

The lengths of the b and c axes in $(\text{NH}_4)\text{Mo}_3\text{O}_9$ and $\text{K}_{1-x}\text{Mo}_3\text{O}_9$ are therefore nearly identical. On the other hand, the difference in the radii of NH_4^+ and K^+ causes an increase of the a axis by 0.54 \AA in going from $\text{K}_{1-x}\text{Mo}_3\text{O}_9$ to $(\text{NH}_4)\text{Mo}_3\text{O}_9$.

Assuming oxidation numbers of -3 for N, $+1$ for H, and -2 for O, a mean oxidation number of $+5.66$ can be calculated for Mo, *i.e.* the formula unit contains two Mo^{6+} and one Mo^{5+} . Keeping in mind the stoichiometric ratio of Mo(1) and Mo(2) as well as the different mean bond lengths Mo(1)—O (1.972 \AA) and Mo(2)—O (1.997 \AA) which are in agreement with the difference in the effective ionic radii for Mo^{6+} (0.59 \AA) and Mo^{5+} (0.61 \AA), both in octahedral coordination (Shannon, 1976), the chemical formula of the new ammonium molybdenum bronze may be written as $(\text{NH}_4)\text{Mo}(\text{1})_2^{\text{6+}}\text{Mo}(\text{2})^{\text{5+}}\text{O}_9$.

Acta Cryst. (1990). C46, 2009–2011

Structure of a Molybdenum(V) Phosphate $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$

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(Received 19 May 1989; accepted 25 September 1989)

Abstract. Dimolybdenum potassium triphosphate, $M_r = 531.90$, monoclinic, $P2_1/c$, $a = 9.701(3)$, $b = 18.848(2)$, $c = 6.389(5) \text{ \AA}$, $\beta = 106.96(3)^\circ$, $V = 1117(2) \text{ \AA}^3$, $Z = 4$, D_m not measured, $D_x = 3.16 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 3.05 \text{ mm}^{-1}$, $F(000) = 252$, $T = 293 \text{ K}$, 2624 reflections, $R = 0.026$, $wR = 0.025$. The lattice is built up of MoO_6 , PO_4 and P_2O_7 groups delimiting tunnels where the K^+ ions lie. The framework is more symmetrical than those of the Rb or Cs compounds.

Introduction. The $A\text{-Mo-P-O}$ ($A = \text{alkaline ions}$) system contains a very large number of compounds with molybdenum in oxidation states less than VI showing the great ability of the PO_4 tetrahedra to form various frameworks with MoO_6 octahedra.

The investigation, by several authors of the $A\text{-Mo}^v\text{-P-O}$ system has shown the formation of $\text{K}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ (or $\alpha\text{-KMo}_2\text{P}_3\text{O}_{13}$) (Leclaire, Monier & Raveau, 1983), α - and $\beta\text{-CsMo}_2\text{P}_3\text{O}_{13}$ (Lii & Haushalter, 1987), $\beta\text{-RbMo}_2\text{P}_3\text{O}_{13}$ (Riou & Goreaud, 1989), $\gamma\text{-CsMo}_2\text{P}_3\text{O}_{13}$ (Chen, Lii & Wang, 1988), $\delta\text{-KMo}_2\text{P}_3\text{O}_{13}$ (Leclaire, Borel, Grandin & Raveau, 1989) and $A\text{Mo}_5\text{P}_8\text{O}_{33}$ ($A = \text{Li, Na, Ag}$) (Lii, Johnston, Goshorn & Haushalter, 1987).

The generous support given by the Fonds der Chemischen Industrie is gratefully acknowledged.

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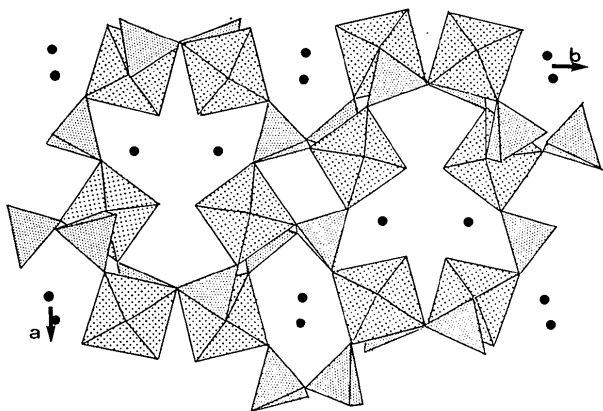
During the investigation of this system we obtained the $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$ compound; its cell parameters correspond to those obtained from powder diffraction by Lii & Haushalter (1987) for $\beta\text{-CsMo}_2\text{P}_3\text{O}_{13}$ but the a and c axes are inverted and the space group is $P2_1/c$ instead of $P2_1$. Intrigued by this result we have determined the crystal structure of $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$.

