TlMo$_2^{IV}$P$_3$O$_{12}$: A Molybdenophosphate with a Tunnel Structure

A. LECLAIRE, J. C. MONIER, AND B. RAVEAU

Laboratoire de Cristallographie, Chimie et Physique des Solides, L.A. 251, ISMRa-Université, 14032 Caen Cedex, France

A molybdenophosphate, TlMo$_2^{IV}$P$_3$O$_{12}$, with an original tunnel structure, has been isolated. Its structure has been determined by X-ray diffraction on a single crystal. It crystallizes in the orthorhombic system with $a = 8.836(1)$, $b = 9.255(1)$, $c = 12.288(1)$ Å, possible space groups *Pbcm* and *Pbc2$_1$* with $Z = 4$. The structure was solved and refined in the centrosymmetric space group *Pbcm*. The host lattice "Mo$_3$P$_3$O$_{12}$" is built up from corner-sharing octahedra and tetrahedra and forms tunnels running along the b axis and cages where the Tl$^+$ ions are located. The relationships of this framework with that of the phosphate tungsten bronze CsP$_8$W$_8$O$_{40}$ and that of the hexagonal tungsten bronze are discussed. © 1985 Academic Press, Inc.

Introduction

The molybdenum phosphorus oxides are known for their ability to form mixed frameworks built up from corner-sharing MoO$_6$ octahedra and PO$_4$ tetrahedra. The ternary system Mo–P–O indeed exhibits either Mo(VI) phosphates (MoO$_2$)$_2$P$_2$O$_7$, MoO$_2$(PO$_3$)$_2$ (*1, 2*) or Mo(V) phosphates (MoO)PO$_4$ (*3*) and (MoO)$_2$P$_4$O$_{13}$ (*4*). The introduction in this system of an alkaline ion with an equal size or a size greater than the one of potassium lead to the formation of tunnel or cage structures. The recent study of the Mo(V) phosphate K$_4$Mo$_8^V$P$_{12}$O$_{52}$ (*5*) is in agreement with this point of view. The replacement of K$^+$ by bigger ions such as Tl$^+$ or Rb$^+$ in K$_4$Mo$_8$P$_{12}$O$_{52}$ does not lead to isostructural oxides contrary to what is generally observed in oxides with a tunnel structure. In order to understand the chemistry of these molybdenum phosphates, we have investigated the system Tl–Mo–P–O. Thus, we report here on a Mo(IV) phos-

phate TlMo$_2^{IV}$P$_3$O$_{12}$ which exhibits an original tunnel structure.

Determination of the Structure

Adequate amounts of ammonium phosphate, (NH$_4$)$_2$HPO$_4$, thallium carbonate, Tl$_2$CO$_3$, and molybdenum oxide, MoO$_3$, were first heated progressively up to 873 K in air in order to decompose the carbonate and the ammonium phosphate. The resulting mixture was then mixed with the adequate amount of molybdenum and heated at 1273 K in evacuated silicon ampoules for several days. A rectangular plate of 0.72 × 0.64 × 0.52 mm was selected for the structural determination.

The Laue patterns showed an orthorhombic symmetry (*mmm*). The cell parameters in "abstract" were determined by diffractometric techniques with a least-squares refinement based on 25 reflections.

The systematic absences in 0kl for $k = 2n + 1$ and in $h0l$ for $l = 2n + 1$ led to *Pbcm*

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or $Pbc2_1$ (other setting for $Pca2_1$) space group. The structure was solved and refined in the centrosymmetric space group $Pbcm$.

The data were collected on a CAD 4 Enraf-Nonius diffractometer using graphite-monochromatized $MoK\bar{\alpha}$ radiation. The intensities were measured up to $\theta = 45°$ with a $\omega - \frac{4}{3}\theta$ scan of $(0.90 + 0.35 \tan \theta)°$ and a counter slit aperature of $(1.00 + \tan \theta)$ mm, all determined after a study of some reflections in the $\omega\theta$ plane.

