A Mixed Valent Molybdenum Monophosphate with a Layer Structure: $CsMo_2O_3(PO_4)_2$

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A new mixed valent molybdenum monophosphate Cs $Mo_2O_3(PO_4)_2$ has been synthesized in the form of single crystals. It crystallizes in the space group $P2_1/c$ with $a = 10.047(2)$ Å, $b = 8.655(1)$ Å, $c = 11.597(2)$ Å, $\beta = 104.27(1)°$. This phase exhibits an original layered structure, in which the $[Mo_2P_2O_{11}]_\infty$ layers consist of $[MoPO_8]_\infty$ chains connected with $[MoPO_7]_\infty$ chains. In the $[MoPo_8]_\infty$ chains, one MoO_6 octahedron alternates with one PO_4 tetrahedron, whereas in the $[MoPO_7]_\infty$ chains one MoO_5 trigonal bipyramid alternates with one PO_4 tetrahedron. The geometry of the MoO_6 octahedra and MoO_5 bipyramids is in agreement with their occupancy by Mo(V) and Mo(VI), respectively. The Cs^+ cations interleaved between these layers exhibit a monocapped distorted cubic coordination. © 1995 Academic Press, Inc.

INTRODUCTION

Begun in 1990, the research on mixed valent molybdenum Mo(V)–Mo(VI) phosphates has allowed four new series of compounds with an original structure to be synthesized to date. In these compounds, the behavior of molybdenum varies dramatically from one series to the other. The monophosphates $A_3Mo_4O_6(PO_4)_4$ with $A =$ Rb, Tl, Cs (1, 2) are the only ones that are characterized by an electronic delocalization at the scale of bioctahedral units Mo_2O_{11}. In the three other series, the Mo(V) and Mo(VI) species are distributed in an ordered way; Mo(V) exhibits an octahedral configuration characteristic of the molybdenyl ion, whereas Mo(VI) exhibits either a tetrahedral coordination as in $Cs_{8+x}Mo_{13}O_{22}(PO_4)_{10}$ (3), or an unusual trigonal bipyramidal coordination as in the series $AMo_3O_4(PO_4)_3$ with $A =$ Na, Ag (4, 5) and $AMo_3O_6(PO_4)_2$ with $A =$ K, Na, Rb, Ag, Sr (6, 7). The wide range of molar ratios Mo(V)/Mo(VI), from 12 to 1/2, obtained for these compounds suggests that we are at the beginning of the discovery of mixed valent molybdenum phosphates. For this reason a systematic reinvestigation of the Cs–Mo–P–O system, varying the Mo(V)–Mo(VI) molar ratio has been carried out. We report here on a new mixed valent monophosphate, $CsMo_2O_3(PO_4)_2$ with a layered

structure, in which Mo(VI) exhibits the trigonal bipyramidal coordination.

EXPERIMENTAL

Single crystals of this new phosphate were grown from a mixture of nominal composition $CsMo_3P_3O_{17}$.

The synthesis was performed in two steps from mixture in adequate ratios to obtain the above formulation. First a mixture of Cs_2CO_3, $H(NH_4)_2PO_4$, and MoO_3 was ground and heated to 673 K to eliminate CO_2, NH_3, and H_2O. In a second step, the appropriate amount of molybdenum was added and the finely ground mixture was sealed in an evacuated silica ampoule, then heated for a day to 920 K, cooled at 4 K/h to 773 K, and then quenched to room temperature. Some yellow plate crystals were extracted from this resulting mixture. The microprobe analysis of the yellow crystals confirms the composition $CsMo_2P_2O_{11}$ in agreement with the structure determination.

Many attempts to prepare this new phase in the form of powder always led to a mixture. Based on visual microscopic examination, there were two phases in the product: the major phase occurred as yellow plates and the minor phase as black needles not yet identified. The yellow crystals were picked out with tweezers using a binocular microscope and the powder X-ray pattern of this phase was indexed with the parameters obtained from the single crystal study (Table 1).

