

## A Molybdenum V Diphosphate, $\text{BaMo}_2\text{P}_4\text{O}_{16}$

G. COSTENTIN, M. M. BOREL, A. GRANDIN, A. LECLAIRE,<sup>1</sup>  
AND B. RAVEAU

*Laboratoire de Cristallographie et Sciences des Matériaux, C.N.R.S.,  
CRISMAT-ISMRA Université de Caen, Boulevard du Maréchal Juin, 14032  
Caen Cédex, France*

Received March 5, 1990

A new Mo(V) phosphate  $\text{BaMo}_2\text{P}_4\text{O}_{16}$  has been synthesized and its structure has been determined from a single crystal X-ray diffraction study. It crystallizes in the space group  $P2_1/c$  with  $a = 6.4394(4)$  Å,  $b = 12.378(1)$  Å,  $c = 9.1613(7)$  Å,  $\beta = 123.92(1)^\circ$ . The original  $[\text{Mo}_2\text{P}_4\text{O}_{16}]_x$  host lattice shows that it is the only diphosphate of pentavalent molybdenum known up to now. Each  $\text{P}_2\text{O}_7$  group shares two corners with the same  $\text{MoO}_6$  octahedron forming  $[\text{MoP}_2\text{O}_{11}]$  units already encountered in the  $A\text{Mo}_2\text{P}_3\text{O}_{13}$  phosphates. The whole structure can be described from these structural units, which share their corners leading to  $[\text{MoP}_2\text{O}_{10}]_x$  chains running along  $\vec{b}$ . One important characteristic of this tridimensional framework deals with the fact that each  $\text{MoO}_6$  octahedron and each  $\text{P}_2\text{O}_7$  group exhibit one free apex, suggesting a great flexibility of the structure. © 1990 Academic Press, Inc.

### Introduction

The recent exploration of the molybdenum phosphates has shown that these compounds form a huge family owing to the various oxidation states of molybdenum. In this respect, Mo(V) was considered until 1983 as an unusual valency for molybdenum in oxides and especially in phosphates, since only two Mo(V) phosphates were known,  $\text{MoPO}_5$  (1) and  $\text{Mo}_2\text{P}_4\text{O}_{15}$  (2). The ability of pentavalent molybdenum to participate to phosphate frameworks was demonstrated these last years with the synthesis of six new structural types, corresponding all to the same formulation  $A\text{Mo}_2\text{P}_3\text{O}_{13}$  (3–11). The variety of these structures results from the particular electronic configuration of

Mo(V), which forms an abnormally short Mo–O bond and makes that each  $\text{MoO}_6$  octahedron always exhibits one free apex, allowing a great flexibility of the “MoPO” framework to be reached. These latter results suggest that the investigation of pseudo-ternary systems involving large A cations like alkaline or alkaline earth should allow new Mo(V) phosphates to be synthesized. We report here on the crystal structure of a new barium molybdenum(V) diphosphate  $\text{BaMo}_2\text{P}_4\text{O}_{16}$ .

### Synthesis

The quantitative synthesis of  $\text{BaMo}_2\text{P}_4\text{O}_{16}$  was performed in two steps: first,  $\text{H}(\text{NH}_4)_2\text{PO}_4$ ,  $\text{MoO}_3$ , and  $\text{BaCO}_3$  were mixed in appropriate ratios to obtain the composition  $\text{Ba}_2\text{Mo}_{1.667}\text{P}_4\text{O}_{16}$  and heated in

<sup>1</sup> To whom correspondence should be addressed.

