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A Molybdenum (V) Monophosphate with a Layer Structure, $BaMo_4O_8(PO_4)_2$

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A new Mo(V) monophosphate $BaMo_4O_8(PO_4)_2$, with a layer structure, has been isolated. It crystallizes in the space group $I\bar{4}2m$, with $a = 7.475(1)$ Å and $c = 11.156(1)$ Å. The close relationships between the structure of this phase and that of the mixed-valent Mo(III)–Mo(IV) phosphate $Cs_3(MoO)_4(PO_4)_3$ are remarkable. Both phosphates are characterized by Mo_4O_{16} octahedral units built up from $Mo_4O_4^{6+}$ cubes, forming identical $[Mo_4P_2O_{16}]_\infty$ layers parallel to (001). The layer structure of the present Mo(V) monophosphate derives from the intersecting tunnel framework of the intermediate valent Mo monophosphate by just suppressing the PO_4 tetrahedra along one direction and by translating two successive $[Mo_4P_2O_{16}]_\infty$ layers by (a + b)/2.

INTRODUCTION

It is now well established that the association of MoO_6 octahedra with PO_4 tetrahedra allows the pentavalent state of molybdenum to be stabilized (1). About 30 Mo(V) phosphates have been isolated up to now. In all of them, Mo(V) is off-centered in its octahedron; i.e., it is strongly displaced toward one corner of its octahedron, leading to an abnormally short Mo–O bond. This specific geometry of the Mo(V) octahedra, that is generally described as molybdenyl ions, requires that one of the corners of the MoO_6 octahedra be free. Most of the Mo(V) anhydrous phosphates isolated up to now by solid state chemistry at high temperature are characterized by isolated MoO_6 octahedra, except for $AgMo_5P_8O_{33}$ (2), $MoPO_5$ (3), and $MoAlP_2O_9$ (4), in which the MoO_6 octahedra form $[MoO_3]_\infty$ chains, and for $A_2Mo_2P_2O_{11}$, with A = K, Tl (5, 6), where one observes Mo_2O_{11} units built up of two corner-sharing octahedra. Such frameworks generally form either cages or tunnels whose walls are partly made up of the free oxygens of the MoO_6 octahedra. Phosphates with a layer structure should also be favorable to the stabilization of those Mo(V) octahedra. Curiously only one phosphate, $Cs_2Mo_4P_6O_{26}$ (7), belongs to this category. The generation of such a layer structure requires the presence of, besides Mo and P, big cations such as Cs^+, Rb^+, K^+, or Ba^{2+}. If a great deal of work has been carried out on Mo(V) phosphates of univalent cations, very few results have been obtained in the system $BaO–Mo_2^VO_5–P_2O_5$. Ba $Mo_2P_4O_{16}$ is the only Mo(V) of this system that has been isolated up to now. We report here on the synthesis and structural study of a new Mo(V) phosphate with a layer structure $BaMo_4O_8(PO_4)_2$, that is closely related to the tunnel structure of mixed-valent Mo(III)–Mo(IV) monophosphates $A_3Mo_4O_4(PO_4)_3$, with A = NH_4,Cs (8, 9).

CHEMICAL SYNTHESIS

Single crystals of $BaMo_4O_8(PO_4)_2$ for the structure determination were extracted from a mixture of nominal composition $BaMo_3P_2O_{14}$. The latter was prepared from an intimate mixture of $BaCO_3$, $H(NH_4)_2PO_4$, and MoO_3 first heated in air at 673 K for 6 hr and then the resulting product, with composition $BaMo_{2.66}P_2O_{14}$, was added to 0.33 mole of metallic Mo, placed in an alumina crucible, and heated in an evacuated silica ampoule at 1173 K for a day; the sample was then cooled slowly (4 K/hr) down to 973 K. From the mixture some red plate crystals were extracted. The composition deduced from the structural determination $BaMo_4P_2O_{16}$ was confirmed by microprobe analysis. Subsequently the synthesis of the pure-phase $BaMo_4P_2O_{16}$ was performed in a similar way in two steps, but started from the exact stoichiometric composition. In this case the second step was carried out during a day at 1023 K and quenched at room temperature.

