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A Mixed Valent Molybdenum Monophosphate with an Original Cage Structure $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$

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A new mixed valent molybdenum monophosphate, $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$, has been synthesized. It crystallizes in the space group $I\bar{4}2d$ with $a = 9.953(2)$ Å, $c = 26.413(4)$ Å. Its original three-dimensional framework $[Mo_8P_4O_{33}]_\infty$ consists of corner-sharing tetraoctahedral units Mo_4O_{20} with the perovskite configuration, ditetrahedral groups Mo_2O_7, MoO_6 octahedra, and single PO_4 tetrahedra. This 3D lattice forms large cages where the Cs^+ ions are located. An important feature of this structure deals also with the fact that the "molybdenum–oxygen" framework is itself three-dimensional. The distribution of the electrons in this structure is discussed on the basis of bond valence calculations and magnetic measurements. © 1997 Academic Press

INTRODUCTION

Among the mixed valent Mo(V)–Mo(VI) phosphates that have been isolated these past eight years, the cesium compounds exhibit very original frameworks with respect to other alkaline phosphates, due to the larger size of Cs^+. Beside the monophosphate $Cs_3Mo_4O_6(PO_4)_4$ (1), isotypic of $K_2Mo_2O_3(PO_4)_2$ (2) which involves bioctahedral units, two cesium phosphates with an original structure were recently synthesized. The first, $CsMo_2O_3(PO_4)_2$ (3), exhibits a layer structure involving isolated MoO_6 octahedra and MoO_5 bipyramids occupied by Mo(V) and Mo(VI), respectively. The second, $Cs_{8+x}(MoO_4)Mo_{12}O_{18}(PO_4)_{10}\ H_2O$ (4), exhibits tetraoctahedral units of corner- and edge-sharing MoO_6 octahedra connected through MoO_4 and PO_4 tetrahedra, forming an opened framework with zeolithic properties. Such results suggest that we are just at the beginning of a fascinating chemistry, and that many other original frameworks should be generated by associating the large size of cesium and the high flexibility of Mo(V)/Mo(VI) polyhedra in a phosphate matrix. For this reason, we have investigated Cs–Mo–P–O regions corresponding to lower cesium contents. The present work deals with the structure and magnetic properties of a new mixed molybdenum monophosphate, $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$, whose complex framework is built up from tetraoctahedral Mo_4O_{20} perovskite units, ditetrahedral groups Mo_2O_7, MoO_6 octahedra, and monophosphate groups PO_4 forming large cages where cesium is located.

SYNTHESIS AND CRYSTAL GROWTH

Single crystals of the title compound were grown from a nominal composition $CsMo_2P_2O_{11}$. The growth was carried out in two steps: first, the $H(NH_4)_2PO_4$, $CsNO_3$, and MoO_3 were mixed in an agate mortar in adequate ratios according to the composition $CsMo_{1.83}P_2O_{11}$ and heated at 673 K in a platinum crucible for 2 h in air. In a second step, the resulting mixture was added to the required amount of molybdenum (0.17 mole) and 5 wt% of CsCl. The intimately ground mixture was sealed in an evacuated silica ampoule heated in a horizontal furnace for 12 h at 953 K, then cooled at 4 K/h down to 853 K, and finally quenched at room temperature.

From the resulting mixture two sorts of crystals were extracted: black needles that have not been identified owing to their poor quality and pink metallic plates of high quality. The latter were studied by X-ray diffraction; microprobe analysis confirmed the composition $CsMo_8P_4O_{33}$ deduced from the structure determination.

The chemical synthesis of this phase in the form of a polycrystalline sample was performed from a sample of nominal composition $CsMo_8P_4O_{33}$ heated at 833 K for 1 day. A pure phase was isolated and the powder X-ray pattern, registered on a PW1711/90 Philips diffractometer, was indexed in a tetragonal cell (Table 1) in agreement with parameters obtained from the single crystal study (Table 2).

STRUCTURE DETERMINATION

A metallic pink plate-like crystal with dimensions $0.077 \times 0.052 \times 0.077$ 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

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TABLE 1
Powder Diffraction Data for $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$

h	k	l	d_{calc}(Å)	d_{obs}(Å)	I_{obs}
1	0	1	9.314	9.325	1
0	0	4	6.603	6.606	8
0	1	3			
1	1	2	6.211	6.218	13
1	0	5	4.662	4.663	26
2	0	2			
2	1	1	4.389	4.395	31
2	0	4	3.974	3.978	182
1	2	3			
1	1	6	3.732	3.735	54
1	0	7	3.528	3.53	118
2	2	0	3.519	3.524	29
1	2	5	3.404	3.407	85
0	0	8	3.302	3.303	56
2	0	6	3.295	3.298	115
3	0	1			
2	2	4	3.106	3.109	29
0	3	3			
3	1	2	3.062	3.066	41
2	1	7	2.878	2.881	7
3	2	1	2.745	2.749	25
1	2	9	2.450	2.452	19
3	2	5			
2	2	8	2.408	2.410	18
3	2	7	2.228	2.229	13
4	2	0			
3	0	9	2.198	2.200	21
1	2	11	2.113	2.115	20
4	2	4	2.109	2.112	17
3	3	6	2.070	2.073	7
3	2	9	2.010	2.013	10
1	0	13	1.991	1.992	13
3	0	11	1.945	1.946	20
5	0	3	1.942	1.944	14
2	2	12	1.866	1.867	12
4	1	9	1.864	1.866	11
2	1	13	1.848	1.849	10
5	0	7	1.761	1.762	12
4	3	7			
5	3	2	1.693	1.695	25
6	0	0	1.659	1.661	23
3	2	13	1.636	1.637	12
2	0	16	1.567	1.568	15
5	2	9	1.564	1.565	13
4	1	13	1.554	1.555	7
6	2	4	1.531	1.532	18
6	0	8	1.482	1.484	8
5	2	11	1.464	1.466	10
5	3	10	1.434	1.435	10
5	0	13	1.422	1.423	8
4	0	16	1.375	1.376	8
8	0	4	1.222	1.224	7