TABLE I  
BaMo<sub>2</sub>P<sub>4</sub>O<sub>16</sub>: X-RAY POWDER PATTERN

<i>h k l</i>	<i>d</i> <sub>obsd</sub>	<i>d</i> <sub>calcd</sub>	<i>I</i> / <i>I</i> <sub>0</sub>	<i>h k l</i>	<i>d</i> <sub>obsd</sub>	<i>d</i> <sub>calcd</sub>	<i>I</i> / <i>I</i> <sub>0</sub>
1 0 0	5.348	5.343	9	1 0 2	2.509	2.506	8.5
0 2 1	4.797	4.799	10.5	0 1 3	2.486	2.483	6
-1 0 2	4.516	4.504	98	1 1 2	2.458	2.457	9
-1 1 2	4.238	4.233	8	2 2 0	2.449	2.453	17
1 2 0	4.051	4.044	29	-1 3 3		2.446	
0 1 2	3.633	3.634	100	1 2 2	2.326	2.323	18.5
1 1 1	3.408	3.403	32	1 5 0	2.248	2.246	3.5
1 3 0	3.273	3.266	3.5	-2 1 4	2.216	2.216	7
-2 0 2	3.173	3.172	6	-1 1 4	2.190	2.190	16
0 4 0	3.091	3.094	46	1 3 2	2.142	2.142	40
-2 1 2	3.068	3.072	58	-2 2 4	2.118	2.116	14
1 2 1		3.073		0 6 0	2.064	2.063	7
-2 1 1	3.033	3.029	20	-2 4 3		2.061	
-1 1 3	2.951	2.951	10	1 5 1	2.029	2.029	10
0 4 1	2.869	2.866	27	0 6 1	1.993	1.991	4.5
-2 2 2	2.825	2.823	37	-3 0 4	1.954	1.952	10
0 3 2	2.791	2.796	24	-2 5 2		1.951	
-2 2 1		2.789		-3 1 4	1.928	1.928	32
-2 1 3	2.699	2.697	10	0 1 4	1.879	1.878	11
1 3 1	2.685	2.687	11.5	-2 5 3	1.845	1.844	10
2 1 0	2.615	2.612	10	0 2 4	1.816	1.817	11
-1 4 2	2.552	2.551	7.5	2 5 0		1.816	

air at 600 K to decompose the carbonate and the ammonium phosphate; in a second step, the resulting product was then added to the required amount of molybdenum and heated up to 1173 K for 2 days in an evacuated silica ampoule. Green crystals of BaMo<sub>2</sub>P<sub>4</sub>O<sub>16</sub> were grown from a mixture corresponding to the normal composition Ba<sub>0.5</sub>Mo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> in the following way: first, a mixture of H(NH<sub>4</sub>)<sub>2</sub>PO<sub>4</sub>, MoO<sub>3</sub>, and BaCO<sub>3</sub> in appropriate ratios was heated in a platinum crucible at 600 K in order to decompose the carbonate and the ammonium phosphate. In a second step, the required amount of molybdenum was added and the product was heated in an evacuated silica ampoule for 5 days at 1073 K.

The powder X-ray diffraction pattern of the phase was indexed in a monoclinic cell (Table I) in agreement with the parameters obtained from the single crystal study.

### Structure Determination

The cell parameters reported in Table II were determined and refined by diffracto-

TABLE II  
SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR BaMo<sub>2</sub>P<sub>4</sub>O<sub>16</sub>

1. Crystal data	
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Cell dimensions	<i>a</i> = 6.4394(4) Å <i>b</i> = 12.378(1) Å β = 123.92(1)° <i>c</i> = 9.1613(7) Å <i>v</i> = 606.0(2) Å <sup>3</sup>
Volume	2
<i>Z</i>	
2. Intensity Measurement	
λ (MoKα)	0.71073 Å
Scan mode	ω - 4/3 θ
Scan width (°)	1 + 0.35 tan θ
Slit aperture (mm)	1 + tan θ
Max θ (°)	45
Standard reflections	3 measured every 2000 sec (no decay)
Reflections with <i>I</i> > 3σ	1152
μ (mm <sup>-1</sup> )	5.82
3. Structure solution and refinement	
Parameters refined	106
Agreement factors	<i>R</i> = 0.031, <i>R</i> <sub>w</sub> = 0.031
Weighting scheme	<i>W</i> = <i>f</i> (sin θ/λ)
Δ/σ <sub>max</sub>	0.005

metric techniques at 294 K with a least-squares refinement based upon 25 reflections with 18 < θ < 22°. The data were collected on a CAD-4 Enraf-Nonius diffractometer with the data collection parameters reported in Table II. The reflections were corrected for Lorentz and polarization ef-

