which matches with a trigonal planar situation. Additionally, the central complex is surrounded by three crystallographically independent potassium ions with K–O distances ranging from $262.4(9)$ to $334.0(4)$ pm. Furthermore, the central nickel borate complex is surrounded by five crystallographically independent nitrate groups as shown in Fig. 2. The N1, N2, and N3 atoms of the nitrate groups show similar N–O distances ranging from $123.2(6)$ to $125.8(7)$ pm, with average values of 124.2 , 124.2 , and 124.8 pm, respectively, which are in good agreement

with values known in literature [13, 14, 16]. The O–N–O bond angles range from $119.1(5)$ to $121.8(6)^\circ$ with averages of 120.0° each.

The nitrate group with the central nitrogen atom N4 allows for six different oxygen positions with N–O distances of $123.6(8)$ pm each. As the site occupancy of the oxygen atoms is 0.5, only three oxygen sites are simultaneously occupied, forming a trigonal planar conformation and thereby allowing for two distinct nitrate groups that differ in their orientation, as illustrated in Fig. 3 (left). For the nitrogen atom N5, two different NO_3^- groups are found, as illustrated in Fig. 3 (right). The nitrogen atom N5 is displaced from the trigonal planar conformation. Regarding the nitrogen atom N5A, the O19A oxygen atoms are closest with N–O distances of $116(2)$ pm and O–N–O bond angles of $117.5(5)^\circ$. The other possible oxygen positions are further away with N–O distances of $128(2)$ pm and O–N–O bond angles of $101(2)^\circ$. The same is obviously true for the position N5B, with interchanged values. A statistical presence of the different possible nitrates seems to be most plausible.

Along the *ab* plane, the nickel borate complex is surrounded by three K1, three K2, and three K3 ions, as well as three H_3BO_3 groups and six nitrate groups as illustrated in Fig. 2 (top). The crystals have a layer-like structure stacked along the *c* axis. As shown in Fig. 2 (bottom), a layer of N3- and N4-centred nitrate groups is followed by a layer of the nickel borate complex along with potassium cations, H_3BO_3 molecules, and the N1-centred nitrate group, then again followed by a layer of N2- and N5-centred nitrate groups. With an additional translation of $[1/3, 1/3, 0]$, an inverted layer of the central

Fig. 2: The central nickel borate complexes are isolated from each other and are each surrounded by six nitrate groups in the ab plane (top). Additionally, the nickel borate complex is surrounded by a layer-like structure of nitrates shown along the ac plane (bottom).

nickel borate units with their environment (K^+ , H_3BO_3 , N1-centred nitrate groups) follows next. Due to the translation along the lattice and the inversion of every layer, six different layers can be identified. However, only two are depicted for clarity. For further clarification, red and blue circles are drawn in Fig. 2 to indicate the positioning directly above each other along the c axis.

To equalize the charges, four hydrogen atoms were found to be located in proximity to the oxygen atoms O5, O6, O8, and O12. For all positions, interconnecting hydrogen bonds were identified, which are listed in Table 6. Each hydrogen atom was fixed to the corresponding oxygen atom at 0.84(2) pm using the DFIX command.

To evaluate our single-crystal structure solution, bond valence sums were calculated for every crystallographically independent non-hydrogen atom utilizing the bond-length/bond-strength concept. The O–H distances were fixed at 95 pm according to Brown and Altermatt [29, 30]. The obtained values agree well with the expected ones, at least within the accuracy of the method, with the exception of the nitrate group formed by the atom N5. Owing to the high degree of distortion of the nitrate anion, the calculated values are unusually high/low, depending on whether the short (A) or the long (B) N–O distances are considered. The exact values for the calculations are listed in Table 7.

Fig. 3: The N4-nitrate appears either as the $N4O18A_3$ (green) or the $N4O18B_3$ (purple) unit (left). For the N5-nitrate, either the $N5AO19A_3$ or the $N5BO19B_3$ nitrate are formed (right). All intermolecular distances and bond angles are identical in both possible arrangements. The difference stems from their orientation and therefore their vicinity.

Table 6: The hydrogen bond parameters (pm, deg) in $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$.

Hydrogen bond	D–H	H...A	D...A	D–H...A
O5–H5...O17	83(2)	193(2)	275.6(6)	171(6)
O6–H6...O12	85(8)	190(8)	269.6(7)	155(7)
O8–H8...O16	84(2)	198(2)	281.1(6)	174(6)
O12–H12...O14	86(5)	186(6)	261.6(8)	145(4)

Table 7: Charge distribution in $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ (space group $R\bar{3}$, no. 148), calculated with the bond-length/bond-strength concept (ΣV)^a [29].

	Ni1	K1	K2	K3	B1	B2	B3	B4	B5	B6
ΣV	2.29	1.37	1.31	1.04	3.05	3.06	3.09	3.09	3.04	3.05
	B7	N1	N2	N3	N4	N5 ^A	N5 ^B			
ΣV	3.04	5.01	5.01	4.93	5.10	6.29	4.48			
	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10
ΣV	1.99	1.96	2.13	2.11	2.38	2.26	1.92	2.35	2.01	2.10
	O11	O12	O13	O14	O15	O16	O17	O18	O19 ^A	O19 ^B
ΣV	2.14	2.06	2.11	1.77	2.01	1.67	1.69	1.96	2.10	1.49

^aThe superscripts ^{A,B} refer to the short (A) and long (B) N5–O19 distances.

4 Conclusion

The synthesis and crystallographic characterization of the novel compound $K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6 \cdot (H_3BO_3)$ is reported in this work. The title compound is one of the few structures to encompass both, the structural motifs of borates as well as of nitrates. The crystal structure consists of nitrate layers and complex nickel borate layers surrounded by boric acid molecules, nitrate anions, and potassium cations stacked along the *c* axis. Hence, the field of nickel borates could be expanded by the incorporation of nitrate groups leading to the first nickel borate nitrate.

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