reflections with $18^\circ \leq \theta \leq 22^\circ$. The systematic absences $h+k+l=2n+1$ for hkl, $k+l=2n+1$ for $0kl$ and $2h+l \neq 4n$ for hhl led to the space groups $I\,4_1md$ (No. 109) and $I\,\bar{4}2d$ (No. 122). The data were collected on a CAD 4 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 with the heavy atom method using the XTAL package (8). A refinement of the occupation factors shows us that the Mo(3), O(9), and Cs sites were half occupied so their occupancy factors were fixed to 0.5 in the further calculations. The refinement of the atomic coordinates and the anisotropic thermal factors was successful in the space group $I\,\bar{4}2d$ and led to $R = 0.041$ and $R_w = 0.032$ for the atomic parameters of Table 3.

TABLE 2
Summary of Crystal Data, Intensity Measurements, and Structure Refinement for $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$

Crystal data	
Space group	$I\,\bar{4}2d$
Cell dimensions	$a = 9.953(2)$ Å
	$c = 26.413(4)$ Å
Volume	2617(1) Å^3
Z	4
d_{calc}	3.94 g/cm^3
Intensity measurements	
λ(Mo$K\alpha$)	0.71073 Å
Scan mode	ω–$2/3\theta$
Scan width (°)	$1.5 + 0.35 \tan\theta$
Max θ (°)	45
Standard reflections	3 measured every hour
Reflections measured	5859
Reflections with $I > 3\sigma$	895 unique reflections
μ (mm^{-1})	5.46
Structure solution and refinement	
Parameters refined	94
Agreement factors	$R = 0.041$ $R_w = 0.033$
Weighting scheme	$w = 1/\sigma^2$
Δ/σ max	< 0.009
$\Delta\rho$ (eÅ^{-3})	< 1.8

RESULTS AND DISCUSSION

Description of the Structure

The projection of this structure along **a** (Fig. 1) shows the high complexity of the $[Mo_8P_4O_{33}]_\infty$ framework that consists of corner-sharing MO_6 octahedra, PO_4 tetrahedra, and ditetrahedral groups Mo_2O_7 forming large cages where the Cs^+ ions are located.

The $[Mo_8P_4O_{33}]_\infty$ framework can be described in a rather simple way by the stacking along **c** of two kinds of layers. The first kind of layer consists of a two-dimensional network $[Mo_4P_4O_{28}]_\infty$ (Fig. 2) built up of tetraoctahedral units Mo_4O_{20} characteristic of the perovskite structure interconnected through PO_4 tetrahedra. The corner-sharing Mo(1) octahedra and P(1) tetrahedra that form this framework can also be described as chains along [1 0 0] and

TABLE 3
Atomic Positional, Isotropic Displacement, Occupation, and Site Parameters for $CsMo_6O_{10}(Mo_2O_7(PO_4)_4$

Atoms	x/a	y/b	z/c	$B(Å^2)$	Occupation	Site
Mo(1)	0.1809(2)	0.1847(2)	0.00729(4)	0.66(3)	1.0	16*e*
Mo(2)	0.4785(4)	0.504(2)	0.10915(6)	0.63(8)	0.5	16*e*
Mo(3)	0.1412(2)	0.6237(3)	0.11410(8)	0.60(6)	0.5	16*e*
Cs	0.0	0.5	0.09897(9)	2.37(8)	0.5	8*c*
P(1)	0.4905(5)	0.2192(3)	0.0420(1)	0.55(8)	1.0	16*e*
O(1)	0.002(2)	0.1824(9)	− 0.0126(3)	1.3(2)	1.0	16*e*
O(2)	0.169(1)	0.226(1)	0.0684(3)	1.5(2)	1.0	16*e*
O(3)	0.198(1)	0.374(1)	− 0.0213(4)	1.8(3)	1.0	16*e*
O(4)	0.385(1)	0.180(1)	0.0029(3)	1.0(2)	1.0	16*e*
O(5)	0.215(1)	0.131(1)	− 0.0754(4)	2.1(3)	1.0	16*e*
O(6)	0.4700(9)	0.3660(9)	0.0574(3)	0.8(2)	1.0	16*e*
O(7)	0.305(1)	0.545(1)	0.1101(3)	1.7(3)	1.0	16*e*
O(8)	0.532(1)	0.633(1)	0.1606(4)	1.7(3)	1.0	16*e*
O(9)	0.0	0.5	0.09897(9)	2.2(3)	0.5	8*c*