TABLE III  
POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ba	0.000	0.000	0.500	1.23(1)
Mo	0.45795(9)	0.18924(5)	0.16072(6)	0.366(8)
P(1)	0.8753(3)	0.3066(2)	0.5674(2)	0.48(3)
P(2)	0.6571(3)	0.4437(2)	0.2509(2)	0.49(3)
O(1)	0.3140(8)	0.1557(5)	-0.0495(6)	1.1(1)
O(2)	0.8063(7)	0.1706(4)	0.1980(5)	0.81(9)
O(3)	0.4659(8)	0.3520(4)	0.1501(6)	0.72(9)
O(4)	0.1551(7)	0.2127(4)	0.1684(6)	0.9(1)
O(5)	0.5054(8)	0.0380(4)	0.2584(6)	0.68(9)
O(6)	0.7234(8)	0.2161(4)	0.4423(6)	0.72(9)
O(7)	0.8196(8)	0.4130(4)	0.4542(6)	1.0(1)
O(8)	0.8224(8)	0.4695(5)	0.1927(6)	1.4(1)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $B_{eq} = \frac{4}{3} [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (ab \cos \gamma)\beta_{12} + (ac \cos \beta)\beta_{13} + (bc \cos \alpha)\beta_{23}]$ .

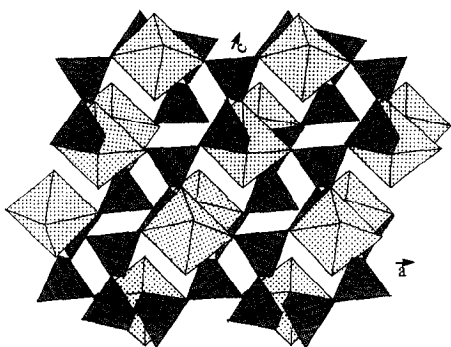


FIG. 1. Projection of the structure of BaMo<sub>2</sub>P<sub>4</sub>O<sub>16</sub> along  $\vec{b}$ .

fects; no absorption corrections were performed.

Atomic coordinates of the molybdenum atom were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to  $R = 0.031$  and  $R_w = 0.031$  and to the atomic parameters of Table III.<sup>2</sup>

### Description of the Structure and Discussion

BaMo<sub>2</sub>P<sub>4</sub>O<sub>16</sub> represents the ninth Mo(V) phosphate which has been discovered up to now, and the first one which can be described as a diphosphate of pentavalent molybdenum. Its host lattice [Mo<sub>2</sub>P<sub>4</sub>O<sub>16</sub>]<sub>∞</sub> (Fig. 1) is indeed built up from corner-sharing MoO<sub>6</sub> octahedron and P<sub>2</sub>O<sub>7</sub> groups, whereas the six forms of AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> (3-11) phosphates always contain single PO<sub>4</sub> (2) besides P<sub>2</sub>O<sub>7</sub> groups, MoPO<sub>5</sub> (1) and Mo<sub>2</sub>P<sub>4</sub>O<sub>15</sub> (2)

being a monophosphate and a tetraphosphate, respectively.

The geometry of the MoO<sub>6</sub> octahedra is characteristic of Mo(V). One observes one very short Mo–O bond (1.658 Å) and one abnormally long Mo–O distance (2.183 Å), whereas the four other Mo–O distances are normal (2.011 to 2.085 Å) (Table IV). The sum of the electrostatic valences calculated with the Zachariasen curves (13) confirms that molybdenum presents the pentavalent state. As in the AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> (3-11) compounds, the Mo<sup>V</sup>O<sub>6</sub> octahedron has one free apex which is not shared with other polyhedra of the host lattice and corresponds to the abnormally short Mo–O bond. The diphosphate groups exhibit an eclipsed configuration. One striking feature concerns the fact that one apex of the P<sub>2</sub>O<sub>7</sub> groups is free, i.e., not linked to another polyhedron but only involved in the barium coordination. This behavior has never been observed in the other Mo(V) AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> phosphates (3-11), nor in the molybdenum diphosphates NaMoP<sub>2</sub>O<sub>7</sub> (14) and KMoP<sub>2</sub>O<sub>7</sub> (15). The geometry of the PO<sub>4</sub> tetrahedra is strongly influenced by their way of linking. For the P(1) tetrahedron one observes the classical geometry for diphosphate groups, i.e., one long P–O bond corresponding to the bridging oxygen and three shorter P–O distances (Table V). However, for the P(2) tetrahedron one observes one long P–O bond corresponding to the same bridging oxygen, two shorter P–O distances, and one very short P–O bond (1.467 Å) correspond-

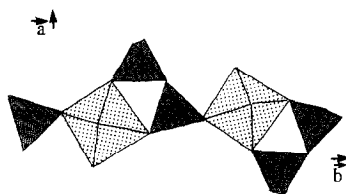


FIG. 2. [MoP<sub>2</sub>O<sub>10</sub>]<sub>∞</sub> chain running along  $\vec{b}$ .

