Crystal structure of potassium ammonium molybdate phosphate, $K_{5-x}(NH_4)_xP[Mo_4O_{14}(OH)]_2 \cdot 2H_2O$ ($x = 2.43$)

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Abstract

$H_{15.72}K_{2.57}Mo_8N_{2.43}O_{32}P$, orthorhombic, *Cmcm* (no. 63), $a = 8.4551(6)$ Å, $b = 22.731(2)$ Å, $c = 15.333(1)$ Å, $V = 2947.0$ Å³, $Z = 4$, $R_{\text{int}}(F) = 0.048$, $wR_{\text{ref}}(F^2) = 0.105$, $T = 293$ K.

Source of material

$Na_2HPO_4 \cdot 2H_2O$ (0.890 g, 5 mmol; Riedel-deHaën, 99.5 %) was first dissolved in 10 ml HNO_3 (10 wt%), and a solution of

$Na_2MoO_4 \cdot 2H_2O$ (10.890 g, 45 mmol; Sigma-Aldrich, 99.5 %) together with H_3BO_3 (0.062 g, 1 mmol; Sigma-Aldrich, 99.5 %) in 20 ml water was added resulting in an overall pale yellow solution. After keeping the solution at room temperature overnight, the resulting precipitate was collected. In a second step, the precipitate (0.500 g) together with KCl (0.230 g, 3 mmol; Alfa, 99.0–100.5 %), $(NH_4)_2HPO_4$ (0.200 g, 1.5 mmol; Sigma-Aldrich, 98+ %) and water (3 ml) was treated by constant magnetic stirring and then placed into a 10 ml Teflon-lined autoclave. After a reaction time of 7 days (autogenous pressure at 170 °C) colorless crystals were isolated as a single phase product after filtration and washing with water.

The presence of ammonium is confirmed by both, chemical analysis (ICP-OES) and thermal gravimetry-mass spectroscopy (TG-MS). The total weight loss of 6.2 % (calculated: 6.5 %) during heating to 600 °C is attributed to the loss of the two moles of crystal water (calculated: 2.5 %), and one mole of water of constitution (calculated: 1.2 %) and 2.43 mole of NH_3 (calculated: 2.8 %) per formula unit.

Experimental details

Hydrogen atoms were not localized during the structure refinement. Lattice parameters were obtained by a least-squares fitting of 40 reflections taken from the X-ray powder diffraction pattern (Cu $K\alpha_1$ radiation, $4^\circ < 2\theta < 100^\circ$, LaB₆ with $a = 4.15692$ Å as internal standard).

Discussion

The title compound is an isotype of $Cs_5P[Mo_4O_{14}(OH)]_2 \cdot 2H_2O$ [1], containing isolated complexes $\{P[Mo_4O_{14}(OH)]_2\}^{5-}$. The anion is made up of two molybdate tetramers which are connected by a phosphate tetrahedron. Each tetramer is built of two pairs of face-sharing octahedra that are linked through common edges. The four molybdenum atoms are coplanar in each tetramer. The MoO_6 octahedra are distorted, with two short (1.701 (3) Å to 1.710 (4) Å), two intermediate (1.914 (2) Å to 1.923 (3) Å) and two long (2.328 (3) Å to 2.4368 (17) Å) Mo—O bonds. P—O bond lengths within the phosphate tetrahedra are nearly equal: 2×1.546 (4) Å and 2×1.548 (4) Å. Potassium and ammonium cations are statistically distributed over the positions corresponding to the Cs sites in the crystal structure of $Cs_5P[Mo_4O_{14}(OH)]_2 \cdot 2H_2O$.

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Table 1. Data collection and handling.

Crystal:	colorless platelet, size 0.015 × 0.030 × 0.060 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	38.28 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC7, φ/ω
2θ _{max} :	62°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	9829, 2476
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1988
<i>N</i> (<i>param</i>) _{refined} :	130
Programs:	SHELXS-97 [2], SHELXL-97 [3], DIAMOND [4], WinCSD [5]

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

Atom	Site	Occ.	<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
Mo(1)	16h		0.19662(5)	0.01271(2)	0.14604(2)	0.0164(2)	0.0172(2)	0.0153(2)	0.0009(2)	0.0013(2)	-0.0011(1)
Mo(2)	16h		0.18877(5)	0.23640(2)	0.14087(2)	0.0215(3)	0.0169(2)	0.0174(2)	-0.0021(2)	0.0018(2)	0.0022(1)
P	4c		0	0.12482(8)	¼	0.016(1)	0.0097(8)	0.014(1)	0	0	0
K(1)	8f	0.66(1)	0	0.13654(9)	0.5246(2)	0.033(2)	0.027(1)	0.034(1)	0	0	0.0046(9)
N(1)	8f	0.34(1)	0	0.13654(9)	0.5246(2)	0.033(2)	0.027(1)	0.034(1)	0	0	0.0046(9)
K(2)	8f	0.48(1)	0	0.3789(1)	0.0357(2)	0.033(2)	0.030(1)	0.033(2)	0	0	0.005(1)
N(2)	8f	0.52(1)	0	0.3789(1)	0.0357(2)	0.033(2)	0.030(1)	0.033(2)	0	0	0.005(1)
K(3)	4c	0.29(2)	0	0.6165(2)	¼	0.038(4)	0.037(3)	0.064(5)	0	0	0
N(3)	4c	0.71(2)	0	0.6165(2)	¼	0.038(4)	0.037(3)	0.064(5)	0	0	0
O(1)	16h		0.3272(4)	0.0568(2)	0.0927(2)	0.022(2)	0.034(2)	0.027(2)	-0.006(2)	0.007(2)	0.002(2)
O(2)	16h		0.2902(5)	0.4457(1)	0.0963(2)	0.038(2)	0.022(2)	0.030(2)	-0.006(2)	-0.003(2)	-0.007(1)
O(3)	8f		0	0.0410(2)	0.1009(3)	0.017(3)	0.024(2)	0.016(2)	0	0	0.003(2)
O(4)	8g		0.1869(5)	0.4942(2)	¼	0.015(3)	0.022(2)	0.019(2)	-0.004(2)	0	0
O(5)	8g		0.1491(5)	0.0854(2)	¼	0.014(2)	0.017(2)	0.016(2)	-0.000(2)	0	0
O(6)	4c		0	0.9808(2)	¼	0.021(4)	0.013(2)	0.020(3)	0	0	0
O(7)	16h		0.2892(5)	0.1925(2)	0.0704(2)	0.033(2)	0.034(2)	0.027(2)	0.004(2)	0.009(2)	0.001(2)
O(8)	16h		0.2776(5)	0.3037(2)	0.1344(2)	0.040(3)	0.029(2)	0.034(2)	-0.011(2)	-0.000(2)	0.008(2)
O(9)	8g		0.2693(6)	0.2084(2)	¼	0.018(3)	0.018(2)	0.021(2)	0.000(2)	0	0
O(10)	8f		0	0.2538(2)	0.0763(3)	0.026(3)	0.025(2)	0.020(2)	0	0	0.007(2)
O(11)	8f		0	0.1644(2)	0.1682(3)	0.020(3)	0.011(2)	0.017(2)	0	0	-0.001(2)
O(12)	4c		0	0.2698(2)	¼	0.025(4)	0.015(3)	0.014(3)	0	0	0
OW(1)	4c		0	0.3915(3)	¼	0.031(5)	0.023(3)	0.108(8)	0	0	0
OW(2)	4c		0	0.8645(3)	¼	0.029(5)	0.022(3)	0.056(5)	0	0	0

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