Crystal structure of sodium nickel diaqua *catena*-[monoboro-diphosphate] monohydrate, $\text{NaNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$, at 293 K and 198 K

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Abstract

$\text{BNaNiO}_{11}\text{P}_2$, hexagonal, $P6_122$ (No. 178), $a = 9.377(1) \text{ \AA}$, $c = 15.848(1) \text{ \AA}$, $V = 1206.8 \text{ \AA}^3$, $Z = 6$, $R_{\text{gt}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.074$, $T = 293 \text{ K}$.

$\text{BNaNiO}_{11}\text{P}_2$, hexagonal, $P6_122$ (No. 178), $a = 9.358(1) \text{ \AA}$, $c = 15.833(1) \text{ \AA}$, $V = 1200.7 \text{ \AA}^3$, $Z = 6$, $R_{\text{gt}}(F) = 0.026$, $wR_{\text{ref}}(F^2) = 0.070$, $T = 198 \text{ K}$.

Source of material

$\text{NaNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$ was prepared by hydrothermal treatment of mixtures of 0.29 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 0.96 g

$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, and 0.37 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (molar ratio 2:1:7). A concentrated aqueous solution of $\text{pH} = 1$ (1.5 ml of 18% HCl) was held at 393 K for two weeks in a sealed glass ampoule (degree of filling 50%).

Discussion

The crystal structure of $\text{NaNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$ reveals an infinite one-dimensional anionic partial structure. Condensation of PO_4 and BO_4 tetrahedra via common vertices leads to tetrahedral ribbons $[\text{BP}_2\text{O}_8]^{3-}$ which are arranged around 6_1 screw axes to form chiral helices [1,2]. The central channel is filled by a helix made up of water molecules. The ribbons are connected via $\text{Ni}^{\text{II}}\text{O}_4(\text{H}_2\text{O})_2$ coordination octahedra and the free threads of the helices are occupied by sodium cations fixed by an irregular surrounding of six oxygen atoms from adjacent phosphate groups. The overall resulting framework is related to the CZP-topology [3,4]. Interatomic distances and angles within the tetrahedral helices are similar to known values for borophosphates [5,6]. The isotropic thermal displacement parameter of O(6) (water molecule in the center of the helical channels) drops significantly at lower temperature from $0.097 \text{ \AA}^2$ (293 K) to $0.063 \text{ \AA}^2$ (198 K). Therefore, the relatively high isotropic thermal displacement parameter could be interpreted as thermal motion of the water of crystallisation.

1. $\text{NaNi}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$, $T = 293 \text{ K}$

Table 1. Data collection and handling.

Crystal:	yellow-green, hexagonal bipyramid, size $0.15 \times 0.15 \times 0.35 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71069 \text{ \AA}$)
μ :	29.19 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8184, 1184
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1152
$N(\text{param})_{\text{refined}}$:	75
Programs:	SHELXS-97 [7], SHELXL-97 [8], DRAWxtl [9], POV-Ray 3.1a [10]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Na(1)	6b	0.1947(2)	2x	1/4	0.060(1)	0.049(2)	0.036(1)	U ₂₂ /2	0.006(1)	0
Ni(1)	6b	0.55421(3)	2x	1/4	0.0127(2)	0.0130(2)	0.0120(2)	U ₂₂ /2	0.0007(2)	0
B(1)	6b	0.8477(2)	2x	1/4	0.011(1)	0.012(2)	0.009(2)	U ₂₂ /2	0.000(1)	0
P(1)	12c	0.39041(8)	0.17057(8)	0.41480(4)	0.0128(3)	0.0119(3)	0.0105(3)	0.0058(2)	0.0007(2)	-0.0001(2)
O(1)	12c	0.2148(2)	0.0220(2)	0.4001(1)	0.0144(9)	0.0093(8)	0.0167(9)	0.0040(7)	-0.0024(7)	0.0002(7)
O(2)	12c	0.2923(3)	0.4927(3)	0.1108(1)	0.0157(9)	0.021(1)	0.0177(8)	0.0087(8)	-0.0013(7)	-0.0023(8)
O(3)	12c	0.3875(3)	0.3194(3)	0.3806(1)	0.024(1)	0.0121(9)	0.0145(8)	0.0101(8)	0.0017(8)	0.0014(7)
O(4)	12c	0.4192(2)	0.1835(2)	0.5126(1)	0.0127(8)	0.0164(9)	0.0086(7)	0.0060(7)	0.0005(6)	-0.0014(6)
O(5)	12c	0.6193(2)	0.1374(3)	0.1233(1)	0.0148(9)	0.020(1)	0.0126(8)	0.0088(8)	0.0034(7)	0.0008(7)
O(6)	6a	0.1359(7)	0	0	0.051(3)	0.072(4)	0.182(8)	U ₂₂ /2	0.031(3)	2U ₁₃

2. NaNi(H₂O)₂[BP₂O₈] · H₂O, T = 198 K**Table 3.** Data collection and handling.

Crystal:	yellow-green, hexagonal bipyramids, size 0.15 × 0.15 × 0.35 mm
Wavelength:	Mo K _α radiation (0.71069 Å)
μ:	29.33 cm ⁻¹
Diffractometer, scan mode:	Siemens P4, ω
2θ _{max} :	60.02°
N(hkl) _{measured} , N(hkl) _{unique} :	7005, 1176
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 1157
N(param) _{refined} :	75
Programs:	SHELXS-97 [7], SHELXL-97 [8] DRAWxtl [9], POV-Ray 3.1a [10]

Table 4. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Na(1)	6b	0.1938(1)	2x	1/4	0.0397(9)	0.035(1)	0.0254(9)	U ₂₂ /2	0.0045(8)	0
Ni(1)	6b	0.55448(3)	2x	1/4	0.0094(2)	0.0094(2)	0.0088(2)	U ₂₂ /2	0.0005(1)	0
B(1)	6b	0.8474(2)	2x	1/4	0.009(1)	0.010(1)	0.006(1)	U ₂₂ /2	-0.001(1)	0
P(1)	12c	0.39080(7)	0.17067(8)	0.41472(4)	0.0100(3)	0.0094(2)	0.0082(2)	0.0045(2)	0.0005(2)	0.0001(2)
O(1)	12c	0.2146(2)	0.0223(2)	0.3999(1)	0.0114(8)	0.0072(7)	0.0118(8)	0.0033(6)	-0.0017(6)	0.0001(6)
O(2)	12c	0.2920(2)	0.4928(3)	0.1106(1)	0.0116(8)	0.0151(8)	0.0128(7)	0.0067(7)	-0.0006(6)	-0.0015(7)
O(3)	12c	0.3880(2)	0.3196(2)	0.3805(1)	0.0170(9)	0.0086(8)	0.0106(7)	0.0073(7)	0.0009(7)	0.0004(6)
O(4)	12c	0.4197(2)	0.1833(2)	0.5126(1)	0.0087(7)	0.0118(8)	0.0070(6)	0.0040(6)	0.0008(6)	-0.0008(5)
O(5)	12c	0.6183(2)	0.1370(2)	0.1232(1)	0.0112(8)	0.0152(9)	0.0088(7)	0.0068(7)	0.0019(6)	0.0007(6)
O(6)	6a	0.1378(5)	0	0	0.039(2)	0.051(3)	0.103(4)	U ₂₂ /2	0.019(2)	2U ₁₃

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