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

[0 1 0], in which one P(1) tetrahedron alternates with two Mo(1) octahedra. The second kind of layer is more difficult to describe due to a partial occupancy of several cationic and anionic sites. The basic framework of this layer which can be formulated as $[Mo_4o_2O_{21}]_\infty$ is represented in Fig. 3a. It can be described as crosslinked chains of Mo(2) octahedra and Mo(3) tetrahedra running along **a** and **b**. One indeed distinguishes infinite chains of corner-sharing Mo(2) octahedra and Mo_2O_7 bitetrahedral Mo(3) running along **a** and chains of corner-sharing Mo(3) tetrahedra running along **b**. The Mo(2) sites are splitted with a classical 50% occupancy. But most important is that 50% of the tetrahedral Mo(3) sites are statistically unoccupied and that 50% of the O(9) site that corresponds to the bridging oxygen atom of the Mo_2O_7 groups is statistically occupied by cesium. Consequently, each $[Mo_4o_2O_{21}]_\infty$ layer cannot be considered as two-dimensional but consists in fact of perfectly ordered "Mo_4O_{17}" units built up of two Mo(2) octahedra interconnected by Mo(3) bitetrahedra (Fig. 3b). Between these units, the Cs^+ cations replace the missing "Mo_2O" groups (2Mo(3) + O(9)) in an ordered way. In two successive layers, that are spaced of $c/4$, the "Mo_4O_{17}" units are 90° oriented, due to the $I\bar{4}2d$ symmetry. Such an ordering should involve a doubling of the a parameter of the tetragonal cell. Such a phenomenon is in fact not observed, because two layers of "Mo_4O_{17}" units spaced of $c/2$ have two fixing points possible, translated $b/2$ with respect to each other, or deduced by a simple $c/2$ translation. The use of either fixing points is done at random. This yields a statistical 50% occupancy of the Mo(3) site and a statistical 50% occupancy of the O(9) site by Cs^+.

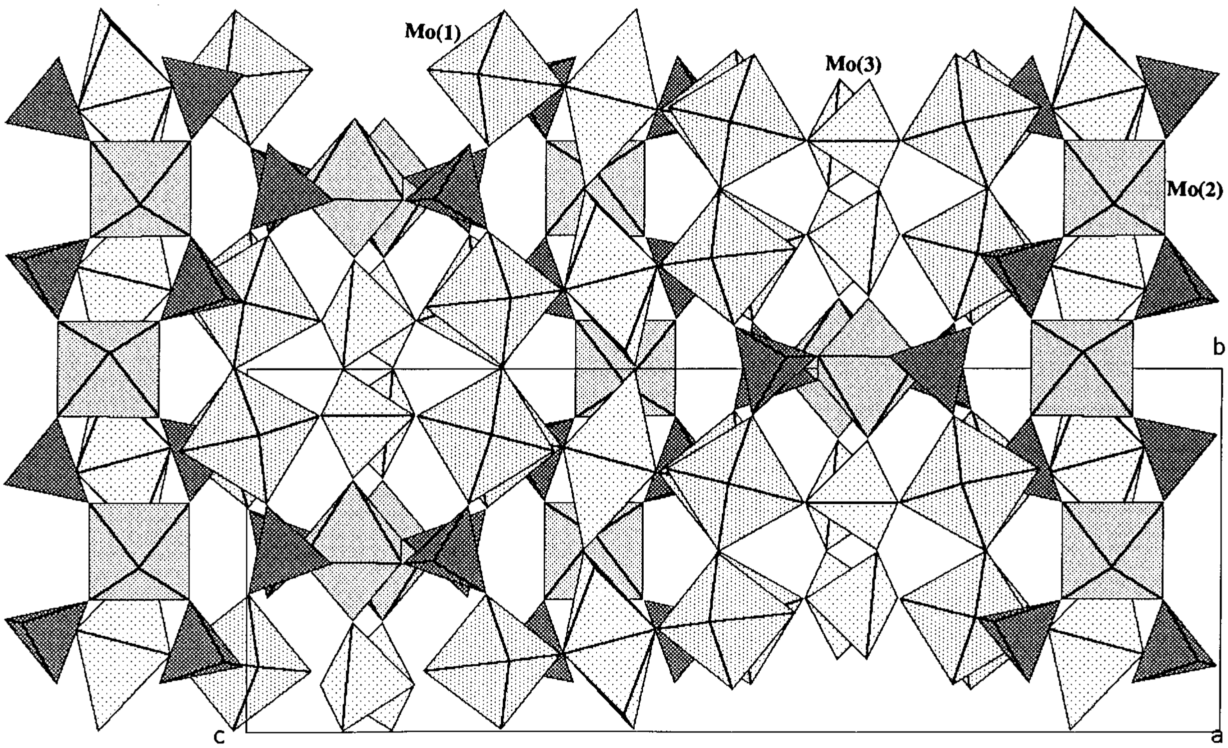

FIG. 1. Projection of the structure of $CsMo_6O_{10}(Mo_2O_7)$ $(PO_4)_4$ along **a**.