Experimental. The preparation was performed in two steps. First, $(\text{NH}_4)_2\text{HPO}_4$, K_2CO_3 and MoO_3 were mixed in an agate mortar in the molecular ratios needed to obtain the composition $\text{KMo}_{1.67}\text{P}_3\text{O}_{13}$ and heated at 600 K to decompose the ammonium phosphate and the carbonate. The resulting mixture was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for several days at 1300 K. Several forms of green crystals were obtained, yellow-green hexagonal prismatic crystals of $\beta\text{-KMo}_2\text{P}_3\text{O}_{13}$ and emerald green polyhedral crystals of $\delta\text{-KMo}_2\text{P}_3\text{O}_{13}$ (Leclaire *et al.*, 1989). Yellow-green crystal $0.168 \times 0.036 \times 0.024 \text{ mm}$. m symmetry with systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$. Space group $P2_1/c$. Enraf-Nonius CAD-4

Table 1. Positional parameters and their estimated standard deviations

$$B_{eq} = (4/3) \sum_i \beta_i a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
Mo(1)	0.06417 (4)	0.16238 (2)	0.38290 (6)	0.520 (5)
Mo(2)	0.61627 (4)	0.37300 (2)	0.18747 (6)	0.518 (5)
P(1)	0.2970 (1)	0.59086 (6)	0.2686 (2)	0.64 (2)
P(2)	0.3053 (1)	0.46506 (6)	0.0082 (2)	0.58 (2)
P(3)	-0.0343 (1)	0.32612 (6)	0.3404 (2)	0.59 (2)
K(1)	0.0521 (3)	0.0034 (2)	-0.0242 (5)	4.50 (8)
K(2)	0.3615 (3)	0.1648 (2)	0.0416 (6)	4.38 (7)
O(1)	0.2141 (3)	0.2106 (2)	0.4483 (5)	1.21 (6)
O(2)	0.0605 (3)	0.1522 (2)	0.0685 (5)	0.93 (5)
O(3)	0.0528 (3)	0.1512 (2)	0.6864 (4)	1.04 (5)
O(4)	0.5127 (3)	0.0632 (2)	0.4154 (5)	0.83 (5)
O(5)	-0.0708 (3)	0.2474 (2)	0.3228 (5)	0.95 (5)
O(6)	-0.1395 (3)	0.1066 (2)	0.2804 (5)	1.12 (6)
O(7)	0.5773 (3)	0.2874 (2)	0.1931 (6)	1.58 (6)
O(8)	0.6249 (3)	0.3715 (2)	-0.1270 (4)	0.88 (5)
O(9)	0.6171 (3)	0.4000 (2)	0.4936 (4)	0.89 (5)
O(10)	0.8296 (3)	0.3706 (2)	0.2885 (5)	1.11 (5)
O(11)	0.4079 (3)	0.4036 (2)	0.0837 (5)	0.96 (5)
O(12)	0.6573 (3)	0.4856 (2)	0.1502 (5)	0.87 (5)
O(13)	0.3087 (3)	0.5073 (2)	0.2258 (5)	0.89 (5)

Fig. 1. Projection of the structure of β - $\text{KMo}_2\text{P}_3\text{O}_{13}$ along c . The dots are the half occupied positions of the K^+ ions.Table 2. Distances (\AA) and angles ($^\circ$) in the MoO_6 octahedra, PO_4 polyhedra and mean $\text{K}-\text{O}$ distances