The powder *XR* diffractogram enregistered with a PW3710 Phillips diffractometer was indexed as a tetragonal cell (Table 1), in agreement with the parameters obtained from a single-crystal study (Table 2).

STRUCTURE DETERMINATION

A red plate with dimensions 0.115 × 0.077 × 0.025 mm was selected for the structure determination. The cell parameters reported in Table 2 were determined and refined by diffractometric techniques at 294 K with a least-

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TABLE 1
Interreticular Distances in $BaMo_4O_8(PO_4)_2$

h	k	l	d_{calc} (Å)	d_{obs} (Å)	I/I_0	h	k	l	d_{calc} (Å)	d_{obs} (Å)	I/I_0
1	0	1	6.212	6.206	16.4	2	2	2	2.389	2.389	10.2
0	0	2	5.575	5.575	69.1	3	1	0	2.365	2.364	2.6
1	1	0	5.289	5.284	25.7	2	0	4	2.235	2.235	6.3
1	1	2	3.837	3.836	31.4	3	1	2	2.177	2.177	13.6
2	0	0	3.740	3.747	11.1	1	0	5	2.137	2.137	40.0
1	0	3	3.328	3.329	100.0	3	2	1	2.040	2.039	11.5
2	1	1	3.204	3.203	39.6	2	2	4	1.918	1.918	7.2
2	0	2	3.106	3.106	16.3	4	0	0	1.870	1.869	6.6
0	0	4	2.787	2.789	12.3	0	0	6	1.858	1.856	15.2
2	2	0	2.644	2.644	3.4	2	1	5	1.855		
2	1	3	2.486	2.486	11.3	3	2	3	1.811	1.811	3.7
1	1	4	2.466	2.466	4	3	1	4	1.803	1.803	8.3
3	0	1	2.433	2.432	23.4						

squares refinement based upon 25 reflections with $18 < \theta < 22°$. The data were collected on a CAD4 Enraf-Nonius diffractometer with the data collection parameters of Table 2. The reflections were corrected for Lorentz, polarization, absorption, and secondary extinction effects. The structure was solved by the heavy atom method. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.0195$ and $Rw = 0.0237$ and to the atomic parameters of Table 3.

TABLE 2
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $BaMo_4O_8(PO_4)_2$

Crystal data	
Space group	$I\bar{4}2m$
Cell dimensions	a = 7.475(1) Å
	c = 11.156(1) Å
Volume	623.5(1) Å^3
Z	2
d_{calc}	4.47
d_{obs}	4.70
Intensity measurements	
λ(Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - \theta$
Scan width (°)	1.06 + 0.35 tan θ
Slit aperture (mm)	1.06 + tan θ
max θ (°)	45
Standard reflections	3 every 3000 sec
Reflections with $I > 3\sigma$	649
Reflections measured	778
μ(mm^{-1})	7.28
Structure solution and refinement	
Parameters refined	34
Agreement factors	R = 0.0195, Rw = 0.0237
Weighting scheme	$w = f(\sin\theta/\lambda)$
Δ/σ max	<0.004
$\Delta\rho$ (eÅ^{-3})	0.7

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the structure of this new phosphate along **a** (Fig. 1) shows that it consists of $[Mo_4P_2O_{16}]_\infty$ layers parallel to (001), whose connection is ensured by barium cations.

The projection of one $[Mo_4P_2O_{16}]_\infty$ layer along **c** (Fig. 2) shows its great similarity with the structure of the monophosphates $A_3(MoO)_4(PO_4)_3$ (8, 9). Both structures consist of Mo_4O_{16} units (Fig. 3) built up from edge-sharing MoO_6 octahedra located at the corners of a Mo_4 tetrahedron. In each $[Mo_4P_2O_{16}]_\infty$ layer the "Mo_4O_{16}" units are linked along **a** and **b** through single PO_4 tetrahedra, and each PO_4 tetrahedron shares two corners with the same "Mo_4O_{16}" unit, so that one PO_4 tetrahedron alternates with one Mo_4O_{16} unit along **a** and **b**. It results in large eight-sided windows (Fig. 2) where the Ba^{2+} cations are located. Absolutely identical $[Mo_4P_2O_{16}]_\infty$ layers parallel to (010), (100), or (001) are observed in the cubic tridimensional framework of the tunnel structure of $A_3(MoO)_4(PO_4)_3$ (8, 9). Such isolated $[Mo_4P_2O_{16}]_\infty$ layers have been also

