

## A novel form of molybdenum (V) phosphate: $\delta$ - $\text{KMo}_2\text{P}_3\text{O}_{13}$

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Potassium molybdenum phosphate and pyrophosphate*

**Abstract.** A new form of molybdenum (V) phosphate has been isolated. The structure of this oxide has been determined from a single crystal X-ray diffraction study. It crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 8.846(8)$  Å,  $b = 8.846(9)$  Å,  $c = 10.01(1)$  Å,  $\alpha = 56.488(8)^\circ$ ,  $\beta = 55.588(7)^\circ$ ,  $\gamma = 68.868(7)^\circ$ ,  $Z = 1$ . The refinement has led to  $R = 0.022$  and  $R_w = 0.026$  for 5243 reflections with  $I \geq 3\sigma(I)$ . The structure consists of corner-sharing  $\text{MoO}_6$  octahedra,  $\text{P}_2\text{O}_7$  tetrahedra forming tunnels running along  $[0\bar{1}1]$  where the  $\text{K}^+$  ions are located. One original feature of this structure, compared to the other forms –  $\alpha$ ,  $\beta$ ,  $\gamma$  – deals with the existence of  $\text{Mo}_2\text{P}_2\text{O}_{15}$  units formed of one  $\text{P}_2\text{O}_7$  group sharing four of its corners with two  $\text{MoO}_6$  octahedra.

### Introduction

The pentavalent state of molybdenum appears as rather unusual in oxides owing to the particular coordination of this cation which requires one abnormally short Mo–O bond, close to 1.60 Å, and is so strongly off centered in its “ $\text{O}_6$ ” octahedron. The strongly covalent character of one of the six Mo–O bonds of the octahedron, implies that the corresponding oxygen be only linked to this element. Such a behaviour should be favoured by realising a mixed framework in which the  $\text{MoO}_6$  octahedra would be isolated, i.e. only linked to more covalent polyhedra such as  $\text{PO}_4$  or  $\text{SiO}_4$  tetrahedra. The recent studies of the molybdenum phosphates show the great ability of phosphorus to stabilize  $\text{Mo}^{\text{V}}$  in oxides. Besides the oxide

MoPO<sub>5</sub> discovered by Kierkegaard (Kierkegaard and Westerlund, 1964), four different forms of molybdenum phosphate of univalent ions were successively isolated with the composition AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub>: ( $\alpha$ -form) for A = K (Leclaire et al. 1983)  $\beta$ -AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> for A = K, Rb, Cs, Tl (Lii and Haushalter, 1987); and  $\gamma$ -AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> for A = Cs (Chen et al., 1988) and  $\alpha$ -form for A = Cs (Lii and Haushalter, 1987). These latter results confirm the great ability of the monophosphate and diphosphate groups to adapt to the MoO<sub>6</sub> octahedra, and suggest that the variation of experimental conditions could allow new forms to be isolated. The present paper deals with the structural study of a third form of the potassium oxide called  $\delta$ -KMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub>.

## Synthesis

The preparation was performed in two steps. First, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, MoO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were mixed in an agate mortar in the molecular ratio to obtain the stoichiometric KMo<sub>1.66</sub>P<sub>3</sub>O<sub>13</sub> and heated at 600 K to decompose the potassium carbonate and the ammonium phosphate. The resulting mixture was then added to the required amount of molybdenum, and placed in an evacuated silica ampoule. This mixture heated for several days yielded at 1073 K  $\alpha$ -KMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> (Leclaire et al., 1983), at 1273 K green crystals of  $\delta$ -KMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub>.

## Determination and refinement of the structure

Weissenberg and precession photographs indicate a triclinic symmetry  $P\bar{1}$ . The cell dimension obtained and refined from single crystal high theta data are:  $a = 8.8464(8)$  Å,  $b = 8.8478(9)$  Å,  $c = 10.01(1)$  Å,  $\alpha = 56.488(8)^\circ$ ,  $\beta = 55.588(7)^\circ$ ,  $\gamma = 68.868(8)^\circ$ .

The cell contains one formula unit KMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub>. The data were collected on a CAD-4 Enraf Nonius diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The intensities were measured up to  $\theta = 45^\circ$  with a  $\omega$ -4/3  $\theta$  scan of  $(0.9 + 0.35 \text{tg} \theta)^\circ$  and a counter slit aperture of  $(1.0 + \text{tg} \theta)$  mm all determined after a study of some reflections in the  $\omega$ - $\theta$  plane. The background intensity was measured on both sides of each reflections. A periodic control of three reflections verified the stability of the sample. 5243 reflections with  $I \geq 3\sigma(I)$ , corrected for Lorentz and polarisation effects were used to solve and refine the structure. No absorption corrections were applied.