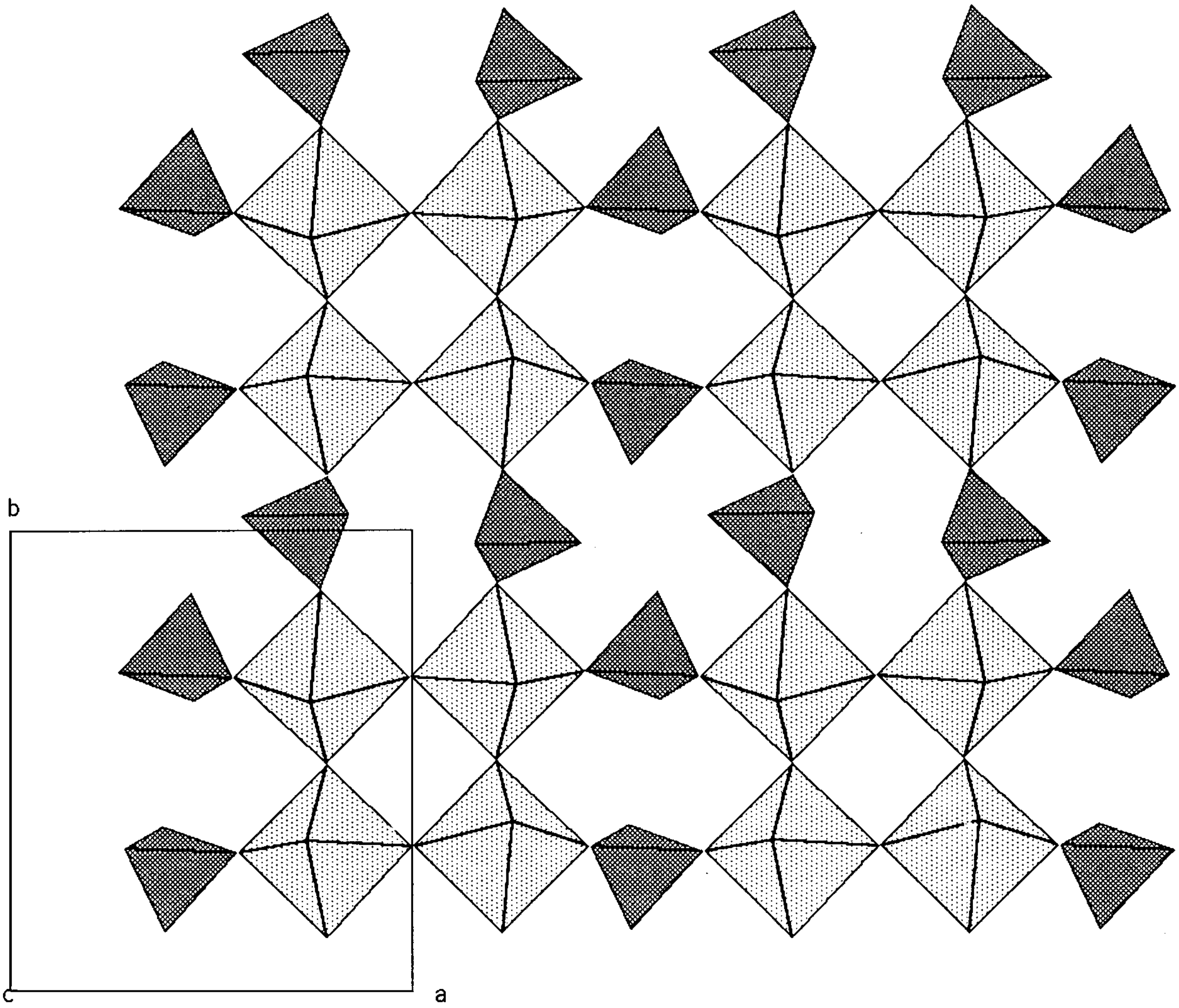

FIG. 2. The $[Mo_4P_4O_{28}]_\infty$ layer.

The "Mo_4O_{17}" units are sandwiched between two $[Mo_4P_4O_{28}]_\infty$ layers ensuring the cohesion of the three-dimensional network. Each Mo(2) octahedron of such units shares two apices with two PO_4 tetrahedra of the above layer and two other apices with two PO_4 tetrahedra of the layer located below. In the same way each Mo_2O_7 group shares two apices with two Mo_4O_{20} units of one layer and two other apices with one Mo_4O_{20} unit of the other layer as schematized in Fig. 4.

An important characteristic of this structure deals with the fact that molybdenum polyhedra form a three-dimensional mixed framework (Fig. 5).

In this complex structure each PO_4 tetrahedron shares four apices with four MoO_6 octahedra (2 Mo(1) + 2 Mo(2)) and is regular (Table 4), the P–O distances ranging from 1.47 to 1.51 Å.

Each Mo(1) octahedron shares two apices with two other Mo(1) octahedra forming the Mo_4O_{20} perovskite units, two apices with two PO_4 tetrahedra, and one apex with one Mo(3) tetrahedron, its sixth apex being free (i.e., not shared with an other octahedron or tetrahedron). The geometry of this octahedron suggests that it is mainly occupied by Mo(V) or at least mixed valent due to the 3D character of the molybdenum oxygen framework. One indeed observes (Table 4) one abnormally short Mo(1)–O bond (1.67 Å) corresponding to the free oxygen atom, opposed to an abnormally long Mo(1)–O bond (2.27 Å), whereas the four equatorial Mo(1)–O bonds exhibit intermediate values (1.86 to 2.04 Å).

In a similar way, each Mo(2) octahedron, which belongs to the "Mo_4O_{17}" units, shares four apices of its basal plane with four PO_4 tetrahedra, leading to four intermediate Mo(2)–O bonds ranging from 1.94 to 1.95 Å (Table 4). The two apical oxygen atoms O(7) and O(7^{ii}), are located at 1.78 and 2.21 Å, respectively. They correspond to the free apex and to the Mo(2)–O(7)–Mo(3) bond, respectively. This configuration of the Mo(2) octahedron is again characteristic of pentavalent molybdenum or at least of mixed valent molybdenum Mo(V)–Mo(VI). The fact that the distance of the free apex Mo(2)–O(7) is slightly longer than the Mo(1)–O(2) bond may be due to the proximity of cesium (Table 4) that forms with O(7) the shortest bond of the CsO_{10} polyhedron (3.08 Å).

Each Mo(3) tetrahedron shares three apices with two Mo(1) octahedra and one Mo(2) octahedron leading to Mo–O distances of 1.84–1.90 Å and 1.81 Å, respectively; the fourth apex O(9) which corresponds to the bridging oxygen atom of the Mo_2O_7 group is located at 1.91 Å (Table 4). Such MoO_4 tetrahedron is typical of hexavalent molybdenum.