STRUCTURE DETERMINATION

A yellow crystal with dimensions $0.077 \times 0.051 \times 0.026$ 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-squares refinement based upon 25 reflections with $18° < \theta < 22°$; the systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ are characteristic of the $P2_1/c$ space group. The data were collected on an Enraf–Nonius CAD4 diffractometer with the data collection parameters

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TABLE 1

$CsMo_2O_3(PO_4)_2$: Guinier X-ray Diffraction Pattern

h	k	l	d_{calc}	d_{obs}	I_{obs}	h	k	l	d_{calc}	d_{obs}	I_{obs}
2	0	0	4.853	4.863	9						
0	2	0	4.324	4.321	22	4	0	0	2.432	2.432	32
2	0	$\bar{2}$	4.228	4.220	40	3	3	0	2.154	2.155	6
1	1	2	3.933	3.928	28	3	2	$\bar{4}$	2.126	2.121	12
1	2	$\bar{1}$	3.849	3.846	2	0	4	$\bar{1}$	2.123		
2	1	1	3.712	3.705	8	1	4	1	2.054	2.054	3
0	2	2	3.426	3.428	7	1	3	$\bar{4}$	2.043	2.042	2
2	0	2	3.297	3.292	18	4	2	$\bar{3}$	2.042		
3	0	0	3.242	3.239	26	1	4	2	1.942	1.942	7
3	0	$\bar{2}$	3.167	3.170	24	2	4	$\bar{2}$	1.925	1.924	6
2	1	$\bar{3}$	3.164			4	3	0	1.859	1.859	8
2	1	2	3.081	3.079	18	3	1	$\bar{6}$	1.789	1.789	4
3	1	0	3.036	3.036	100	3	2	4	1.742	1.743	4
1	1	$\bar{4}$	2.746	2.752	10	5	3	$\bar{2}$	1.641	1.642	8
2	2	$\bar{3}$	2.672	2.670	3	1	1	$\bar{7}$	1.621	1.623	20
0	1	$\bar{4}$	2.672			6	1	1	1.527	1.528	3

reported in Table 2. The reflections were corrected for Lorentz, polarization, and absorption effects.

Atomic coordinates of the molybdenum were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the

TABLE 2

Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $CsMo_2O_3(PO_4)_2$

Crystal data	
Space group	$P2_1/c$
Cell dimensions	a = 10.047(2) Å
	b = 8.655(1) Å
	c = 11.597(2) Å
	β = 104.27(1)°
Volume	977.2(5) Å^3
Z	4
d_{calc}	3.83
Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 2/3\theta$
Scan width (°)	1.32 + 0.35 tan θ
Slit aperture (mm)	1.25 + tan θ
Max θ (°)	45
Standard reflections	3 every hour
Reflections measured	8642
Reflections with $I > 2.5\sigma$	1236
μ (mm^{-1})	6.53
Structure solution and refinement	
Parameters refined	90
Agreement factors	R = 0.037 R_w = 0.037
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	<0.004
$\Delta\rho$ (e Å^{-3})	1.3
S	1.004

TABLE 3

Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B (Å^2)
Cs	0.09345(8)	0.2362(1)	0.07226(7)	1.76(1)
Mo(1)	0.38233(8)	0.2557(1)	0.38781(8)	0.64(1)
Mo(2)	0.80420(9)	0.2240(1)	0.27332(9)	0.88(2)
P(1)	0.4752(3)	0.0810(4)	0.1646(3)	0.65(5)
P(2)	0.7077(3)	0.0863(4)	0.5121(3)	0.75(5)
O(1)	0.2360(9)	0.346(1)	0.3225(8)	1.4(2)^a
O(2)	0.3880(9)	0.120(1)	0.2509(8)	1.2(1)^a
O(3)	0.5043(9)	0.405(1)	0.3313(9)	1.6(2)^a
O(4)	0.2861(8)	0.083(1)	0.4504(8)	1.2(1)^a
O(5)	0.397(1)	0.369(1)	0.5435(9)	1.7(2)^a
O(6)	0.5659(9)	0.150(1)	0.4741(8)	1.4(2)^a
O(7)	0.953(1)	0.134(1)	0.2752(9)	1.9(2)^a
O(8)	0.846(1)	0.387(1)	0.358(1)	2.5(2)^a
O(9)	0.6157(9)	0.158(1)	0.2001(8)	1.5(2)^a
O(10)	0.7966(9)	0.318(1)	0.1161(9)	1.5(2)^a
O(11)	0.7847(9)	0.094(1)	0.4120(8)	1.2(1)^a