The positions of molybdenum atoms were determined from a Patterson synthesis. The phosphorus and oxygen atoms were located by subsequent Fourier syntheses. The refinement of the coordinates and the anisotropic thermal factors of all the atoms led to  $R = 0.022$ ,  $R_w = 0.026$  and to the

**Table 1.** Atomic parameters.

Atom	x	y	z	B (Å <sup>2</sup> )
Mo(1)	0.00751(2)	0.17364(2)	0.16264(2)	0.527(4)
Mo(2)	0.34382(2)	0.33738(2)	0.32635(2)	0.522(4)
P(1)	0.26056(7)	0.48946(7)	-0.01052(7)	0.46(1)
P(2)	0.08727(7)	-0.26151(7)	0.35204(7)	0.54(1)
P(3)	-0.1780(2)	-0.1480(2)	0.2390(2)	0.53(1)
K(1)	0.500	0.000	0.000	4.81(6)
K(2)	0.500	0.500	0.500	4.82(8)
O(1)	-0.0816(2)	0.3959(2)	0.0006(2)	0.75(4)
O(2)	0.1977(2)	0.1501(3)	-0.1011(2)	1.01(5)
O(3)	0.2327(2)	0.2916(2)	0.0600(3)	0.87(5)
O(4)	0.1477(2)	-0.0693(2)	0.2543(2)	0.89(5)
O(5)	-0.1649(2)	0.0411(2)	0.1981(3)	1.05(6)
O(6)	-0.1220(3)	0.1973(3)	0.3516(3)	1.58(7)
O(7)	0.3147(2)	0.4996(2)	0.1041(2)	0.78(5)
O(8)	0.5842(2)	0.4398(3)	0.2087(2)	0.88(5)
O(9)	0.2462(2)	0.6009(2)	0.3503(3)	0.98(5)
O(10)	0.3327(2)	0.2453(2)	0.5695(2)	0.90(5)
O(11)	0.0741(2)	0.3017(3)	0.4590(2)	1.05(5)
O(12)	0.4264(3)	0.1490(3)	0.3023(3)	1.60(7)
O(13)	0.0109(2)	-0.2605(2)	0.2392(2)	0.79(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $4/3 \cdot [a^2 B_{11} + \dots bc \cos \alpha B_{23}]$ .

atomic parameters Table 1<sup>1</sup>. The scattering factors are taken from International Tables for X-ray Crystallography (1974).

## Discussion

$\delta$ -KMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> exhibits a complex structure whose host lattice [Mo<sub>2</sub>P<sub>3</sub>O<sub>13</sub>] is formed of corner-sharing MoO<sub>6</sub> octahedra, P<sub>2</sub>O<sub>7</sub> groups and PO<sub>4</sub> tetrahedra (Fig. 1). This three-dimensional framework delimits tunnels running along [0 $\bar{1}$ 1] where the potassium ions are located (Fig. 2).

The geometry of the MoO<sub>6</sub> octahedra is characteristic of that generally observed for Mo<sup>V</sup>, i.e. very similar to those of Mo<sup>V</sup> in the forms  $\alpha$  (Leclaire et al., 1983),  $\beta$ -CsMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> (Lii and Haushalter, 1987) and  $\gamma$ -CsMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> (Chen et al., 1988) or AgMo<sub>5</sub>P<sub>8</sub>O<sub>33</sub> (Lii et al., 1987). The "O<sub>6</sub>" octahedron is very regular, but the molybdenum is strongly off-centered towards one oxygen atom forming a very short Mo-O bond (1.657–1.654 Å), whereas four Mo-O distances are normal (1.982–2.047 Å) and one is abnormally

<sup>1</sup> Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 53504, the names of the authors and the title of the paper.

