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$K_2Mo_3AlP_8O_{28}$: a Tunnel Structure Isotypic with $Na_{0.5}MoP_2O_7$

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Abstract. $K_2Mo_3AlP_8O_{28}$, $M_r = 544{\cdot}39$, triclinic, $P\bar{1}$, $a = 4{\cdot}8171\ (8)$, $b = 7{\cdot}133\ (2)$, $c = 7{\cdot}998\ (2)$ Å, $\alpha = 90{\cdot}53\ (2)$, $\beta = 92{\cdot}95\ (2)$, $\gamma = 105{\cdot}18\ (2)^\circ$, $V = 264{\cdot}8\ (2)$ Å^3, $Z = 0{\cdot}5$, $D_x = 3{\cdot}41$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}568$ mm^{-1}, $T = 294$ K, $F(000) = 260{\cdot}50$, $R = 0{\cdot}061$, $wR = 0{\cdot}068$ for 856 observed reflections. The host lattice of this phase is built up from MoO_6 and AlO_6 octahedra sharing corners with PO_4 tetrahedra and belongs to the $Na_{0.5}MoP_2O_7$-type structure. The tunnels are fully occupied by K^+ ions and one kind of octahedral site is only occupied by molybdenum, whereas molybdenum and aluminium are distributed at random over the second kind of site.

Introduction. The structural study of the mixed-valence molybdenum phosphate $Na_{0.30}MoP_2O_7$, (Leclaire, Grandin & Raveau, 1988), has shown the possibility of formation of non-stoichiometric oxides, with large tunnels partly occupied by sodium. In spite of the great size of such octagonal tunnels, no isostructural potassium compound was obtained in the system K–Mo–P–O. In this latter system, another phase, $K_{0.17}MoP_2O_7$, with a different structure was indeed isolated (Leclaire, Borel, Grandin & Raveau, 1989). Considering the mixed valence of molybdenum Mo^{III}/Mo^{IV}, the substitution of aluminium for Mo^{III} was investigated. The present study reports on the structure of a new diphosphate $K_2Mo_3AlP_8O_{28}$, isotypic with $Na_{0.5}MoP_2O_7$.

Experimental. The crystals of this phase were isolated from a nominal composition $K_2Mo_2P_8O_{25}$. This synthesis was performed in two steps. Firstly, an appropriate mixture of K_2CO_3, $H(NH_4)_2PO_4$ and MoO_3 was heated to 673 K in air to eliminate CO_2, H_2O and NH_3. Secondly, the resulting finely ground product, mixed with an appropriate amount of molybdenum, was placed in an alumina crucible and sealed in an evacuated silica ampoule. This sample was then heated to 1073 K for 48 h and quenched at room temperature.

Purple crystals 0·148 × 0·024 × 0·024 mm. Enraf–Nonius CAD-4 diffractometer. Mo $K\alpha$ radiation. Unit cell: least squares on 25 reflections $\pm 2\theta$: $36 \le 2\theta \le 44^\circ$. Intensity: measurement by ω–θ scan of $(1{\cdot}25 + 0{\cdot}35\tan\theta)^\circ$ and with a $(1 + \tan\theta)$ mm counter slit; determined by a study of some reflections in the $\omega\theta$ plane. Scan speed adjusted so as to obtain $\sigma(I)/I \le 0{\cdot}018$ or to approach it in a time limited to 60 s. Three standard reflections (332, 323, 046) monitored for count, every 2000 s, and for orientation every 600 reflections; no appreciable trends. 4552 reflections measured, 4552 unique. 856 reflections ($h_{\max} = 9$, $k_{\max} = 14$, $l_{\max} = 15$), $2 \le \theta \le 45^\circ$ with $I/\sigma(I) \ge 3$ used to solve and refine the structure. No correction made for extinction or absorption. Structure solved by heavy-atom method. Refinement by full-matrix least squares using F's. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on a MicroVAX II with the *SDP* system (B.A. Frenz & Associates Inc., 1982). 65 parameters refined. $w = 1/\sigma(I)$. $(\Delta/\sigma)_{\max} = 0{\cdot}004$, $\Delta\rho \le 1{\cdot}8$ e Å^{-3}, $R = 0{\cdot}061$, $wR = 0{\cdot}068$, $S = 0{\cdot}98$. Atomic parameters are given in Table 1.* The refinement of the occupancy factor of the 0·5, 0·5, 0·5 position using molybdenum diffusion tables leads to a number of electrons corresponding to $\frac{1}{2}$ Mo and $\frac{1}{2}$ Al distributed at random over this position in agreement with microprobe analysis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52811 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. The host lattice of $K_2Mo_3AlP_8O_{28}$ ($K_{0\cdot5}Mo_{0\cdot75}Al_{0\cdot25}P_2O_7$) is similar to that of $Na_{0\cdot3}MoP_2O_7$ (Leclaire *et al.*, 1988) (Fig. 1). One observes MoO_6 and $(Mo,Al)O_6$ octahedra sharing their corners with diphosphate groups in such a way that each octahedron is surrounded by six PO_4 tetrahedra and reciprocally each PO_4 tetrahedron is linked to three octahedra and one PO_4 tetrahedron. This framework delimits large octagonal tunnels where the K^+ ions are located.