MoO ₆ octahedra						
Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.662 (3)	2.685 (4)	2.721 (4)	2.837 (4)	2.733 (4)	3.823 (4)
O(2)	93.6 (1)	2.008 (3)	3.970 (4)	2.715 (4)	2.948 (4)	2.805 (4)
O(3)	96.1 (1)	167.7 (1)	1.985 (3)	2.769 (4)	2.915 (4)	2.845 (4)
O(4)	99.4 (1)	84.2 (1)	86.8 (1)	2.043 (3)	4.045 (4)	2.833 (4)
O(5)	94.9 (1)	93.7 (1)	93.0 (1)	165.7 (1)	2.034 (3)	2.730 (4)
O(6)	175.3 (1)	84.4 (1)	86.5 (1)	84.6 (1)	81.1 (1)	2.164 (3)
Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1.660 (3)	2.731 (4)	2.812 (4)	2.819 (4)	2.705 (4)	3.841 (4)
O(8)	94.8 (1)	2.036 (3)	4.024 (4)	2.814 (4)	2.875 (4)	2.745 (4)
O(9)	99.2 (1)	166.0 (1)	2.019 (3)	2.802 (4)	2.808 (4)	2.841 (4)
O(10)	101.1 (1)	88.9 (1)	88.9 (1)	1.980 (3)	3.964 (4)	2.722 (4)
O(11)	94.1 (1)	90.3 (1)	88.1 (1)	164.7 (1)	2.019 (3)	2.798 (4)
O(12)	175.1 (1)	81.1 (1)	85.0 (1)	81.5 (1)	83.4 (1)	2.184 (3)
PO ₄ tetrahedra						
P(1)	O(6 ⁱ)	O(8 ⁱⁱ)	O(9 ⁱⁱⁱ)	O(13)		
O(6 ⁱ)	1.496 (3)	2.556 (4)	2.534 (4)	2.483 (4)		
O(8 ⁱⁱ)	116.1 (2)	1.516 (3)	2.462 (4)	2.505 (4)		
O(9 ⁱⁱⁱ)	114.6 (2)	108.7 (2)	1.514 (3)	2.457 (4)		
O(13)	106.1 (2)	106.5 (2)	103.7 (2)	1.609 (3)		
P(2)	O(4 ^{iv})	O(11)	O(12 ^v)	O(13)		
O(4 ^{iv})	1.521 (3)	2.475 (4)	2.482 (4)	2.497 (4)		
O(11)	109.4 (2)	1.512 (3)	2.539 (4)	2.466 (4)		
O(12 ^v)	110.7 (2)	115.2 (2)	1.495 (3)	2.522 (4)		
O(13)	106.6 (2)	105.1 (2)	109.4 (2)	1.594 (3)		
P(3)	O(2 ^{vi})	O(3 ^{vii})	O(5)	O(10 ^{viii})		
O(2 ^{vi})	1.535 (3)	2.421 (4)	2.550 (4)	2.463 (4)		
O(3 ^{vii})	104.2 (2)	1.533 (3)	2.542 (4)	2.472 (4)		
O(5)	113.1 (2)	112.6 (2)	1.522 (3)	2.500 (4)		
O(10 ^{viii})	107.6 (2)	108.3 (2)	110.7 (2)	1.517 (3)		
K—O distances (\AA)						
K(1)—O(2 ^{vi})	3.114 (4)	K(2)—O(1 ^{iv})	2.724 (4)			
K(1)—O(2)	2.863 (4)	K(2)—O(2)	2.985 (4)			
K(1)—O(3 ^{vii})	3.344 (4)	K(2)—O(3 ^{vii})	3.197 (4)			
K(1)—O(4 ^{iv})	2.978 (4)	K(2)—O(7)	3.079 (4)			
K(1)—O(4)	2.917 (4)	K(2)—O(8 ⁱⁱ)	2.885 (4)			
K(1)—O(6 ⁱ)	2.917 (4)	K(2)—O(9 ⁱⁱⁱ)	2.859 (4)			
K(1)—O(10 ^{viii})	3.198 (4)	K(2)—O(11 ^v)	3.344 (4)			
K(1)—O(10 ^v)	2.974 (4)					
K(1)—O(12 ^v)	3.137 (4)					
K(1)—O(13 ^{ix})	3.333 (4)					

Symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $x - 1, y, z$; (vii) $-x, -y, -z$; (viii) $x, y, z - 1$; (ix) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$; (x) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Associates Inc., 1982), $(\Delta/\sigma)_{\max} = 0.01$, $\Delta\rho = 2.8 \text{ e } \text{\AA}^{-3}$, $R = 0.026$, $wR = 0.025$, $S = 1.31$, $w = 1/\sigma^2 F_o$. Atomic parameters given in Table 1.*

