Gd···W9	3.818 (2)	W4—O14	2.34 (2)
Gd—O15	2.39 (2)	W5—O36	1.73 (2)
Gd—O16	2.39 (2)	W5—O35	1.87 (2)
Gd—O17	2.42 (2)	W5—O32	1.90 (2)
Gd—O18	2.41 (2)	W5—O33	1.90 (2)
Gd—O19	2.40 (2)	W5—O34	1.90 (2)
Gd—O20	2.42 (2)	W5—O23	2.27 (2)
Gd—O21	2.42 (2)	W6—O24	1.69 (2)
Gd—O22	2.42 (2)	W6—O19	1.78 (2)
W0—O1	1.72 (2)	W6—O28	1.93 (2)
W0—O2	1.87 (2)	W6—O31	1.96 (2)
W0—O5	1.89 (2)	W6—O32	2.04 (2)
W0—O3	1.90 (2)	W6—O23	2.31 (2)
W0—O4	1.93 (2)	W7—O25	1.75 (2)
W0—O14	2.31 (1)	W7—O20	1.76 (2)
W1—O6	1.73 (2)	W7—O29	1.94 (2)
W1—O15	1.79 (1)	W7—O28	1.96 (2)
W1—O13	1.96 (2)	W7—O33	2.02 (2)
W1—O10	1.97 (2)	W7—O23	2.31 (2)
W1—O2	2.01 (2)	W8—O26	1.73 (2)
W1—O14	2.34 (2)	W8—O21	1.79 (1)
W2—O7	1.74 (2)	W8—O30	1.89 (2)
W2—O16	1.79 (1)	W8—O29	1.96 (2)
W2—O11	1.94 (2)	W8—O34	2.03 (2)
W2—O10	1.94 (2)	W8—O23	2.32 (2)
W2—O3	2.02 (2)	W9—O27	1.73 (2)
W2—O14	2.31 (2)	W9—O22	1.80 (2)
W3—O8	1.75 (2)	W9—O31	1.91 (2)
W3—O17	1.77 (2)	W9—O30	1.96 (2)
W3—O11	1.95 (2)	W9—O35	2.04 (2)
W3—O12	1.95 (2)	W9—O23	2.33 (2)

Data collection: *RCRYSTAN* (Rigaku Corporation, 1985). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AS1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Mo^V Monophosphate, $Rb_2Mo_2P_2O_{11}$

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Abstract

Molybdenum rubidium phosphate, $Rb_2Mo_2P_2O_{11}$, has been synthesized and the growth of single crystals allowed its structure to be determined. This compound is isotypic with $Tl_2Mo_2P_2O_{11}$ and $K_2Mo_2P_2O_{11}$, and contains a framework built from $Mo_2P_2O_{15}$ units formed by one Mo_2O_{11} group sharing four of its corners with two PO_4 tetrahedra, leading to $[Mo_2P_2O_{13}]_\infty$ chains running along **c**, or to $[Mo_2P_2O_{13}]_\infty$ double layers. The $[Mo_2P_2O_{11}]_\infty$ framework forms two different intersecting tunnels along [001] and ⟨110⟩ where the Rb^+ ions are located. Although different from $Rb_{1.5}Mo_2P_2O_{11}$, the two structures exhibit some close relationships.

Comment

The synthesis and determination of the structure of the title compound were undertaken in order to test the possibility of replacing potassium by rubidium in the phase $K_2Mo_2P_2O_{11}$ (Gueho, Borel, Grandin, Leclaire & Raveau, 1993). The replacement of K^+ by Cs^+ was only partial and led to $Cs_{1.5}Mo_2P_2O_{11}$ with the same framework structure (Borel, Leclaire, Grandin & Raveau, 1994), whereas the replacement of K^+ by Tl^+ was complete (Guesdon, Borel, Grandin, Leclaire & Raveau, 1993). Attempts to substitute rubidium for potassium allowed $Rb_2Mo_2P_2O_{11}$ to be prepared in the form of a microcrystalline powder (Gueho *et al.*, 1993), but the first single crystals that were obtained were those of the monophosphate $Rb_{1.5}Mo_2P_2O_{11}$ (Borel, Leclaire, Guesdon, Grandin & Raveau, 1994) with a structure which, in contrast to $Cs_{1.5}Mo_2P_2O_{11}$, was different to that of $K_2Mo_2P_2O_{11}$. In the present work, single crystals of $Rb_2Mo_2P_2O_{11}$ were synthesized as a minor phase from a batch of nominal composition $Rb_6Mo_7P_2O_{37}$ heated at 923 K for one day in an evacuated silica ampoule and cooled at 2 K h^{-1} to 823 K. The sample was then quenched to room temperature and reddish purple crystals were extracted.