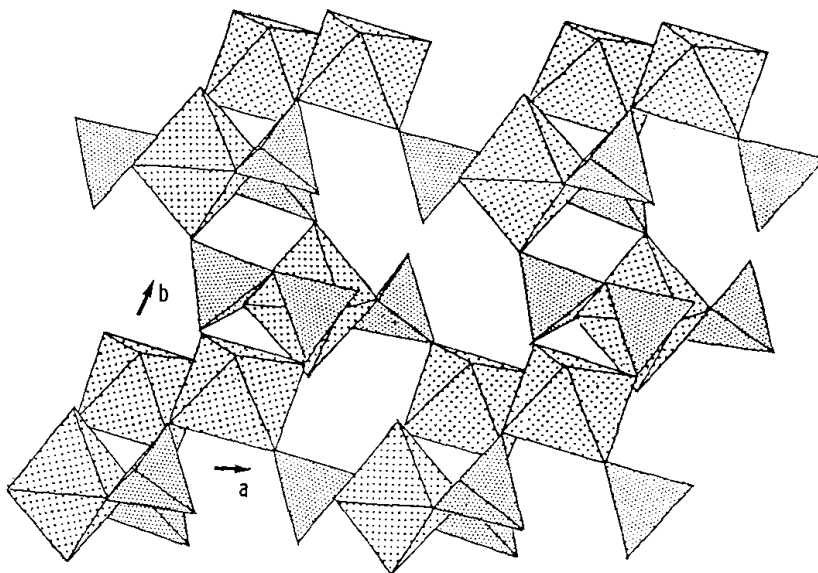


Fig. 1. Structure of  $\delta\text{-KM}_2\text{P}_3\text{O}_{13}$  projected onto (001).

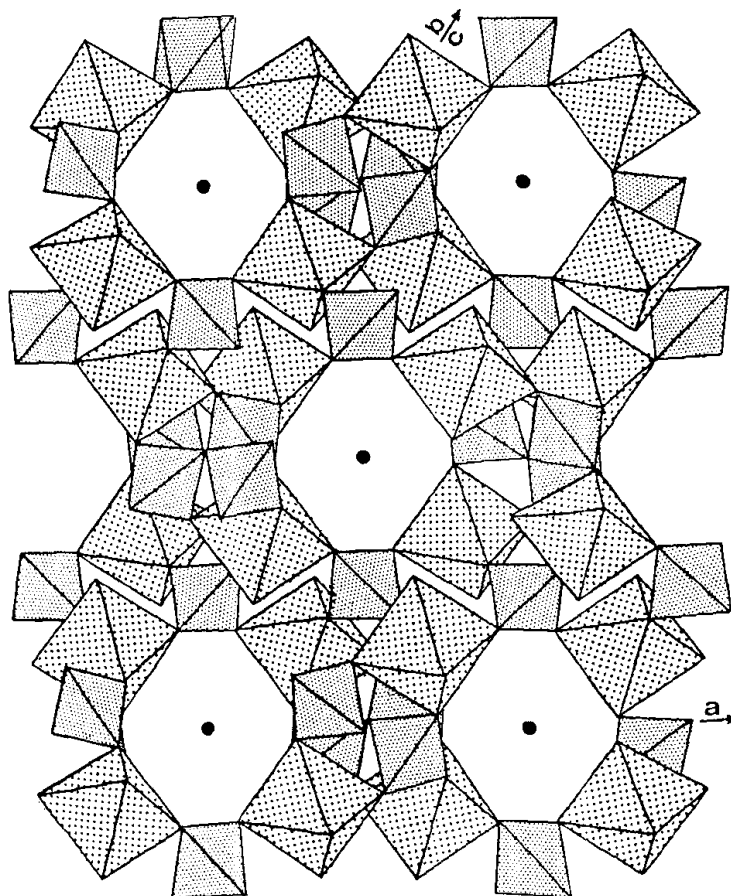
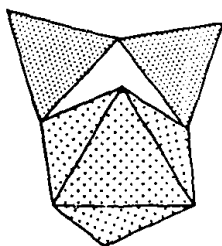
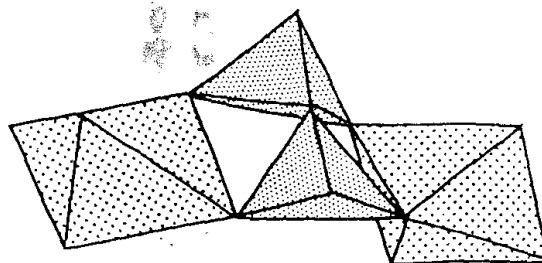


Fig. 2. Projection of the structure along [011] showing the tunnels.