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3 \Sigma_i \Sigma_j$ $\mathbf{a}_i \cdot \mathbf{a}_j \beta_{ij}$.
^{a} Refined isotropically.

atomic coordinates, of the anisotropic thermal factor for cesium, molybdenum, and phosphorus atoms and of the isotropic thermal factor for oxygen atoms led to R = 0.037 and R_w = 0.037 and to the atomic parameters of Table 3.
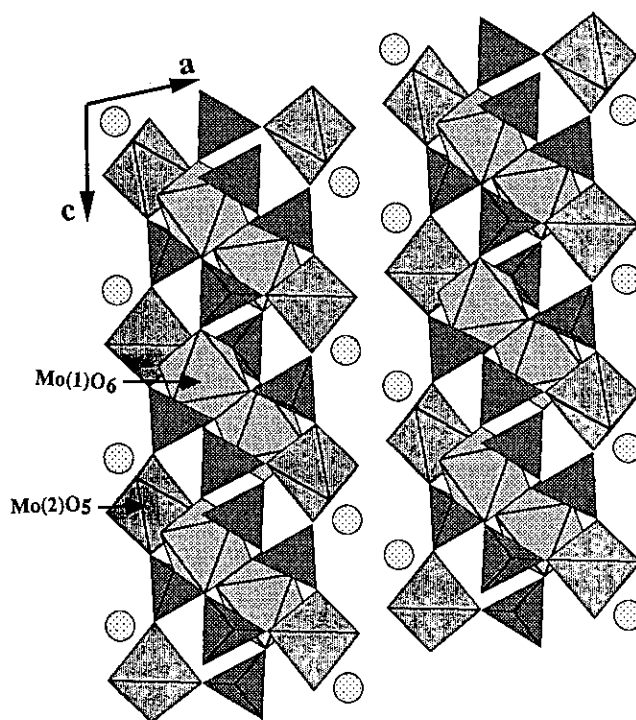

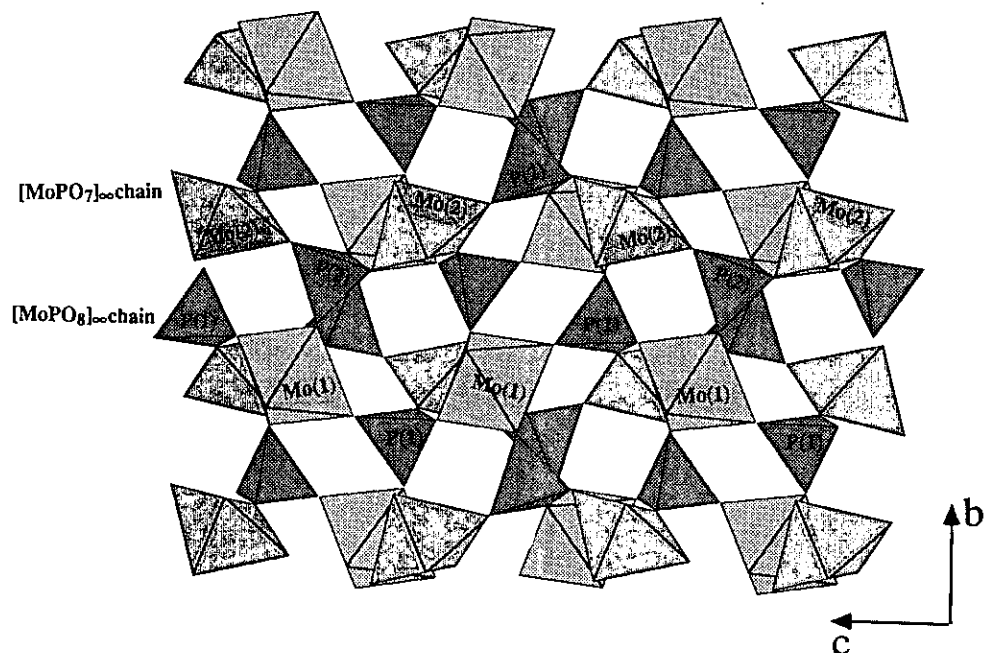FIG. 1. Projection of the structure of $CsMo_2O_3(Po_4)_2$ along **b**.