The interatomic Cs–O distances, ranging from 3.08 to 3.43 Å (Table 4), are those usually observed for Cs^+ cations.

Electronic Distribution in the Molybdenum–Oxygen Framework

An important issue deals with the distribution of the electrons in the molybdenum oxygen framework of this phase, whose formula implies a mean valency of molybdenum of 5.62. Although they are difficult to interpret, the bond valence calculations based on a Brown and Altermatt expression (5) allow a first rough distribution to be proposed. One obtains for the octahedral sites Mo(1) and Mo(2) values of 5.52 and 5.12, respectively. Such values indicate that Mo(V) is preferentially localized an Mo(2). In contrast, the Mo(1) site is better characterized by a mixed valence Mo(V)–Mo(VI). Such a feature can be explained by the fact that Mo(1) belongs to Mo_4O_{20} units, so that in the latter *d* electrons would be delocalized over four octahedra. Calculations assuming that the Mo(3) site is occupied by hexavalent molybdenum lead to a resultant mean value of 5.56 for all the Mo sites of the structure in perfect agreement with the mean valence of 5.62 deduced from the chemical formula.

In order to better understand the electronic distribution over the molybdenum sites, a magnetic investigation was performed. The magnetization of $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$ was measured. The magnetic moment of a sample made of randomly oriented small pink crystals was measured with a SQUID magnetometer between 4.5 and 350 K under 1 T after zero field cooling. The sample holder signal measured in the same experimental conditions was subtracted. The resulting magnetic susceptibility is shown in Fig. 6. One can see in Fig. 6 that at $T \approx 5$ K an antiferromagnetic transition seems to appear.

The $X(T)$ curve was fitted with the law

$$X_M = X_0 + \frac{C_M}{T - \theta}$$

TABLE 4
Main Distances (Å) and Angles (°) in the Polyhedra in $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(1^{i})
O(1)	1.86(2)	2.74(2)	2.73(2)	3.84(2)	2.74(2)	2.65(2)
O(2)	102.0(5)	1.670(9)	2.80(1)	2.79(2)	3.94(1)	2.70(2)
O(3)	89.2(4)	97.9(5)	2.03(1)	2.75(2)	2.81(2)	3.85(2)
O(4)	160.2(4)	97.5(5)	85.2(4)	2.04(1)	2.72(1)	2.72(2)
O(5)	82.4(4)	175.5(5)	81.3(4)	77.9(4)	2.274(2)	2.69(2)
O(1^{i})	90.9(5)	99.9(4)	161.7(4)	88.6(4)	80.5(4)	1.86(2)

Mo(2)	O(6)	O(7)	O(8)	O(6^{ii})	O(7^{ii})	O(8^{ii})
O(6)	1.94(1)	2.79(2)	3.85(2)	2.73(1)	2.78(1)	2.72(2)
O(7)	97.5(5)	1.78(1)	2.76(2)	2.78(1)	3.98(2)	2.75(1)
O(8)	166.6(5)	95.9(7)	1.94(1)	2.72(2)	2.75(1)	2.72(1)
O(6^{ii})	89.3(4)	96.4(6)	89.0(8)	1.95(1)	2.79(2)	3.85(2)
O(7^{ii})	83.9(5)	178.5(5)	82.7(4)	84.2(1)	2.21(1)	2.76(2)
O(8^{ii})	89.7(8)	95.9(5)	89.2(4)	167.7(6)	83.5(5)	1.92(1)

Mo(3)	O(5^{iii})	O(5^{iv})	O(7)	O(9)
O(5^{iii})	1.84(1)	2.71(2)	2.96(2)	3.20(1)
O(5^{iv})	92.7(5)	1.90(2)	3.09(2)	3.18(1)
O(7)	108.4(5)	112.4(5)	1.81(2)	3.08(1)
O(9)	117.2(4)	112.9(4)	111.8(4)	1.911(3)

P(1)	O(3^{vi})	O(4)	O(6)	O(8^{v})
O(3^{iv})	1.47(2)	2.45(2)	2.47(2)	2.47(2)
O(4)	110.2(6)	1.52(1)	2.49(1)	2.47(2)
O(6)	111.0(6)	109.3(6)	1.53(1)	2.47(1)
O(8^{v})	110.7(6)	108.2(6)	107.4(5)	1.54(1)

Cs–O distances (Å)

Cs	O(7)	: 3.08(2)
	O(7^{vii})	: 3.08(2)
	O(5^{iv})	: 3.18(1)
	O(5^{viii})	: 3.18(1)
	O(5^{iii})	: 3.20(2)
	O(5^{ix})	: 3.20(2)
	O(2)	: 3.30(2)
	O(2^{vii})	: 3.30(2)
	O(4^{iv})	: 3.431(9)
	O(4^{viii})	: 3.431(9)

Symmetry code

i:	y;	$-x$;	$-z$
ii:	$1-x$;	$1-y$;	$1+z$
iii:	y;	$1/2+x$;	$1/4+z$
iv:	y;	$1-x$;	$-z$
v:	$1-x$;	$-1/2+y$	$1/4-z$
vi:	$1-y$;	x;	$-z$
vii:	$-x$;	$1-y$;	$1+z$
viii:	$-y$;	x;	$-z$
ix:	$-y$;	$1/2-x$;	$1/4+z$

Note. The Mo–O or P–O distances are on the diagonal, above it are the $O_i \cdots O_j$ distances, and below it are the $O_i \cdots Mo \cdots O_j$ or $O_i \cdots P \cdots O_j$ angles.