The background intensity was measured on both sides of each reflection. A periodic intensity control on 0 0 6, 2 0 0, and 1 5 0 reflections verified the stability of the sample. The 1115 independent reflections which had $I > 3\sigma(I)$ were corrected for Lorentz and polarization effect; absorption correction were applied using the program AGNOSTC (6, 7). The Mo atomic coordinates were deduced from a three-dimensional PATTERSON map. The remaining atoms were located in subsequent Fourier syntheses.

Scattering factors and anomalous-dispersion corrections for the different atoms of the compound were taken from International Tables for X-Ray Crystallography (8).

The atomic parameters with anisotropic thermal factors and an isotropic extinction parameter (9) were refined by full-matrix least squares, and a linear weighting scheme $w = f(\sin \theta/\lambda)$ was adjusted by using the program POND (10). The reliability factors were lowered to $R = 0.055$ and $R_w = 0.062$ with the extinction coefficient $g = 49(9)$. Final atomic parameters are given in Table I.[1]

Description of the Structure and Discussion

The examination of the structure along b

TABLE I

$TlMo_2^{IV}P_3O_{12}$: ATOMIC COORDINATES

Atom	x	y	z	$B_{eq} = \frac{4}{3} \Sigma \Sigma \beta_{ij}a_ia_j$
Mo	0.24728(18)	0.029874(9)	0.10109(7)	0.40(1)
Tl	−0.18018(23)	0.16397(13)	0.25	2.99(3)
P(1)	−0.0255(5)	0.25	0	0.55(7)
P(2)	0.4084(4)	0.3602(3)	0.1296(2)	0.50(4)
O(1)	0.2147(16)	0.0175(14)	0.25	0.77(21)
O(2)	0.1234(19)	−0.1507(14)	0.0703(9)	1.86(25)
O(3)	0.2986(14)	0.0495(10)	−0.0606(8)	0.94(17)
O(4)	0.3866(14)	0.1994(9)	0.1222(9)	1.01(18)
O(5)	0.4287(12)	−0.1052(11)	0.1153(10)	1.12(18)
O(6)	0.0666(16)	0.1624(13)	0.0803(8)	1.45(21)
O(7)	0.3564(20)	0.4099(18)	0.25	1.18(27)

(Fig. 1) shows that it exhibits a three-dimensional framework "$Mo_2P_3O_{12}$" built up from corner-sharing octahedra and tetrahedra, which forms tunnels running along b and cages where the Tl^+ ions are located.

The MoO_6 octahedra form units of two octahedra (Mo_2O_{11}). In each octahedron the five Mo–O distances which correspond to the oxygen atoms linked to PO_4 tetrahedra, are almost equal: their values, ranging from 2.02(1) to 2.05(1) Å (Table II), are close to
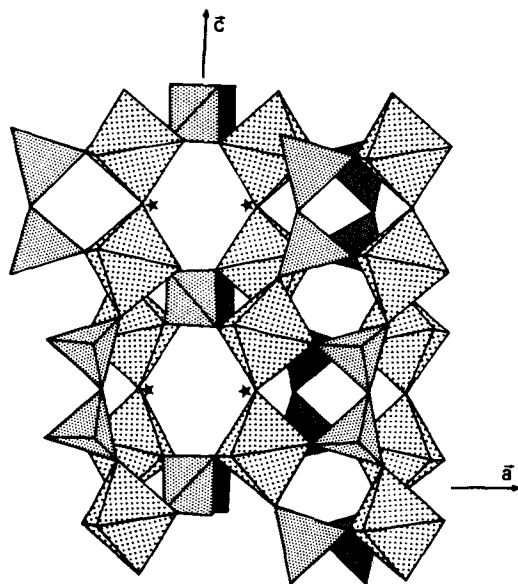

FIG. 1. Projection of the structure along b showing the tunnels. The stars point out the thallium atoms.