FIG. 2.   Projection of a [Mo₂P₂O₁₁]ₓ layer along **a**.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of this structure along **b** shows its lamellar character (Fig. 1). It consists of [Mo₂P₂O₁₁]ₓ layers of corner-sharing PO₄ tetrahedra, MoO₆ octahedra, and MoO₅ trigonal bipyramids, parallel to (100), interleaved with Cs⁺ cations.

The projection of a [Mo₂P₂O₁₁]ₓ layer onto the (100)

plane (Fig. 2) shows that it consists of two kinds of chains waving along **c**. In the first type, formulated as [MoPO₈]ₓ, one MoO₆ octahedron (Mo(1)) alternates with one PO₄ tetrahedron (P(1)), whereas in the second kind of chain, (MoPO₇)ₓ, one MoO₅ bipyramid (Mo(2)) alternates with one PO₄ tetrahedron (P(2)). In fact, each [MoPO₇]ₓ chain shares the apices of its polyhedra with two [MoPO₈]ₓ chains in such a way that a PO₄ tetrahedron of one chain

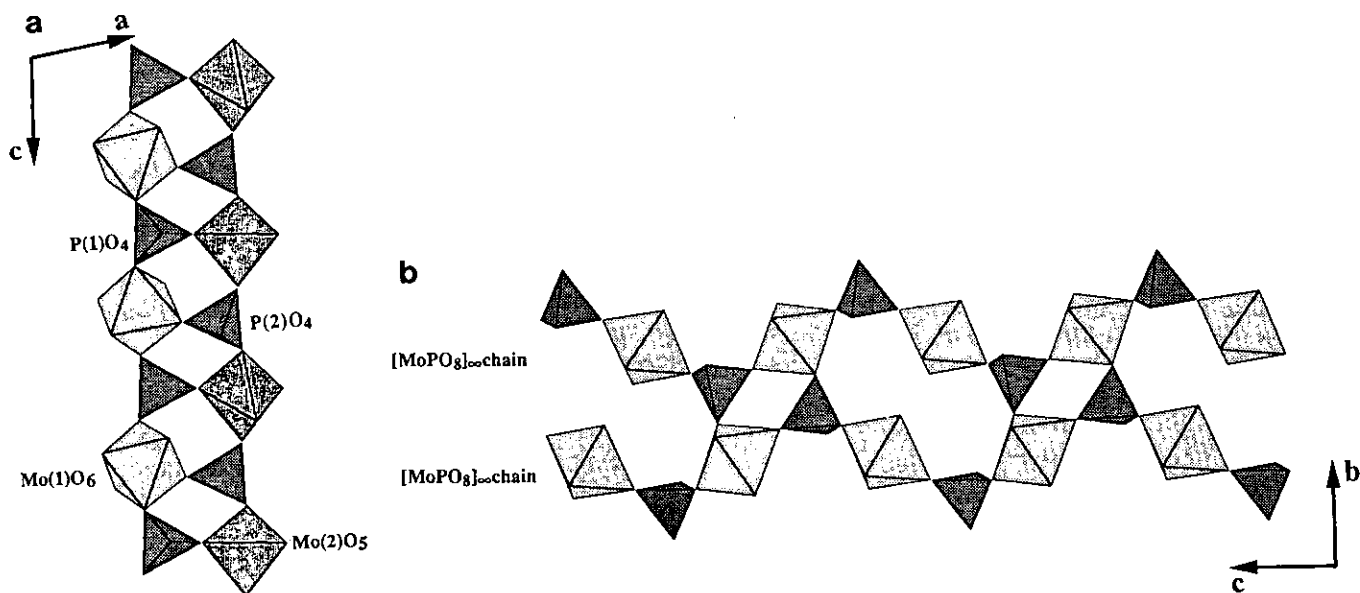FIG. 3.   (a) The [Mo₂P₂O₁₃]ₓ double chain running along **c**, (b) the [Mo₂P₂O₁₄]ₓ double chain running along **c**.