$Rb_2Mo_2P_2O_{11}$ is isotypic with the 'K_2', '$Cs_{1.5}$' and 'Tl_2' phases; its framework is built from $Mo_2P_2O_{15}$ units formed by one Mo_2O_{11} group sharing four of

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its corners with two PO_4 tetrahedra, leading to $[Mo_2P_2O_{13}]_\infty$ double layers parallel to (001). It differs from $Rb_{1.5}Mo_2P_2O_{11}$ in the stacking of the double layers along **c**. The thickness of these layers determines the periodicity along **c** in the 'Rb_2' phase, while every other layer is rotated by 180° around **a** in the '$Rb_{1.5}$' structure. This framework forms two different intersecting tunnels running along [001] and ⟨110⟩. As in the other isotypic phases, the Rb^+ cations are distributed over three kinds of sites. The Rb(1) cations are located on a centre of symmetry and exhibit eightfold coordination with Rb—O distances ranging from 2.76 (3) to 2.89 (3) Å; they are strongly linked to the surrounding O atoms and have low equivalent isotropic displacement factors of 1.18 $Å^2$. The Rb(2) cations, located in the [001] tunnels, are characterized by ninefold coordination with Rb—O distances ranging from 2.93 (3) to 3.39 (3) Å. The Rb(3) cations, located near the axis of the ⟨110⟩ tunnels, also sit in the [001] tunnels and are split over two positions with respect to the centre of symmetry; they exhibit sevenfold coordination with Rb—O distances ranging from 2.88 (3) to 3.25 (3) Å. The equivalent isotropic displacement factors for Rb(2) and Rb(3) [2.48 (3) and 2.95 (7) $Å^2$, respectively] are in accordance with the longer Rb—O distances observed for Rb(2) than for Rb(1). It is noted that the equivalent isotropic displacement factors for the Rb^+ cations are smaller than those for the Tl^+ cations in $Tl_2Mo_2P_2O_{11}$ (3.69 and 4.78 $Å^2$, respectively) in spite of the Rb—O and Tl—O distances being similar; this can be explained by the particular $6s^2$ lone-pair configuration of Tl^+ which leads to a non-spherical symmetry for the thallium ion.

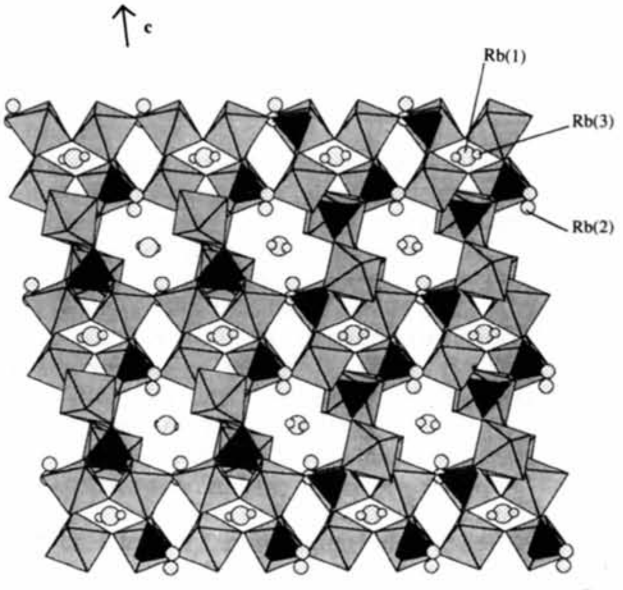

Fig. 1. A projection of the structure of $Rb_2Mo_2P_2O_{11}$ along $[1\bar{1}0]$.

Experimental

Crystal data

$Rb_2Mo_2P_2O_{11}$
$M_r = 600.76$
Monoclinic
$P2_1/c$
$a = 9.973\ (2)$ Å
$b = 10.180\ (2)$ Å
$c = 10.012\ (1)$ Å
$\beta = 97.70\ (1)°$
$V = 1007.2\ (5)\ Å^3$
$Z = 4$
$D_x = 3.96$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18–22°$
$\mu = 12.144\ mm^{-1}$
$T = 274$ K
Polyhedral
0.077 × 0.070 × 0.060 mm
Reddish purple

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: analytical
$T_{min} = 0.429$, $T_{max} = 0.556$
8881 measured reflections
8881 independent reflections