<sup>2</sup> Lists of structure factors and anisotropic thermal motion parameters are available on request to the authors.

TABLE IV  
DISTANCE (Å) AND ANGLES (°) IN THE MoO<sub>6</sub> OCTAHEDRON

Mo	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.658(5)	2.684(7)	2.865(7)	2.795(8)	2.779(7)	3.815(8)
O(2)	90.9(2)	2.085(5)	2.995(7)	4.081(8)	2.819(7)	2.635(7)
O(3)	101.9(3)	93.7(2)	2.020(5)	2.717(7)	3.985(8)	2.792(7)
O(4)	98.8(2)	170.3(2)	84.8(2)	2.011(5)	2.893(7)	3.073(7)
O(5)	97.5(3)	86.7(2)	160.5(2)	91.6(2)	2.023(5)	2.652(7)
O(6)	166.5(2)	76.2(2)	83.1(2)	94.1(2)	78.1(2)	2.183(5)

Note. The diagonal terms are the Mo–O(*i*) distances, the terms above the diagonal are the O(*i*)–O(*j*) distances, and those below are the O(*i*)–Mo–O(*j*) angles.

ing to the free corner of the diphosphate group (Table V).

Although being different from the other Mo(V) phosphates, the [Mo<sub>2</sub>P<sub>4</sub>O<sub>16</sub>]<sub>∞</sub> framework has a common feature with the AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> phosphates (3-11), which also contain diphosphate groups. All those frameworks exhibit indeed [MoP<sub>2</sub>O<sub>11</sub>] units built up from one P<sub>2</sub>O<sub>7</sub> groups sharing two of its apices with the same MoO<sub>6</sub> octahedron.

TABLE V  
DISTANCES (Å) AND ANGLES (°) IN THE PO<sub>4</sub> TETRAHEDRA

P(1)	O(2 <sup>i</sup> )	O(4 <sup>ii</sup> )	O(6)	O(7)
O(2 <sup>i</sup> )	1.517(5)	2.464(7)	2.519(7)	2.506(7)
O(4 <sup>ii</sup> )	108.7(3)	1.516(5)	2.524(7)	2.492(7)
O(6)	112.7(3)	113.1(3)	1.508(5)	2.502(7)
O(7)	105.6(3)	106.7(3)	107.8(3)	1.588(6)
P(2)	O(3)	O(5 <sup>iii</sup> )	O(7)	O(8)
O(3)	1.545(5)	2.421(7)	2.537(7)	2.556(7)
O(5 <sup>iii</sup> )	103.5(3)	1.538(3)	2.453(7)	2.536(7)
O(7)	107.9(3)	103.2(3)	1.592(5)	2.506(8)
O(8)	116.1(3)	115.1(3)	109.9(3)	1.467(6)

Note. The diagonal terms are the P–O(*i*) distances, the terms above the diagonal are the O(*i*)–O(*j*) distances, and those below are the O(*i*)–P–O(*j*) angles. (i):  $x; \frac{1}{2} - y; \frac{1}{2} + z$ . (ii):  $1 + x; \frac{1}{2} - y; \frac{1}{2} + z$ . (iii):  $1 - x; \frac{1}{2} + y; \frac{1}{2} - z$ . (iv):  $x - 1; \frac{1}{2} - y; \frac{1}{2} + z$ . (v):  $1 - x; y - \frac{1}{2}; \frac{1}{2} - z$ . (vi):  $x - 1; y; z$ . (vii):  $1 - x; -y; 1 - z$ . (viii):  $-x; y - \frac{1}{2}; \frac{1}{2} - z$ .