TABLE 3
Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	Beq (Å^2)
Ba	0	0	0	0.953(4)
Mo	0.87680(3)	0.87680	0.62921(3)	0.452(2)
P	0.5	0	0.5	0.55(2)
O(1)	0.8704(3)	1.1296	0.5872(3)	0.61(2)
O(2)	0.6127(3)	0.8742(4)	0.5783(2)	0.84(3)
O(3)	0.8591(4)	0.8591	0.7793(3)	1.07(3)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $Beq = 4/3 \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \cdot \beta_{ij}$.

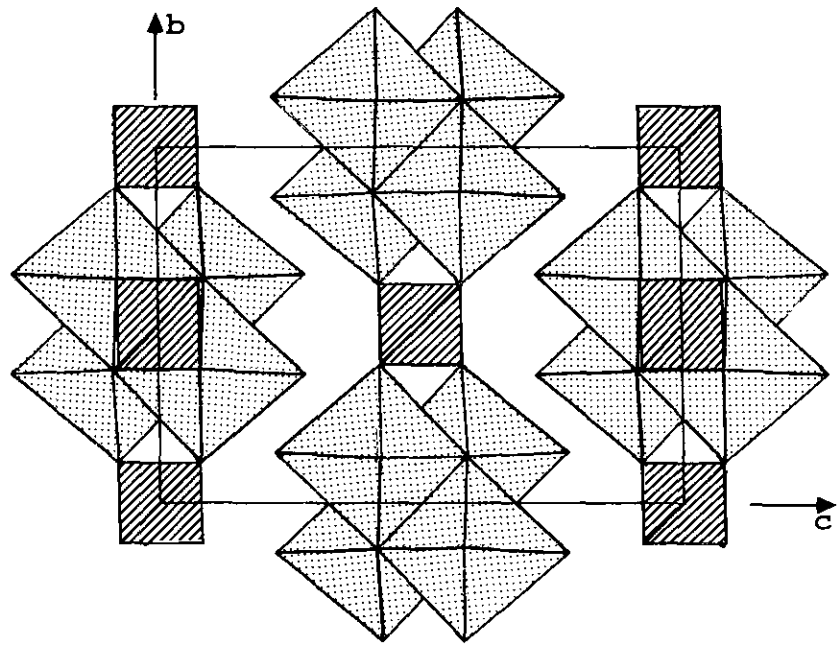

FIG. 1. Projection of the structure of $BaMo_4O_8(PO_4)_2$ along **a**.

observed, interleaved with ammonium cations in $Pr_4N(NH_4)[Mo_4O_8(PO_4)_2]$ (11), $(Et_2NH_2)_2[Mo_4O_8(PO_4)_2]$ (12), or (4-phenylpyridine)$_2$ $[Mo_4O_8(PO_4)_2]$ (12). Thus the structure of $BaMo_4O_8(PO_4)_2$ is directly derived from the $A_3(MoO)_4(PO_4)_3$ structure in a very simple way. Let us take the axes of the first structure as a reference for the description of $Cs_3(MoO)_4(PO_4)_3$ in spite of its cubic symmetry. Both structures can then be described as built up from identical $[Mo_4P_2O_{16}]_\infty$ layers parallel to (001) (Fig. 2). Then the view of the structure of $Cs_3(MoO)_4(PO_4)_3$ along **c** (Fig. 4) is similar to that observed for one (001) layer (Fig. 2): the structure of this phase can be described as a stacking along **c** of identical $[Mo_4P_2O_{16}]_\infty$ parallel to (001) and connected through PO_4 tetrahedra, forming intersecting tunnels. The structure of $BaMo_4O_8(PO_4)_2$ is then deduced from the latter by just supressing the PO_4 tetrahedra between the (001) layers along **c** and by translating one $[Mo_4P_2O_{16}]_\infty$ layer out of two of (**a** + **b**)/2 as shown