TABLE 4
Distances (Å) and Angles (°) in Polyhedra[a]

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.67(1)	2.73(1)	2.72(1)	2.70(1)	2.68(1)	3.75(6)
O(2)	96.2(4)	1.99(1)	2.79(1)	2.77(1)	4.00(6)	2.77(1)
O(3)	95.3(4)	88.9(4)	2.00(1)	4.00(6)	2.94(1)	2.74(1)
O(4)	93.6(4)	87.7(4)	170.8(4)	2.01(1)	2.82(1)	2.82(1)
O(5)	92.3(4)	170.9(5)	93.6(4)	88.6(4)	2.03(1)	2.80(1)
O(6)	177.9(5)	85.8(4)	84.4(4)	86.9(4)	85.8(4)	2.08(1)

Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)
O(7)	1.68(1)	2.72(2)	3.30(1)	2.64(1)	2.61(1)
O(8)	106.5(5)	1.71(1)	3.25(2)	2.79(2)	2.72(2)
O(9)	129.3(5)	124.2(5)	1.96(1)	2.65(1)	2.68(1)
O(10)	91.9(5)	97.9(6)	84.6(4)	1.98(1)	3.96(6)
O(11)	89.6(5)	93.5(5)	84.8(4)	167.5(4)	2.01(1)

P(1)	O(2)	O(3)[i]	O(5)[ii]	O(9)
O(2)	1.52(1)	2.46(1)	2.43(1)	2.52(1)
O(3)[i]	107.2(6)	1.53(1)	2.49(1)	2.48(1)
O(5)[ii]	107.4(6)	110.5(6)	1.50(1)	2.50(1)
O(9)	111.7(5)	108.6(6)	111.5(6)	1.52(1)

P(2)	O(4)[iii]	O(6)	O(10)[iv]	O(11)
O(4)[iii]	1.52(1)	2.53(1)	2.50(1)	2.44(1)
O(6)	114.0(6)	1.49(1)	2.50(1)	2.52(1)
O(10)[iv]	108.5(5)	110.9(6)	1.55(1)	2.46(1)
O(11)	105.4(5)	112.4(5)	105.2(5)	1.55(1)

Cs–O distances

Cs–O(1)	3.05(1)
O(4)[ii]	3.09(1)
O(8)[i]	3.15(1)
O(7)[v]	3.15(1)
O(10)[v]	3.23(1)
O(8)[vi]	3.23(1)
O(5)[ii]	3.28(1)
O(11)[vii]	3.32(1)
O(2)	3.32(1)

Note. Symmetry codes: (i) $1 - x$; $-1/2 + y$; $1/2 - z$; (ii) $-x$; $3/2 + y$; $1/2 - z$; (iii) $1 + x; y; 1 + z$; (iv) $-x; 3/2 + y; 3/2 - z$; (v) $-1 + x; y; z$; (vi) $-1 - x; 3/2 + y; 1/2 - z$; and (vii) $1 - x; 1/2 + y; 1/2 - z$.