TABLE II

INTERATOMIC DISTANCES AND BOND ANGLES IN MoO$_6$ OCTAHEDRON

Mo	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.855(3) Å	2.82(1) Å	3.90(2) Å	2.76(2) Å	2.76(2) Å	2.80(1) Å
O(2)	93.1(5)°	2.02(1) Å	2.90(2) Å	4.04(2) Å	2.79(2) Å	2.94(2) Å
O(3)	175.5(5)°	90.9(4)°	2.05(1) Å	2.75(1) Å	2.84(2) Å	2.88(2) Å
O(4)	90.7(5)°	174.4(5)°	85.2(4)°	2.02(1) Å	2.85(1) Å	2.89(2) Å
O(5)	90.2(5)°	86.7(5)°	88.0(5)°	89.2(4)°	2.03(1) Å	4.07(2) Å
O(6)	92.1(5)°	92.9(6)°	89.7(4)°	91.1(5)°	177.7(4)°	2.04(1) Å

those observed for the silicomolyb-denophosphates AMo$_3^{IV}$P$_{5.8}$Si$_2$O$_{25}$ (A = Rb, Tl) which exhibit isolated MoO$_6$ octahedra only linked to PO$_4$ tetrahedra (11); on the other hand, the sixth Mo–O distance, which corresponds to the oxygen atom common to the two octrahedra is much shorter (1.855(2) Å).

The PO$_4$ tetrahedra are almost regular (Table III): the isolated PO$_4$ tetrahedra exhibit four nearly equal P–O distances ranging from 1.51(1) to 1.53(1) Å whereas in the tetrahedra belonging to the P$_2$O$_7$ groups the phosphorus atoms are off-centered giving three nearly equal P–O bonds (1.49(1) to 1.54(1) Å) and one longer P–O distance (1.616(8) Å).

The view of this structure along axis b (Fig. 1), shows also that the host lattice "Mo$_2$P$_3$O$_{12}$" can be described as planes of MoO$_6$ octahedra and planes of PO$_4$ tetrahedra perpendicular to a which alternate according to the following sequence: ‖(MoO$_3$)$_2$|(P$_2$O$_4$)$_2$|(MoO$_3$)$_2$|(PO$_2$)$_2$‖ where (MoO$_3$)$_2$ represents the composition of the octahedral layers, and (P$_2$O$_4$)$_2$ and (PO$_2$)$_2$ the composition of the pyrophosphate planes and of the monophosphate planes, respectively. The consideration of the structure along a (Fig. 2), shows that this framework exhibits also layers of MoO$_6$ octahedra and of PO$_4$ tetrahedra perpendicular to b; however, in this direction, the
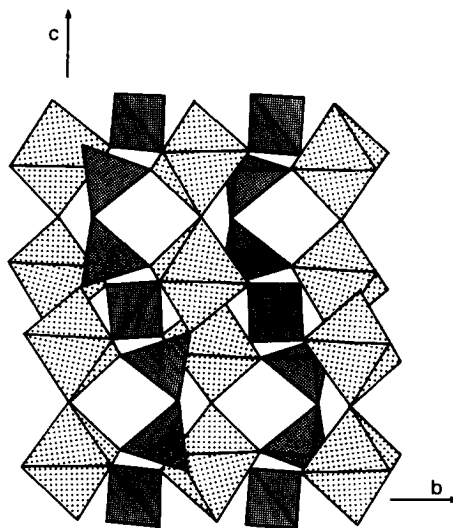
TABLE III

INTERATOMIC DISTANCES AND BOND ANGLES IN PO$_4$ TETRAHEDRA

P(1)	O(2^i)	O(2^{ii})	O(6)	O(6^{iii})
O(2^i)	1.53(1) Å	2.52(2) Å	2.50(2) Å	2.41(2) Å
O(2^{ii})	111.1(9)°	1.53(1) Å	2.41(2) Å	2.50(2) Å
O(6)	110.5(7)°	104.9(6)°	1.51(1) Å	2.55(2) Å
O(6^{iii})	104.9(6)°	110.5(7)°	115.0(8)°	1.51(1) Å

P(2)	O(3^{iii})	O(4)	O(5^{iv})	O(7)
O(3^{iii})	1.54(1) Å	2.57(1) Å	2.55(2) Å	2.41(1) Å
O(4)	115.1(6)°	1.504(9) Å	2.44(1) Å	2.52(2) Å
O(5^{iv})	115.5(6)°	109.3(6)°	1.49(1) Å	2.52(2) Å
O(7)	99.9(7)°	107.5(7)°	108.8(8)°	1.616(8) Å