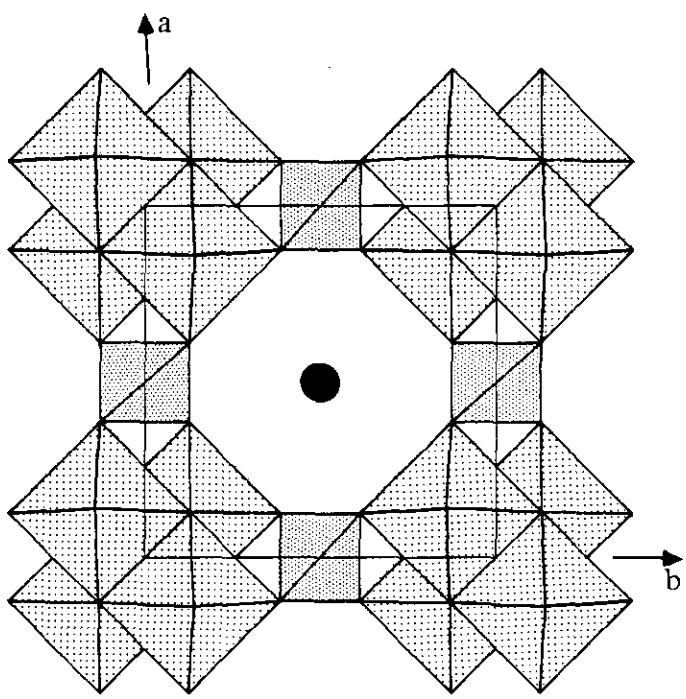

FIG. 2. Projection along **c** of a layer.

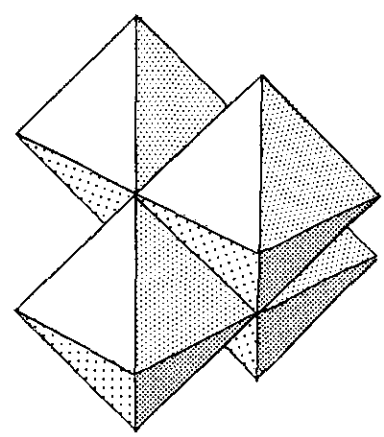

FIG. 3. The Mo_4O_{16} unit.

TABLE 4
Distances in Å and Angles (°) in Octahedra and Tetrahedra

Mo	O(1)	O(1^{i})	O(1^{ii})	O(2)	O(2^{iii})	O(3)
O(1)	1.948(1)	2.741(4)	2.746(7)	2.714(5)	3.866(6)	2.948(5)
O(1^{i})	89.4(1)	1.948(1)	2.741(4)	3.866(6)	2.714(3)	2.948(5)
O(1^{ii})	77.2(1)	77.2(2)	2.415(4)	2.746(6)	2.668(3)	4.090(6)
O(2)	85.4(2)	150.0(1)	72.8(1)	2.054(3)	2.765(5)	2.904(5)
O(2^{iii})	150.0(1)	85.4(1)	72.8(1)	84.6(2)	2.054(3)	2.904(5)
O(3)	108.3(1)	108.3(1)	172.0(1)	101.4(2)	101.4(2)	1.685(1)

P	O(2^{iv})	O(2^{v})	O(2^{vi})	O(2^{vii})
O(2^{iv})	1.536(3)	2.526(5)	2.428(5)	2.568(6)
O(2^{v})	110.6(2)	1.536(3)	2.568(6)	2.428(5)
O(2^{vi})	104.5(3)	113.5(3)	1.536(3)	2.526(5)
O(2^{vii})	113.5(3)	104.5(3)	110.6(2)	1.536(3)

Note. Symmetry codes: (i) $2 - x, 2 - y, z$; (ii) $x, 2 - y, 1 - z$; (iii) y, x, z; (iv) $x, y - 1, z$; (v) $1 - x, 1 - y, z$; (vi) $1 - x, y - 1, 1 - z$; (vii) $x, 1 - y, 1 - z$.

from the projection of the structure of $BaMo_4O_8(PO_4)_2$ along **a** (Fig. 1).