[a] The Mo–O or P–O distances are on the diagonal, above it are the O $\cdots$ O distances, and below it are the O–M–O or O–P–O angles.

be linked either with a MoO_5 bipyramid or with a MoO_6 octahedron of the other chain as schematized in Fig. 3a. Each $[MoPO_8]_\infty$ chain is linked in the same way (Fig. 3a) to two $[MoPO_7]_\infty$ chains, and to two other identical $[MoPO_8]_\infty$ chains as schematized on Fig. 3b. As a result, the corners of half of the PO_4 tetrahedra (P(1) and P(2)) point up and down the (010) plane alternatively (Fig. 3).

Each P(1) tetrahedron shares three apices with the Mo(1) octahedra and one apex with one Mo(2) trigonal bipyramid, whereas each P(2) tetrahedron is linked to two Mo(1) octahedra and two Mo(2) trigonal bipyramids. The P–O bond lengths of both tetrahedra, ranging from 1.49 to 1.55 Å (Table 4) are characteristic of regular monophosphate groups.

Each Mo(1) octahedron has its free apex directed toward the cesium layers (Fig. 1) and shares three apices
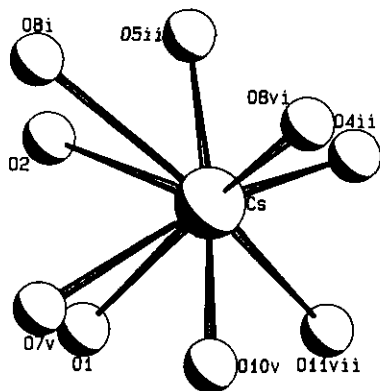
FIG. 4. The Cs$^+$ environment.

with the P(1) tetrahedron and two apices with the P(2) tetrahedron. Its geometry (Table 4) is characteristic of Mo(V) with one abnormally short Mo–O bond (1.67 Å) corresponding to the free apex, the opposite bond being very long (2.08 Å), whereas the four equatorial Mo–O bonds are intermediate (1.99 to 2.03 Å), according to the bond order calculations (5.16) (8).

The Mo(2) trigonal bipyramid has two free apices directed toward the cesium layers (Fig. 1); it shares two apices with the P(2) tetrahedra and one apex with a P(1) tetrahedron. Its geometry (Table 4) is very similar to that observed in the structure of the monophosphates AMo$_3$O$_6$(PO$_4$)$_2$ (4, 5), with three normal and almost equal Mo–O distances corresponding to the oxygen atoms linked shared with three PO$_4$ tetrahedra (1.96 to 2.01 Å), whereas the two other Mo–O bonds, corresponding to the free apices O(7) and O(8) are very short, ranging from 1.68 to 1.71 Å. The bond order calculations (5.99) (9) indicate that the hexavalent molybdenum is located in this bipyramid.

The Cs$^+$ cations which ensure the cohesion between the layers are surrounded by nine oxygen atoms with distances ranging from 3.05 to 3.32 Å, forming a mono-capped distorted cube (Fig. 4).

CONCLUDING REMARKS

The monophosphate CsMo$_2$O$_3$(PO$_4$)$_2$ represents the second kind of mixed valent molybdenum phosphates, with Mo(V)–Mo(VI) that exhibit a layered structure, to date. It is remarkable that in this phase, Mo(VI) is characterized by the unusual trigonal bipyramidal coordination, as in the first series of layered monophosphates AMo$_3$O$_6$(PO$_4$)$_2$ (6, 7). The difficulty in stabilizing such layered structures may be connected with the unusual trigonal bipyramidal coordination of molybdenum. The study of the quantitative synthesis of these phases and of their ion exchange and intercalation properties is in progress.

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