$i = -x; -y; -z$
$ii = -y; \frac{1}{2} + y; z$
$iii = x; \frac{1}{2} - y; -z$
$iv = 1 - x; \frac{1}{2} + y; z$

FIG. 2. Projection of the structure along a showing the layers of MoO$_6$ octahedra and PO$_4$ tetrahedra.
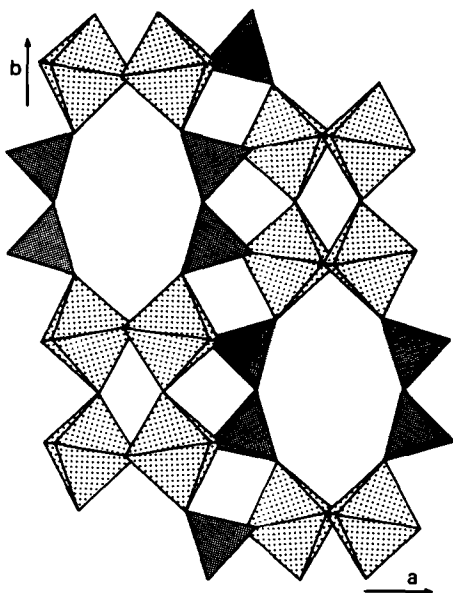
FIG. 3. Projection along c of the $CsP_8W_8O_{40}$ structure.

planes of tetrahedral PO_4 and P_2O_7 groups coincide, leading to the sequence $||(MoO_3)_2|$ $(PO_2)(P_2O_4)|(MoO_3)_2|(PO_2(P_2O_4)|||$.

The "$Mo_2P_3O_{12}$" framework presents some similarity with that of the bronze $CsP_8W_8O_{40}$ (12) (Fig. 3). Both frameworks "$Mo_2P_3O_{12}$" and "$P_8W_8O_{40}$" exhibit similar chains formed of corner-sharing (Mo_2O_{11}) (or W_2O_{11}) units and P_2O_7 groups running along [001] and [010], respectively (Fig. 4). In both structures one observes that two adjacent chains can be linked one to the other by sharing the corners of one P_2O_7 groups of one chain with the corners of a Mo_2O_{11} (or W_2O_{11}) unit of the adjacent chain (Fig. 4). However, the relative orientation of two successive chains is different in both structures. Moreover, the framework $P_8W_8O_{40}$ is only built up from such identical chains so that two adjacent chains can also be linked through the corners of two octahedral units (W_2O_{11}) (Fig. 4b), whereas the remaining corners of the (Mo_2O_{11}) units of the chains are shared with

single PO_4 tetrahedra (Fig. 4a) in the "$Mo_2P_3O_{12}$" framework.

The structure of $TlMo_2P_3O_{12}$ is also related to that of the hexagonal tungsten bronze of Magnéli. The framework "$Mo_2P_3O_{12}$" can be described as being composed of identical layers L (Fig. 5) of polyhedra parallel to ($1\bar{1}0$); these layers are characterized by hexagonal rings similar to those observed in HTB's, which are deduced from the HTB structure by replacing two octahedra by two PO_4 tetrahedra.

Along [110] two successive hexagonal rings are linked through a P_2O_7 group instead of an octahedron in HTB's, forming a P-substituted HTB ribbon. In the layer L the P-substituted HTB ribbons are linked
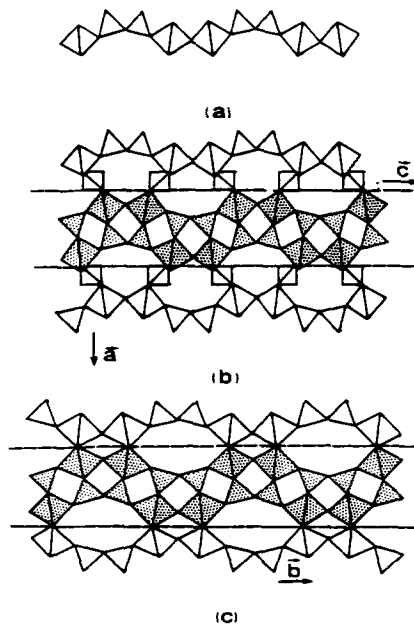