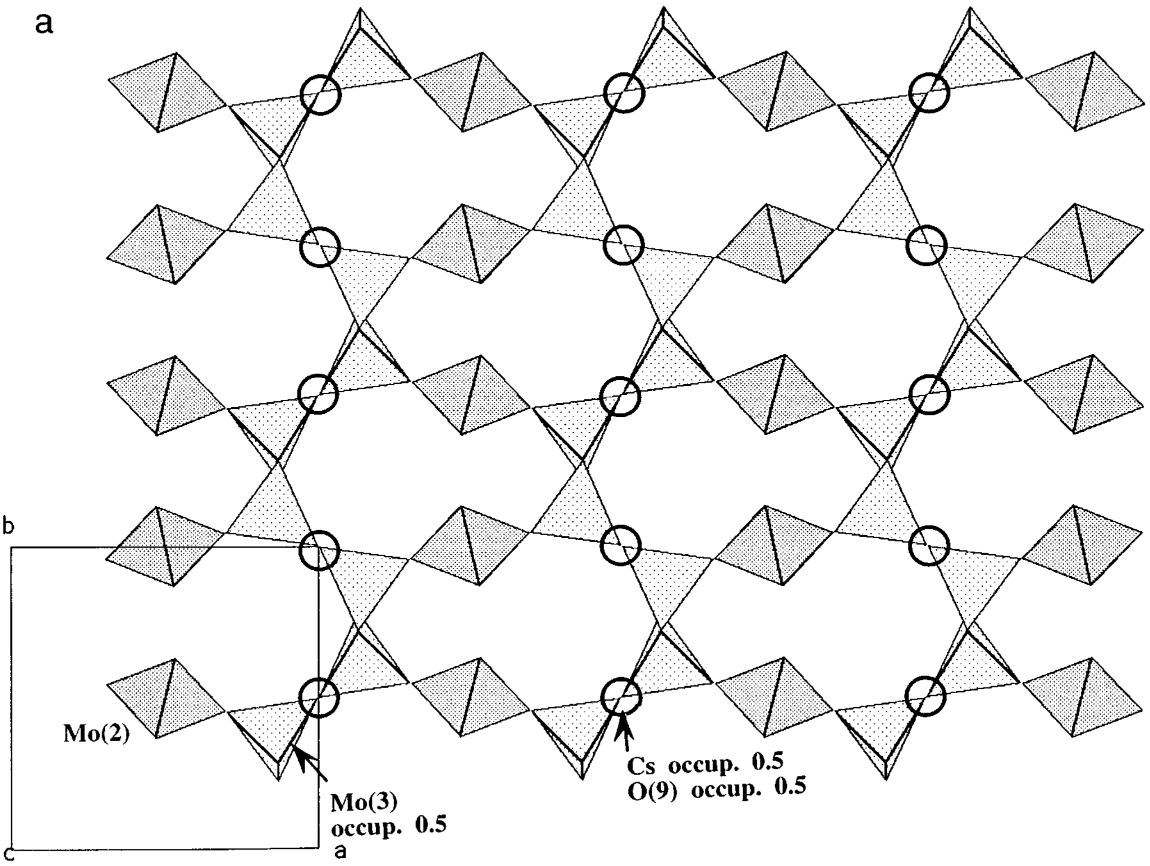

FIG. 3. (a) The sites available in the $[Mo_4o_2O_{21}]_\infty$ layer. (b) The most probable feature of the $[Mo_4o_2O_{21}]_\infty$ layer in agreement with the structural results.

excluding the low temperature values in the antiferromagnetic ordering range. The fitting C_M parameter corresponds to 1.76 μ_B. This value corresponds to one Mo(V) atom (theoretical value 1.73 μ_B). As the formula $CsMo_8P_4O_{33}$ leads to 5 Mo(VI) and 3 Mo(V), the experimental value is much lower than the expected value for 3 Mo(V) atoms.

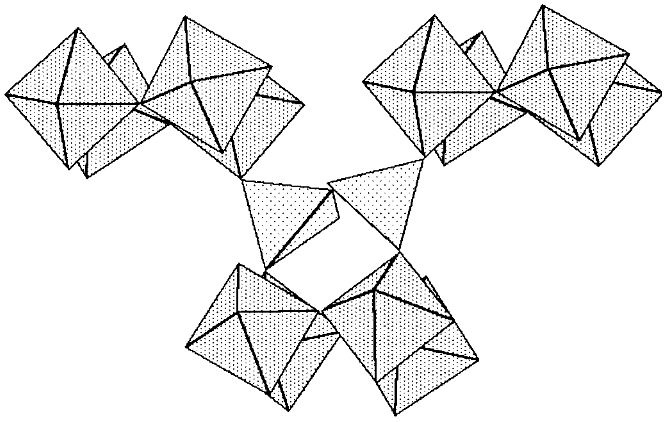

FIG. 4. The connection between the Mo_2O_7 and Mo_4O_{20} groups.

Recently, a combined experimental and theoretical study of numerous molybdenum phosphates containing either only Mo(V) or mixed valent molybdenum (Mo(V)/Mo(VI) and Mo(IV)/Mo(V)) has been performed (6, 7). Different structural units made of one, two, three, and four MoO_6 octahedra were present in the compounds investigated. A new structural classification was proposed, based on the number of octahedra in the unit built from the greater number of octahedra.

