

Crystal structure of potassium vanadium (monophosphate-hydrogenmonoborate-monophosphate), KV[BP₂O₈(OH)]

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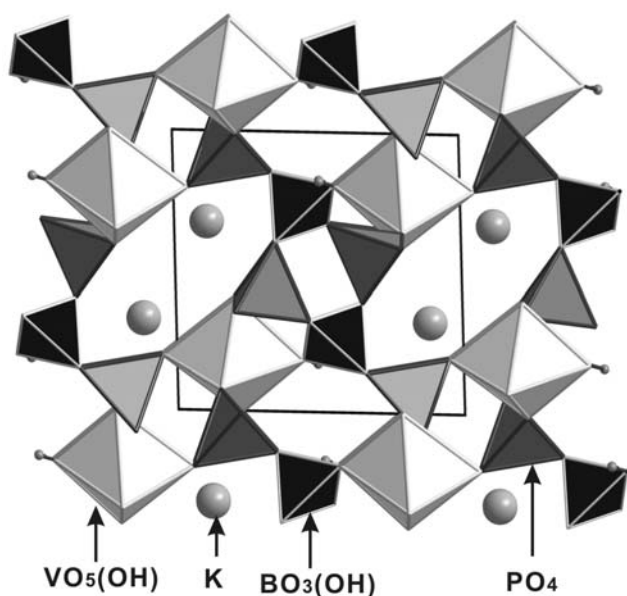
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Abstract

HBKO₉P₂V, triclinic, $P\bar{1}$ (no. 2), $a = 5.1647(1)$ Å, $b = 8.0585(2)$ Å, $c = 8.3567(2)$ Å, $\alpha = 86.847(4)^\circ$, $\beta = 80.196(3)^\circ$, $\gamma = 86.330(3)^\circ$, $V = 341.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.045$, $wR_{\text{ref}}(F^2) = 0.091$, $T = 295$ K.

Source of material

KV[BP₂O₈(OH)] was synthesized under a mild hydrothermal condition. The reaction was performed with a mixture of 3.06 g K₂B₄O₇ · 4H₂O, 0.20 g VCl₃, 0.25 ml 85 % H₃PO₄, and 2 ml H₂O heated at 553 K for 5 days in a Teflon-lined stainless-steel autoclave ($V = 25$ ml). After reaction, the autoclave was moved out of the oven and cooled down to ambient temperature. The reaction product was washed with hot water (333 K) until soluble substances were completely removed. Finally, the reaction product was dried in air at 333 K.

Experimental details

Hydrogen position was initially located from the difference Fourier map close to O9 atom, but for the final refinement step O9—H9 distance was restrained to the value of 0.90 Å with an estimated standard deviation and its displacement parameter was derived from those of O9 atom: $U_{\text{iso}}(\text{H9}) = 1.5 U_{\text{eq}}(\text{O9})$. The lat-

tice parameters were obtained by a least-square fitting of 190 reflections extracted from the X-ray powder pattern (Cu K α_1 radiation, $10 < 2\theta < 100$, LaB₆ with $a = 4.15692$ Å as internal standard).

Discussion

Borophosphates are of particular interest and have attracted considerable attention during the past decades, due to their variable structural chemistry with a large number of connection patterns and their use in the fields of catalysis [1–3]. The title compound belongs to the isotypic series $AM^{\text{III}}[\text{BP}_2\text{O}_8(\text{OH})]$ ($A = \text{NH}_4, \text{K}, \text{Rb}$ and $M^{\text{III}} = \text{Sc}, \text{Fe}, \text{In}$) [4–9]. The crystal structure comprises isolated open-branched four-membered rings $[\text{B}_2\text{P}_4\text{O}_{16}(\text{OH})_2]^{8-}$, which are formed by condensation of two trimers, $[\text{BP}_2\text{O}_9(\text{OH})]$ by sharing common O corners. These oligomers are interconnected by VO₅(OH) octahedra to form a three-dimensional framework with 8-membered ring channels running along [100]. The 8-membered rings consist of two hydrogenborate tetrahedra, four phosphate tetrahedra, and two vanadium coordination octahedra. The negative charge of the framework is balanced by potassium cations occupying the cavities. The V—O and V—OH bond distances vary from 1.96 Å to 2.06 Å. Bond lengths and angles of the BO₃(OH) and the PO₄ groups represent typical values known from related borophosphates [4–9].

Table 1. Data collection and handling.

Crystal:	greenish platelet, size 0.018 × 0.050 × 0.080 mm
Wavelength:	Mo K α radiation (0.7107 Å)
μ :	25.6 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC7, φ/ω
$2\theta_{\text{max}}$:	61.6°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	5001, 2022
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1765
$N(\text{param})_{\text{refined}}$:	131
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

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

Atom	Site	x	y	z	U_{iso}
H(9)	2i	0.455(5)	0.173(6)	0.509(5)	0.022

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
K(1)	2i	0.7209(2)	0.3258(1)	0.1140(1)	0.0131(3)	0.0183(4)	0.0228(4)	-0.0010(3)	-0.0014(3)	-0.0020(3)
V(1)	2i	0.2660(1)	0.19689(7)	0.80713(7)	0.0077(2)	0.0084(3)	0.0085(3)	-0.0009(2)	-0.0012(2)	0.0002(2)
B(1)	2i	0.1234(7)	0.2635(5)	0.4466(5)	0.011(2)	0.009(2)	0.010(2)	0.001(1)	-0.001(1)	-0.002(1)
P(1)	2i	0.2006(2)	0.5798(1)	0.3034(1)	0.0078(3)	0.0082(4)	0.0087(4)	-0.0014(3)	-0.0010(3)	0.0004(3)
P(2)	2i	0.2171(2)	0.0628(1)	0.1854(1)	0.0067(3)	0.0077(4)	0.0091(4)	-0.0008(3)	-0.0015(3)	0.0000(3)
O(1)	2i	0.4486(4)	0.6443(3)	0.2048(3)	0.009(1)	0.009(1)	0.012(1)	-0.0035(8)	0.0004(8)	0.0000(8)
O(2)	2i	0.0266(4)	0.4077(3)	0.7918(3)	0.011(1)	0.009(1)	0.014(1)	-0.0005(8)	-0.0038(9)	-0.0003(9)
O(3)	2i	0.2712(4)	0.3956(3)	0.3486(3)	0.011(1)	0.010(1)	0.013(1)	0.0004(9)	0.0000(9)	0.0026(9)
O(4)	2i	0.1287(4)	0.6736(3)	0.4635(3)	0.013(1)	0.013(1)	0.011(1)	0.0008(9)	-0.0019(9)	-0.0034(9)
O(5)	2i	0.0602(4)	0.9209(3)	0.1502(3)	0.010(1)	0.011(1)	0.015(1)	-0.0048(8)	-0.0021(9)	-0.0012(9)
O(6)	2i	0.4908(4)	0.0035(3)	0.2184(3)	0.009(1)	0.011(1)	0.017(1)	0.0021(9)	-0.0055(9)	-0.0022(9)
O(7)	2i	0.2418(5)	0.1986(3)	0.0493(3)	0.015(1)	0.009(1)	0.010(1)	-0.0019(9)	-0.0032(9)	-0.0004(8)
O(8)	2i	0.0556(5)	0.1427(3)	0.3396(3)	0.013(1)	0.012(1)	0.010(1)	-0.0031(9)	0.0018(9)	-0.0040(9)
O(9)	2i	0.2914(5)	0.1878(3)	0.5592(3)	0.016(1)	0.018(1)	0.009(1)	0.005(1)	-0.0009(9)	0.0009(9)

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