Discussion. The β - $\text{Mo}_2\text{P}_3\text{O}_{13}$ framework of the potassium oxide (Fig. 1) is very similar to those of the Rb or Cs compounds but it is more symmetrical than those latter phases, leading to the space group $P2_1/c$ instead of $P2_1$. It is built up from MoO_6 octahedra,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52709 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

diffractometer. Unit cell: least squares on 25 reflections $36 < 2\theta < 44^\circ$. Intensity: measurement by ω - θ scan of $(0.9 + 0.35 \tan \theta)^\circ$ with a $(1 + \tan \theta)$ mm counter slit; determined by a study of some reflections in the $\omega\theta$ plane. Scan speed adjusted to obtain $\sigma(I)/I < 0.018$ or to approach it in a time limited to 60 s. Three standards: for count, every 2000 s, and for orientation every 600 reflections; no appreciable trends. 4387 reflections measured. 2624 reflections ($h_{\max} = 19$, $k_{\max} = 37$, $l_{\max} = 12$), $2 < \theta < 45^\circ$, with $I/\sigma(I) > 3$ used to solve and refine the structure. No correction made for extinction and absorption. Structure solved by heavy-atom method. Refinement by full-matrix least squares using F^2 s. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The two independent positions of the K ions are half occupied. Calculation on a MicroVAX II with the SDP system (B. A. Frenz &

PO₄ tetrahedra and P₂O₇ groups allowing the formula K(MoO)₂(PO₄)(P₂O₇) and delimiting various tunnels.

Each K⁺ ion is statistically distributed over two positions. In the half occupied K(1) sites, potassium is distributed at random in the six-sided tunnels, two adjacent sites which correspond to each other by a symmetry center not being occupied simultaneously. In the larger tunnels two identical cages are available for one K(2) ion so that the latter is distributed at random over these two equivalent sites which are half occupied.

This main difference from the rubidium and caesium molybdenophosphate is easily explained by the size of K⁺ which is smaller than Rb⁺ and Cs⁺. This cation, unlike the other alkaline cations, does not induce any distortion of the β-Mo₂PO₃O₁₃ framework; consequently, as higher crystal symmetry is observed, no ordering of the K⁺ ions in the tunnels is obtained, in contrast to Rb⁺ and Cs⁺ for which the two sorts of cages exhibit a different size and geometry.

The MoO₆ octahedra correspond to those observed in the literature for Mo^v with one very short Mo—O bond, four medium ones and a very long one (Table 2).

The P(3)—O distances correspond to those of a monophosphate, *i.e.* four almost equal distances. The P(1)—O and the P(2)—O distances correspond to those observed in the tetrahedra of the diphosphate groups, *i.e.* one long distance and three medium ones (Table 2).

K(1) is surrounded by ten O atoms with K—O distances ranging from 2.863 (4) to 3.344 (4) Å and K(2) is bonded to seven O atoms with 2.724 (4) < K—O < 3.344 (4) Å (Table 2).

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Acta Cryst. (1990). **C46**, 2011–2013

Structure of (Na_{2/3}Zr_{1/3})₂P₂O₇

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(Received 28 June 1989; accepted 22 January 1990)

Abstract. Sodium zirconium diphosphate, $M_r = 265.4$, orthorhombic, $Fddd$, origin on $\bar{1}$, $a = 6.867$ (5), $b = 12.345$ (4), $c = 27.527$ (5) Å, $V = 2333$ (2) Å³, $Z = 16$, $D_x = 3.022$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70107$ Å, $\mu = 17.76$ cm⁻¹, $F(000) = 2037.33$, $T = 293$ K, $R = 0.07$ for 420 independent reflections. The asymmetric unit contains a single, disordered metal site. In the crystal, two thirds of these sites are occupied by Na⁺ ions and the remainder by Zr⁴⁺ ions. Each metal site is surrounded by a distorted octahedron of diphosphate O atoms. The two PO₄ tetrahedra in each diphosphate anion are related by a diad axis passing through the O atom linking the P

atoms. The structure can be described as a piling up of slices parallel to (001) with thickness $c/8$. In each slice, diphosphate anions are aligned parallel to $\langle 110 \rangle$ and distributed in a pseudotrigonal grid ($b/a \approx 3^{1/2}$). (Na,Zr) octahedra form strips parallel to $\langle 110 \rangle$ by sharing edges, and connect three different anions in the slice and two anions in adjacent slices.

Introduction. Crystals of the title compound were prepared in teflon liners by the hydrothermal method using Morey-type autoclaves at 423 K and 15 MPa. A typical starting mixture consisted of NaOH (5 g), ZrOCl₂ (1 g) and 85% H₃PO₄ (12 ml). The resulting