Due to the great variety of the molybdenum units concerned in this previous study (6, 7) different magnetic behaviors occurred. These various magnetic behaviors correspond to a large scattering of the magnetic moment per Mo(V) ranging from 0.1 to 1.73 μ_B which is the theoretical value for the spin only contribution of a Mo^{5+} isolated ion. These values were analyzed on the basis of qualitative arguments and confirmed by the results of numerical computations (6) using either tight binding calculations for the 3D lattices or molecular orbital calculations, calculations

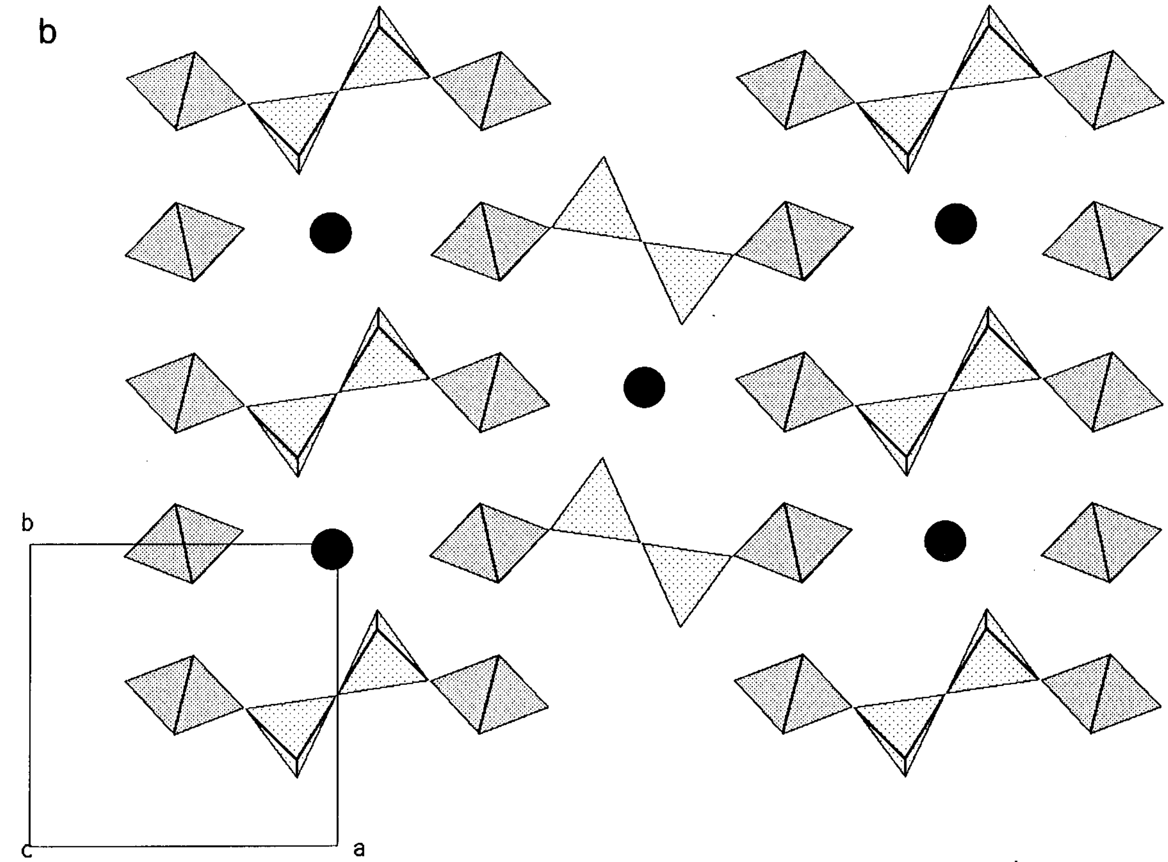

FIG. 3—*Continued*

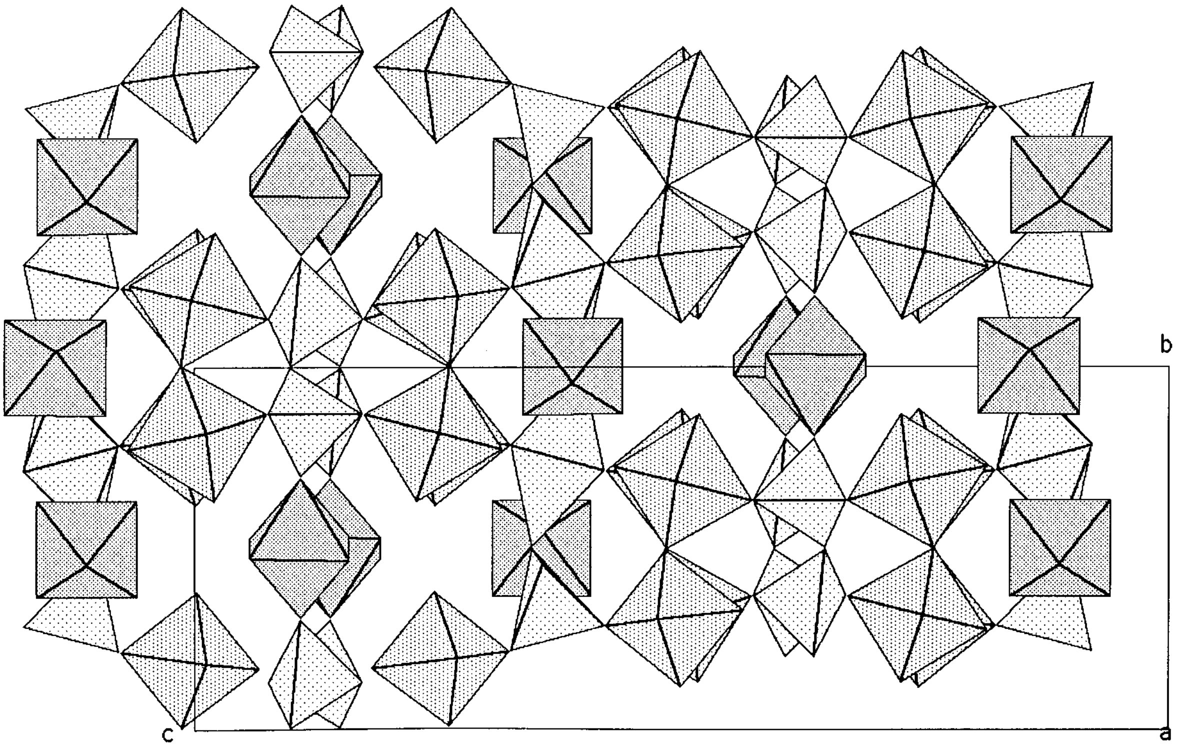

FIG. 5. The three-dimensional framework of Mo polyhedron.

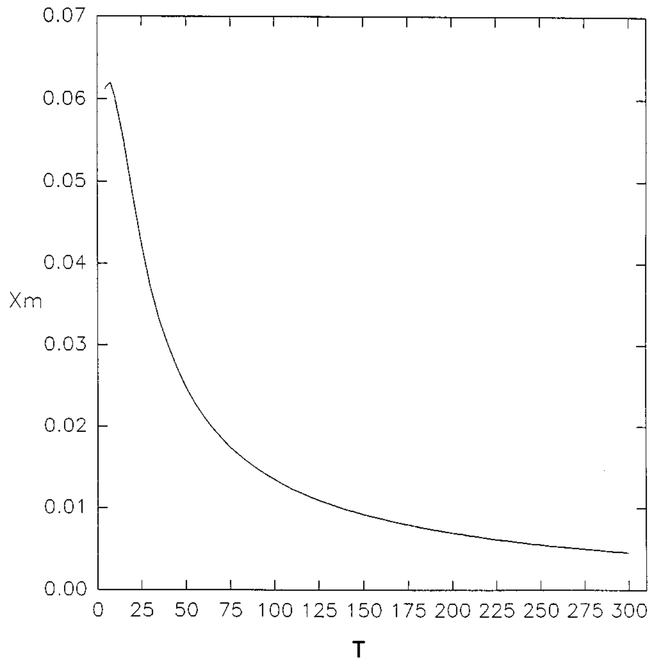

FIG. 6. X_M versus T curve for $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$ showing an antiferromagnetic ordering at about $T \approx 5$ K.

restricted to the polyoctahedral molybdenum uits. The experimental values were well interpreted, the lowest moment values measured corresponding to Mo–Mo bonds and coupling of the unpaired electron of the $Mo(V)O_6$ octahedra.

The monophosphate $CsMo_6O_{10}(Mo_2O_7)(PO_4)_4$ studied here belongs to the group IV, involving tetraoctahedral units, but the situation concerning the molybdenum–oxygen polyhedral units is more complex in this compound than in the previously reported (6). In the present compound we find a new tetraoctahedral unit made of four MoO_6 octahedra sharing one corner (Fig. 2). The four crystallographic Mo(1) sites of this unit are equivalent and, as seen above, the valence calculation using Brown and Altermatt expression leads to the 5.52 valence for Mo(1), i.e., two electrons for the four Mo(1) atoms. Moreover the $Mo(1)O_6$ octahedra show a strong O–Mo–O bond alternation and with such an octahedral distortion, two of the t_{2g} levels of the regular MoO_6 octahedron are raised and only one low lying energy level $dx^2 - y^2$ remains. Under these conditions, the low lying orbital of two neighbor Mo(1) atoms can mix with the shared oxygen atom p orbital. This bonding interaction can lead to diamagnetic-like behavior and lowers the resultant magnetic moment.