The consideration of the "Mo_4O_{16}" units shows their great similarity with those observed for $A_3(MoO)_4(PO_4)_3$. One indeed recognizes $Mo_4O_4^{6+}$ cubes described by Haushalter (9, 10), and by King *et al.* (8), in which the Mo(V) involves elongated Mo_4 tetrahedra characterized by two Mo–Mo contacts of 2.650 Å and four Mo–Mo distances of 3.421 Å instead of six Mo–Mo contacts of 2.57 Å in $A_3(MoO)_4(PO_4)_3$ phosphates. The four oxygen atoms, O(1), O(2) and O(3), that form the Mo_4O_4 cube are bonded to three, two or one molybdenum atoms respectively. This similarity between the two structures is really unexpected if one takes into account the different oxidation states of molybdenum, i.e., Mo(V) in $BaMo_4O_8(PO_4)_2$ and Mo(III)–Mo(IV) in $A_3(MoO)_4(PO_4)_3$. Nevertheless, the geometry of the MoO_6 octahedron (Table 4) in our structure is different and characteristic of Mo(V). One indeed observes a very short apical Mo–O bond (1.685 Å) corresponding to the molybdenyl ion, i.e., to the free oxygen atom pointing out of the layers. Like in most of the Mo(V) octahedra, the opposite apical Mo–O bond is very long (2.415 Å), whereas the four equatorial Mo–O bonds are intermediate (1.948–2.054 Å). The sum of the electrostatic valences calculated with the Zachariasen curves (13) confirms the oxidation state of five for molybdenum (4.96).

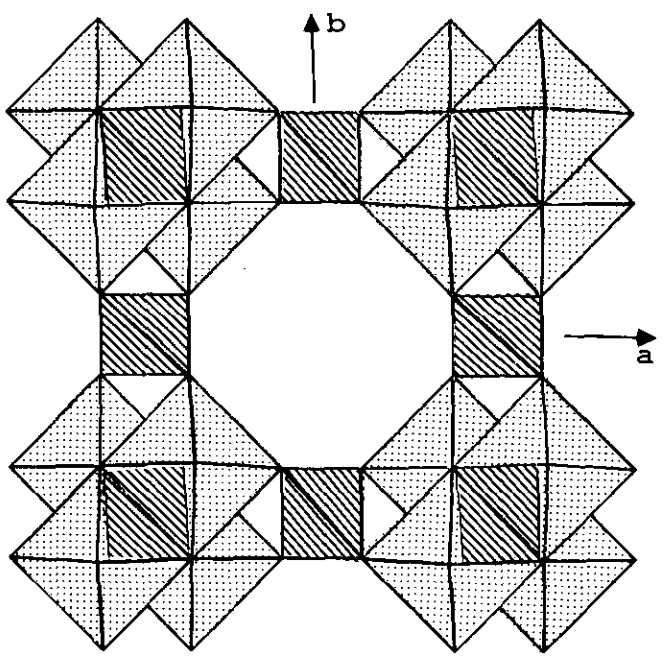

FIG. 4. View of $Cs_3Mo_4P_3O_{16}$ along **c**.

The geometry of the PO_4 tetrahedra is characteristic of monophosphates (Table 4). The barium atoms, that sit at the center of the eight-sided windows, are surrounded by 12 oxygen atoms. Four oxygen atoms correspond to the molybdenyl ions and are located 2.878 Å from Ba^{2+}, whereas the 18 other atoms that form the eight-sided window are sitting further at 3.049 Å.

CONCLUSION

The close relationships between the layer structure of this Mo(V) phosphate and the intersecting tunnel structure of the mixed-valent Mo(III)–Mo(IV) phosphates $A_3(MoO)_4(PO_4)_3$ are a remarkable feature. These relationships and other ones reported by Haushalter and Mundi (10) indicate that it should be possible to generate a number of microporus molybdenum phosphates with closely related structures and intermediate valences of molybdenum using soft chemistry or hydrothermal synthesis.

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