The geometry of the PO_4 tetrahedra (Table 2) is very similar to that previously observed in other molybdenum phosphates or silicophosphates involving diphosphate groups. They are characterized by three short P—O distances ranging from 1·50 to 1·53 Å which correspond to the O atom common to an octahedron and a tetrahedron, and one longer P—O distance ranging from 1·60 to 1·61 Å, which corresponds to the bridging oxygen of the P_2O_7 group.

One original feature of the phase $K_2Mo_3AlP_8O_{28}$ concerns the semi-ordered distribution of molybdenum and aluminium. One observes two sorts of octahedral sites. One kind of site, called 'Mo', is only occupied by molybdenum, whereas in the second,

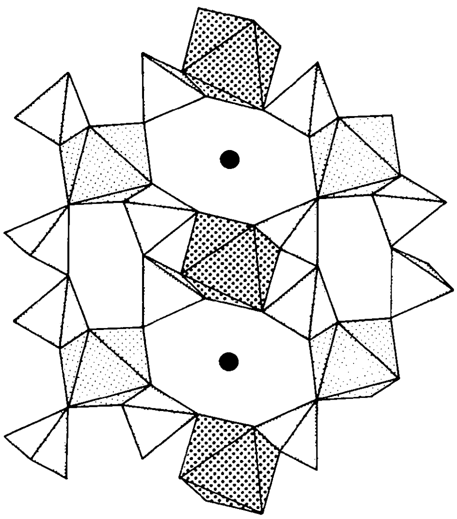

Fig. 1. Projection of the structure of $K_2Mo_3AlP_8O_{28}$ along **a**.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mo(1)	0·000	0·000	0·000	0·97 (2)
Mo,Al	0·500	0·500	0·500	0·65 (3)
K	0·000	0·000	0·500	3·3 (1)
P(1)	−0·3795 (6)	0·2417 (4)	0·1953 (4)	0·65 (4)
P(2)	0·0161 (6)	−0·3816 (4)	0·2532 (4)	0·65 (4)
O(1)	−0·190 (2)	0·102 (1)	0·186 (1)	0·8 (1)
O(2)	0·094 (2)	−0·201 (1)	0·153 (1)	1·2 (1)
O(3)	0·368 (2)	0·192 (1)	0·071 (1)	0·9 (1)
O(4)	0·155 (2)	0·351 (1)	0·597 (1)	1·0 (1)
O(5)	0·278 (2)	0·550 (1)	0·305 (1)	0·9 (1)
O(6)	0·544 (2)	0·260 (1)	0·375 (1)	1·0 (1)
O(7)	−0·197 (2)	0·450 (1)	0·138 (1)	0·7 (1)

Table 2. *Principal bond lengths* (Å) *and angles* (°) *in the different polyhedra*

P(1)	O(1)	O(3^{iii})	O(6^{iii})	O(7)
O(1)	1·52 (1)	2·51 (1)	2·47 (1)	2·52 (1)
O(3^{iii})	112·8 (5)	1·50 (1)	2·54 (1)	2·43 (1)
O(6^{iii})	109·1 (5)	114·5 (5)	1·52 (1)	2·53 (1)
O(7)	107·8 (5)	103·5 (5)	108·0 (5)	1·60 (1)

P(2)	O(2)	O(4^{iv})	O(5^{v})	O(7^{v})
O(2)	1·50 (1)	2·49 (1)	2·48 (1)	2·52 (1)
O(4^{iv})	110·5 (6)	1·53 (1)	2·52 (1)	2·51 (1)
O(5)	111·5 (5)	112·4 (5)	1·51 (1)	2·52 (1)
O(7)	108·1 (5)	106·2 (4)	107·9 (5)	1·61 (1)