FIG. 4. $|Mo_2P_2O_{16}|_\infty$ chains (a) observed in the structure of $TlMo_2P_3O_{12}$ (b), and $CsP_8W_8O_{40}$ (c): in both structures, the $|Mo_2P_2O_{16}|_\infty$ chains form layers (shaded octahedra and tetrahedra between two dashed lines) by sharing the corners of the Mo_2O_{11} groups of one chain with the corners of the P_2O_7 groups of an adjacent chain. The connection between these layers is ensured by sharing corners of octahedra and tetrahedra in $TlMo_2P_3O_{12}$ (a) and by sharing the corners only of octahedra in $CsP_8W_8O_{40}$ (b).
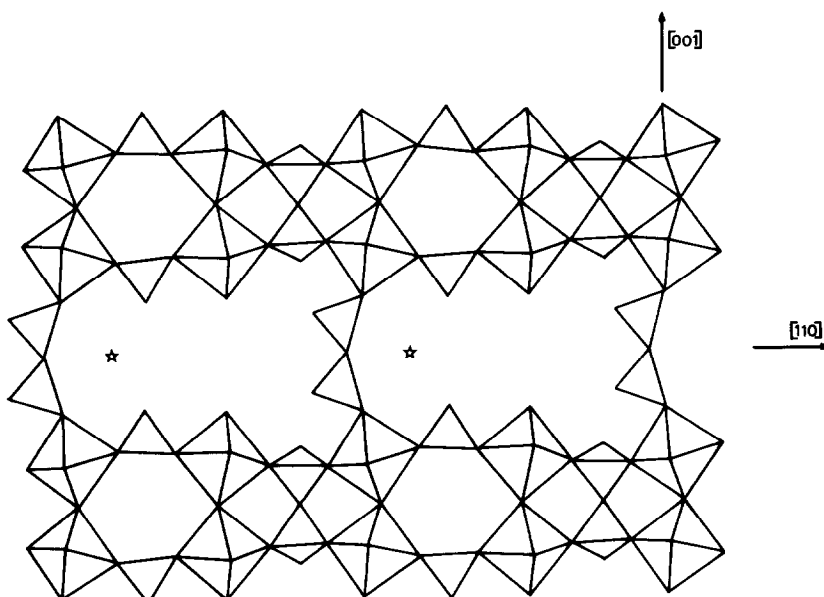
FIG. 5. Layer ($1\bar{1}0$) of the TlMo$_2$P$_3$O$_{12}$ structure. The stars point out the thallium atoms.

along c through P$_2$O$_7$ groups, leaving large spaces where the Tl$^+$ ions are located. The successive L layers which are stacked along ($1\bar{1}0$) are deduced one from the other either by a symmetry center. Thus this framework forms wide cages bounded by 17 oxygen atoms, which communicate through the previously described hexagonal windows, i.e., through tunnels parallel to b. The Tl$^+$ ions lie approximatively at the center of the cage, so that they are located near the "walls" of the tunnels. Each Tl$^+$ ion is mainly bonded to three oxygen atoms with Tl–O distances ranging from 2.82 to 2.84 Å; the distances to the other oxygen atoms delimiting the cage are greater than 3 Å: 3.02 Å ($\times$2) for O(6), 3.23 Å ($\times$2) for O(3), 3.29 Å for O(1), and 3.50 Å ($\times$2) for O(5). It must be emphasized that Tl$^+$ is displaced about 0.33 Å in the direction perpendicular to the plane formed by its three nearest neighbors, so that its lone pair could be directed toward the axis of the tunnel. Nevertheless, the values of the Tl–O distances, which are normal, show that the stereo-

chemical activity of its lone pair is rather weak.

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