Different from AMo<sub>2</sub>P<sub>3</sub>O<sub>13</sub> phosphates, the [Mo<sub>2</sub>P<sub>4</sub>O<sub>16</sub>]<sub>∞</sub> framework can be described from the only association of these MoP<sub>2</sub>O<sub>11</sub> units. The latter units share indeed the corners of their polyhedra forming infinite [MoP<sub>2</sub>O<sub>10</sub>]<sub>∞</sub> chains running along  $\vec{b}$  (Fig. 2). Thus the structure of BaMo<sub>2</sub>P<sub>4</sub>O<sub>16</sub> can be described as the association of identical [MoP<sub>2</sub>O<sub>10</sub>]<sub>∞</sub> chains. Each chain shares corners of its polyhedra with four identical chains which are orientated at 180°. In the same way, these chains form [MoP<sub>2</sub>O<sub>9</sub>]<sub>∞</sub> layers parallel to (100) (Fig. 3). The stacking of these layers along *a* leads to the tridimensional framework [Mo<sub>2</sub>P<sub>4</sub>O<sub>16</sub>]<sub>∞</sub>. The fact that each MoO<sub>6</sub> octahedron and each P<sub>2</sub>O<sub>7</sub> group exhibit one free apex suggests for this structure a great flexibility.

The barium ions in the cages are sur-

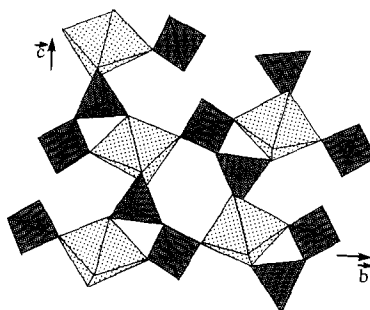


FIG. 3. [MoP<sub>2</sub>O<sub>9</sub>]<sub>∞</sub> layer parallel to (100).

TABLE VI  
OXYGEN ATOMS  
SURROUNDING Ba<sup>2+</sup>

---

Ba–O(8 <sup>iv</sup> ) = 2.611(5) Å
Ba–O(8 <sup>v</sup> ) = 2.611(5)
Ba–O(5 <sup>vi</sup> ) = 2.720(5)
Ba–O(5 <sup>vii</sup> ) = 2.720(5)
Ba–O(6 <sup>vi</sup> ) = 3.092(5)
Ba–O(6 <sup>vii</sup> ) = 3.092(5)
Ba–O(3 <sup>viii</sup> ) = 3.105(5)
Ba–O(3 <sup>i</sup> ) = 3.105(5)
Ba–O(2 <sup>vi</sup> ) = 3.113(5)
Ba–O(2 <sup>vii</sup> ) = 3.113(5)

---

*Note.* Symmetry codes are given in the footnote to Table V.

rounded by 10 oxygen atoms with Ba–O distances ranging from 2.611 to 3.333 Å (Table VI). It is worth pointing out that the shortest Ba–O distances correspond to the O(8) free apex of the P<sub>2</sub>O<sub>7</sub> group whereas the free apex of the MoO<sub>6</sub> octahedron is not involved in the barium coordination.

## References

1. P. KIERKEGAARD AND J. M. LONGO, *Acta Chem. Scand.* **24**, 427 (1970).
2. L. KH. MINACHEVA, A. S. ANTSYSHKINA, A. V. LAVRO, V. G. SAKHAROVA, V. P. NIKOLAEV, AND M. A. PORAI-KOSHITS, *Russ. J. Inorg. Chem.* **24**, 51 (1979).
3. A. LECLAIRE, J. C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **48**, 147 (1983).
4. K. H. LIU AND R. C. HAUSHALTER, *J. Solid State Chem.* **69**, 320 (1987).
5. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Acta Crystallogr.*, in press (1990).
6. J. J. CHEN, K. J. LIU, AND S. L. WANG, *J. Solid State Chem.* **46**, 204 (1988).
7. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Z. Kristallogr.* **188**, 77 (1989).
8. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **80**, 250 (1989).
9. K. H. LIU, D. C. JOHNSTON, D. P. GOSHORN, AND R. C. HAUSHALTER, *J. Solid State Chem.* **71**, 31 (1987).
10. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.*, **89**, 10 (1990).
11. G. COSTENTIN, M. M. BORIN, A. GRANDIN, A. LECLAIRE, AND B. RAVEAU, *J. Solid State Chem.*, **89**, 30 (1990).
12. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Eur. J. Solid State Inorg. Chem.* **26**, 45 (1989).
13. W. H. ZACHARIASEN, *J. Less-Common Met.* **62**, 1 (1978).
14. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **76**, 131 (1988).
15. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **78**, 220 (1989).