**Table 2.** Distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the "MoO<sub>6</sub>" octahedra.

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.981(2)	2.756(3)	2.889(3)		2.734(2)	2.787(3)
O(2)	80.41(7)	2.274(2)	2.708(4)	2.798(3)	2.893(2)	
O(3)	92.20(8)	77.8(1)	2.028(2)	2.787(2)		2.812(2)
O(4)	160.76(9)	80.53(7)	86.30(8)	2.046(2)	2.850(4)	2.838(3)
O(5)	86.43(9)	84.66(9)	162.35(9)	89.23(9)	2.011(3)	2.792(5)
O(6)	99.7(1)	176.7(1)	98.9(1)	99.5(1)	98.6(1)	1.657(3)
Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1.982(2)	2.892(4)	2.756(4)		2.736(2)	2.783(3)
O(8)	92.29(8)	2.028(2)	2.711(2)	2.787(2)		2.810(4)
O(9)	80.41(9)	77.89(8)	2.274(2)	2.800(2)	2.893(4)	
O(10)	160.81(8)	86.30(9)	80.58(9)	2.047(2)	2.852(4)	2.839(5)
O(11)	86.42(8)	162.4(1)	84.60(9)	89.19(9)	2.014(2)	2.789(3)
O(12)	99.5(1)	99.0(1)	176.9(1)	99.6(1)	98.5(1)	1.654(3)

**Fig. 3.** The  $\text{MoP}_2\text{O}_{11}$  unit.**Fig. 4.** The  $\text{Mo}_2\text{P}_2\text{O}_{15}$  unit.

long (2.274  $\text{\AA}$ ) (Table 2). The sum of the electrostatic valences calculated with the Zachariazen curve (1978) confirms the valence V of molybdenum. It must be pointed out that like in the other  $\text{Mo}^{\text{V}}$  phosphates, the abnormally short Mo–O distance correspond to the oxygen atom which is not shared with other polyhedra in this framework.

The  $\text{PO}_4$  tetrahedra are regular: one observes four almost equal P–O distances in the monophosphate groups, whereas the diphosphate groups

which exhibit an eclipsed configuration are characterized by one long P—O bond corresponding to the bridging oxygen and three shorter P—O bonds. The coordination of potassium can be deduced from the maximum bond length calculated with Donnay and Allman's procedure (1970) using the revised ionic radii of Shannon (1976). From this maximum distance of 3.35 Å it appears that  $K^+$  has six nearest neighbours with K—O distances ranging from 2.693 to 2.992 Å.

The structure of  $\delta$ - $KMo_2P_3O_{13}$  is very different from those of the  $\alpha$ - $\beta$ - $\gamma$  forms, in spite of its identical composition. The framework of those latter oxides is indeed characterized by the presence of  $MoP_2O_{11}$  units which correspond to the association of one  $MoO_6$  octahedron and one  $P_2O_7$  group, sharing two of their corners (Fig. 3). The  $\delta$ -form differs from these phosphates by the fact that one diphosphate group shares two of its corners with the same  $MoO_6$  octahedron and two other corners with a second  $MoO_6$  octahedron forming original  $Mo_2P_2O_{15}$  units (Fig. 4). Thus the host lattice of  $\delta$ - $KMo_2P_3O_{13}$  consists of  $Mo_2P_2O_{15}$  units sharing four of their corners with single  $PO_4$  tetrahedra, whereas the framework of  $\alpha$ - $KMo_2P_3O_{13}$  is formed of corner-sharing  $MoP_2O_{11}$  units and single  $PO_4$  tetrahedra, and those of  $\beta$ - and  $\gamma$ - $CsMo_2P_3O_{13}$  are built up from  $MoP_2O_{11}$  units,  $MoO_6$  octahedra and single  $PO_4$  tetrahedra. Such  $Mo_2P_2O_{15}$  units seem to be observed for the first time in mixed frameworks involving a transition element, whereas the  $MoP_2O_{11}$  units are very current and not only limited to  $Mo^V$  phosphates but are also observed for other oxidation states of molybdenum as for instance in  $NaMoP_2O_7$  (Leclaire et al., 1988),  $Na_xMoP_2O_7$  (Leclaire et al., 1988),  $KMoP_2O_7$ ,  $K_{0.17}MoP_2O_7$  (Leclaire et al., 1989),  $RbMoP_2O_7$  (Leclaire et al., in the press) and  $CsMoP_2O_7$  (Lii and Haushalter, 1987).

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