1243 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 45°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.046$
$S = 0.997$
1243 reflections
161 parameters
$w = 1/\sigma(F)$
$(\Delta/\sigma)_{max} < 0.02$
$\Delta\rho_{max} = 2.3$ e $Å^{-3}$
$\Delta\rho_{min} = -1.4$ e $Å^{-3}$

Extinction correction: Zachariasen (1963)
Extinction coefficient: 4.28×10^{-8}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mo(1)	0.3458 (1)	0.0854 (1)	0.1344 (1)	0.48 (2)
Mo(2)	0.0794 (1)	0.3223 (1)	0.1474 (1)	0.43 (1)
P(1)	0.3968 (3)	0.3743 (4)	0.3171 (3)	0.51 (5)
P(2)	0.1263 (3)	0.0754 (4)	0.3541 (3)	0.48 (5)
Rb(1)	0	0	0	1.18 (3)
Rb(2)	0.7620 (2)	0.1852 (2)	0.2901 (2)	2.48 (3)
Rb(3)*	0.5132 (4)	0.0685 (5)	0.5069 (3)	2.95 (7)
O(1)	0.2846 (9)	−0.058 (1)	0.064 (1)	1.1 (2)
O(2)	0.4286 (9)	0.1493 (9)	−0.029 (1)	0.7 (2)
O(3)	0.2681 (9)	0.053 (1)	0.317 (1)	1.1 (2)
O(4)	0.5255 (9)	−0.004 (1)	0.221 (1)	0.9 (2)
O(5)	0.1952 (9)	0.1957 (9)	0.0958 (9)	0.6 (2)
O(6)	0.4436 (9)	0.255 (1)	0.2434 (9)	0.9 (2)
O(7)	−0.070 (1)	0.262 (1)	0.068 (1)	1.3 (2)
O(8)	−0.0261 (9)	0.478 (1)	0.2232 (9)	0.8 (2)
O(9)	0.1340 (9)	0.4489 (9)	0.0063 (9)	0.7 (2)
O(10)	0.068 (1)	0.216 (1)	0.3227 (9)	0.9 (2)
O(11)	0.2470 (9)	0.4043 (9)	0.2748 (9)	0.7 (2)