Based on these qualitative arguments the experimental magnetic moment focused in $CsMo_8P_4O_{33}$ should be mainly related to the unpaired of the $Mo(2)O_6$ octahedra in which, following Brown and Altermatt, the expression should be Mo(V). As there are two Mo(2) atoms for one formular unit $CsMo_8P_4O_{33}$, the magnetic moment should be twice the experimental value if the Mo(2) atoms should be considered independent. The present qualitative reasons do not take account of unpaired electrons coupling through the Mo_2O_7 units. The coupling through PO_4 tetrahedra has been found to be negligible in the previous study (6).

As the Mo lattice of $CsMo_8P_4O_{33}$ is not far from being a 3D lattice, it is obvious that numerical computations in the 3D lattice are necessary to enlighten the present analysis. Such numerical computations are going to be performed to refine the present analysis.

CONCLUDING REMARKS

A new mixed valent molybdenum monophosphate with an opened framework built up from tetraoctahedral units Mo_4O_{20} with the perovskite structure and ditetrahedral Mo_2O_7 groups has been synthesized for the first time. The association of MoO_4 tetrahedra and MoO_6 octahedra which was previously observed in the mixed valent monophosphate $Cs_{8+x}(MoO_4)Mo_{12}O_{18}(PO_4)_{10}$ H_2O (4) opens the route to the investigation of new opened frameworks. The magnetic study and bond valence calculations suggest a complex electronic distribution that will be further studied by taking into consideration the fact that the "molybdenum–oxygen" mixed framework is three-dimensional.

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