Mo(1)	O(1)	O(1^{i})	O(2)	O(2^{i})	O(3)	O(3^{i})
O(1)	2·012 (9)	4·02 (1)	2·86 (1)	2·83 (1)	2·80 (1)	2·85 (1)
O(1^{i})	180·0	2·012 (9)	2·83 (1)	2·86 (1)	2·85 (1)	2·80 (1)
O(2)	90·6 (4)	89·4 (4)	2·016 (10)	4·03 (1)	2·86 (1)	2·80 (1)
O(2^{i})	89·4 (4)	90·6 (4)	180·0	2·016 (10)	2·80 (1)	2·86 (1)
O(3)	88·9 (3)	91·1 (3)	91·3 (4)	88·7 (4)	1·986 (8)	3·97 (1)
O(3^{i})	91·1 (3)	88·9 (3)	88·7 (4)	91·3 (4)	180·0	1·986 (8)

Mo,Al	O(4)	O(4^{ii})	O(5)	O(5^{ii})	O(6)	O(6^{ii})
O(4)	1·928 (8)	3·86 (1)	2·75 (1)	2·71 (1)	2·84 (1)	2·78 (1)
O(4^{ii})	180·0	1·928 (8)	2·71 (1)	2·75 (1)	2·78 (1)	2·84 (1)
O(5)	91·0 (4)	89·0 (4)	1·934 (9)	3·87 (1)	2·76 (1)	2·86 (1)
O(5^{ii})	89·0 (4)	91·0 (4)	180·0	1·934 (9)	2·86 (1)	2·76 (1)
O(6)	91·2 (4)	88·8 (4)	87·8 (4)	92·2 (4)	2·040 (9)	4·08 (1)
O(6^{ii})	88·8 (4)	91·2 (4)	92·2 (4)	87·8 (4)	180·0	2·040 (9)

K—O (4)	2·52 (1)	K—O (6)	3·01 (1)
K—O (4^{iv})	2·52 (1)	K—O (6^{iv})	3·01 (1)
K—O (1)	2·80 (1)	K—O (2)	3·22 (1)
K—O (1^{iv})	2·80 (1)	K—O (2^{iv})	3·22 (1)

Symmetry code: (i) $-x, y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $-x, y, 1-z$; (v) $1-x, y, 1-z$.

called 'Mo,Al', aluminium and molybdenum ions are distributed at random. It is worth pointing out that the 'Mo' octahedra which share their corners with six different P_2O_7 groups are almost regular (Table 2) with Mo—O distances ranging from 1·986 to 2·016 Å. The 'Mo,Al' octahedra exhibit much smaller distances in agreement with the size of aluminium. Moreover they are more distorted owing to the fact that each 'Mo,Al' octahedron shares the four corners of its basal plane with two P_2O_7 groups (Fig. 2), the two other opposite apices being linked to two different diphosphate groups. The molybdenum valency in the different sites is not clearly established. The calculation of the sum of the electrostatic bond strengths according to the theory developed by Zachariasen (1978) leads to the valent state of 4·18 for the octahedra only occupied by molybdenum. This suggests that the 'Mo' octahedra are occupied by tetravalent molybdenum in agreement with the Mo—O distances (Table 2), whereas trivalent molybdenum and aluminium are statistically distributed over the same octahedral site. Nevertheless the latter distribution is rather unexpected owing to the large size of Mo^{III} compared to aluminium.

A second characteristic of this structure deals with the behaviour of K^+ cations which is different from that of Na^+. This cation is indeed surrounded by eight O atoms with K—O distances ranging from 2·52 to 3·22 Å (Table 2) against six for Na^+ (2·33 to 3·20 Å). This can be explained by the fact that the K^+ cations are located at a centre of symmetry, *i.e.* on the axis of the tunnels, while the Na^+ cations are off-centre. Consequently, the vibration of K^+ is preferentially oriented along the axis of the tunnel. Its thermal factor, B_{eq}, smaller than that of Na^+, is consistent with its larger size.

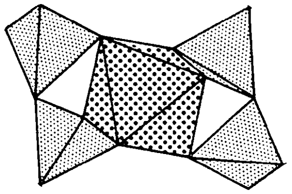

Fig. 2. The $(Mo,Al)P_4O_{16}$ unit.

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Thomsonite, a Neutron Diffraction Study at 13 K

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Abstract. The crystal structure of the natural thomsonite, $Na_{1\cdot00}Ca_{1\cdot88}Sr_{0\cdot12}Al_5Si_5O_{20}.6H_2O$, at 13 K [$M_r$ = 812·3, orthorhombic, *Pncn*, a = 13·1043 (14), b = 13·0569 (18), c = 13·2463 (30) Å, V = 2266 (1) Å^3, Z = 4, D_x = 2·381 g cm^{-3}, μ = 0·886 cm^{-1}] has been refined from neutron diffraction data [λ = 1·1588 (1) Å]. 4513 (3004 unique) reflections resulted in $R(F^2)$ = 0·0369. The structure is generally very close to the room-temperature structure [Pluth, Smith & Kvick, (1985). *Zeolites*, **5**, 74–80] and shows no sign of

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