* Site occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Mo(1)—O(1)	1.70 (3)	Rb(1)—O(5^{iv})	2.86 (3)
Mo(1)—O(2)	2.03 (3)	Rb(1)—O(5)	2.86 (3)
Mo(1)—O(3)	2.11 (3)	Rb(1)—O(7)	2.86 (3)
Mo(1)—O(4)	2.09 (3)	Rb(1)—O(7^{iv})	2.86 (3)
Mo(1)—O(5)	1.87 (3)	Rb(1)—O(8^{v})	2.76 (3)
Mo(1)—O(6)	2.20 (3)	Rb(1)—O(8^{iii})	2.76 (3)
Mo(2)—O(5)	1.85 (3)	Rb(2)—O(1^{ii})	3.05 (3)
Mo(2)—O(7)	1.70 (3)	Rb(2)—O(4)	3.05 (3)
Mo(2)—O(8)	2.10 (3)	Rb(2)—O(6)	3.23 (3)
Mo(2)—O(9)	2.04 (3)	Rb(2)—O(7^{vi})	3.06 (3)
Mo(2)—O(10)	2.08 (3)	Rb(2)—O(7^{vii})	3.10 (3)
Mo(2)—O(11)	2.13 (3)	Rb(2)—O(8^{viii})	3.39 (3)
P(1)—O(2^{i})	1.55 (3)	Rb(2)—O(9^{viii})	3.23 (3)
P(1)—O(4^{ii})	1.54 (3)	Rb(2)—O(10^{vi})	3.04 (3)
P(1)—O(6)	1.53 (3)	Rb(2)—O(11^{viii})	2.93 (3)
P(1)—O(11)	1.53 (3)	Rb(3)—O(2^{i})	3.00 (3)
P(2)—O(3)	1.53 (3)	Rb(3)—O(3)	2.89 (3)
P(2)—O(8^{iii})	1.54 (3)	Rb(3)—O(3^{ix})	2.89 (3)
P(2)—O(9^{i})	1.54 (3)	Rb(3)—O(4)	2.97 (3)
P(2)—O(10)	1.56 (3)	Rb(3)—O(4^{ix})	2.88 (3)
Rb(1)—O(1^{iv})	2.89 (3)	Rb(3)—O(6)	3.25 (3)
Rb(1)—O(1)	2.89 (3)	Rb(3)—O(6^{i})	3.12 (3)
O(2^{i})—P(1)—O(4^{ii})	109 (2)	O(3)—Mo(1)—O(4)	88 (1)
O(2^{i})—P(1)—O(6)	109 (2)	O(3)—Mo(1)—O(5)	84 (1)
O(2^{i})—P(1)—O(11)	112 (2)	O(3)—Mo(1)—O(6)	83 (1)
O(4^{ii})—P(1)—O(6)	109 (2)	O(4)—Mo(1)—O(5)	165 (1)
O(4^{ii})—P(1)—O(11)	106 (2)	O(4)—Mo(1)—O(6)	81 (1)
O(6)—P(1)—O(11)	112 (2)	O(5)—Mo(1)—O(6)	86 (1)
O(3)—P(2)—O(8^{iii})	110 (2)	O(5)—Mo(2)—O(7)	99 (1)
O(3)—P(2)—O(9^{i})	107 (2)	O(5)—Mo(2)—O(8)	171 (1)
O(3)—P(2)—O(10)	115 (2)	O(5)—Mo(2)—O(9)	91 (1)
O(8^{iii})—P(2)—O(9^{i})	110 (2)	O(5)—Mo(2)—O(10)	89 (1)
O(8^{iii})—P(2)—O(10)	107 (2)	O(5)—Mo(2)—O(11)	88 (1)
O(9^{i})—P(2)—O(10)	108 (2)	O(7)—Mo(2)—O(8)	90 (1)
O(1)—Mo(1)—O(2)	96 (1)	O(7)—Mo(2)—O(9)	102 (1)
O(1)—Mo(1)—O(3)	94 (1)	O(7)—Mo(2)—O(10)	93 (1)
O(1)—Mo(1)—O(4)	92 (1)	O(7)—Mo(2)—O(11)	170 (1)
O(1)—Mo(1)—O(5)	101 (1)	O(8)—Mo(2)—O(9)	88 (1)
O(1)—Mo(1)—O(6)	172 (1)	O(8)—Mo(2)—O(10)	90 (1)
O(2)—Mo(1)—O(3)	170 (1)	O(8)—Mo(2)—O(11)	83 (1)
O(2)—Mo(1)—O(4)	93 (1)	O(9)—Mo(2)—O(10)	165 (1)
O(2)—Mo(1)—O(5)	92 (1)	O(9)—Mo(2)—O(11)	85 (1)
O(2)—Mo(1)—O(6)	87 (1)	O(10)—Mo(2)—O(11)	80 (1)

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

Calculations were performed with the *SDP* system (Frenz, 1982) using a MicroVAX II computer. Molecular graphics: *MOLVIEW*.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Thallous Nitrate (III); a Single-Crystal Neutron Study

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Abstract

The structure of $TlNO_3$ (III) is refined from single-crystal neutron diffraction data with significantly improved accuracy compared to the reported X-ray structure. Rigid-body thermal-motion analysis indicates that the largest amplitude of libration is about the plane normal to one of the nitrate ions and about an in-plane axis for the other. The maximum librational frequencies for both nitrate groups, however, are about the in-plane axes, and are in close agreement with the values reported from a Raman scattering study.

Comment

$TlNO_3$ is known to exhibit interesting high-temperature structural phase transitions from the room-temperature orthorhombic phase (III) to a hexagonal phase (II) and then to a cubic phase (I), involving reorientation of the planar nitrate ions (Brown & McLaren, 1962; Fraser, Kennedy & Snow, 1975). However, the structural details of these high-temperature phases have not been reported. In order to understand the mechanism of these transitions, a neutron study of $TlNO_3$ was initiated. This paper reports the results of a single-crystal neutron study of $TlNO_3$ (III).

The structural parameters obtained using neutron data, although essentially in agreement with the values obtained from X-ray data (Fraser, Kennedy & Snow, 1975), are far more accurate for all of the atoms with the exception of the Tl atom. As shown in Table 2, there are no significant differences in the atomic coordinates obtained from the neutron study and the X-ray study. Only the values for the x coordinates of the atoms N(2) and O(2) differ by more than their respective e.s.d.'s. A view of the structure is shown in Fig. 1, which shows that the nitrate ions are enclosed within distorted cubes formed by a pseudo-cubic lattice of Tl ions. The edge lengths of each cube range from 3.9 to 4.7 Å. The nitrate ions are oriented such that the planes through the ions are almost normal to one of the cube edges

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