A New Mixed-Valence Molybdenum Phosphate with a Tunnel Structure: $Cs_3Mo_6P_{10}O_{38}$

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The crystal structure of $Cs_3Mo_6P_{10}O_{38}$ has been determined from single-crystal X-ray diffraction data. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.511(3)$, $b = 14.232(4)$, $c = 6.437(5)$ Å, $\alpha = 91.15(5)$, $\beta = 105.92(5)$, $\gamma = 90.04(2)°$, $V = 838(1)$ Å^3, $Z = 1$, $R = 0.057$, $R_w = 0.066$, GOF = 1.97 for 1460 reflections with $I > 2.5 \sigma(I)$. The structure contains several different types of tunnels of which two are occupied by Cs^+. The structural formula is $Cs_3(Mo)_2(Mo_2O)_2(PO_4)_2(P_2O_7)_4$. It is a mixed-valence molybdenum phosphate in which Mo^{3+} and Mo^{4+} are simultaneously present. The structural relationship between the title compound and $Cs_4Mo_8P_{12}O_{52}$ is discussed. © 1988 Academic Press, Inc.

Introduction

During the investigation of molybdenum phosphates containing molybdenum in oxidation states less than +6, a large number of new structures were discovered. The frameworks of these phosphates are built up from MoO_6 octahedra and PO_4 tetrahedra. In the Mo^{5+}-containing compounds (see, e.g., (*1*)), the MoO_6 octahedra are only linked to PO_4 tetrahedra, but Mo_2O_{11} units exist in the Mo^{4+}-containing phosphate, $TlMo_2P_3O_{12}$ (*2*). Unusual isolated $Mo^{3+}O_6$ octahedra have been observed in $CsMoP_2O_7$ (*3*) and MoP_3SiO_{11} (*4*). A mixed framework consisting of cubane-like Mo_4O_4 clusters and isolated MoO_6 octahedra, which are connected by pyrophosphate groups, was found in $Cs_3Mo_5P_6O_{25}$ (*5*). The cubane-like cluster consists of four MoO_6 octahedra each sharing its three common edges. More recent examples containing cubane-like clusters were $Cs_3Mo_5P_7O_{24}$ (*6*) and $Cs_3Mo_4P_3O_{16}$ (*7*). A confacial bioctahe-

dral Mo_2O_9 cluster with a Mo–Mo bond was observed in $Mo_3P_5SiO_{19}$ (*8*).

$TlMo_2P_3O_{12}$ was unique with respect to the Mo_2O_{11} units in its framework. In an attempt to prepare a cesium analog of the thallium compound, we discovered a novel mixed-valence molybdenum phosphate, $Cs_3Mo_6P_{10}O_{38}$, which contains both MoO_6 and Mo_2O_{11} units. Mixed-valence molybdenum phosphates are relatively rare although several series of mixed-valence tungsten phosphates have been synthesized (see, e.g., (*9*)). Interestingly, $Cs_3Mo_6P_{10}O_{38}$ is structurally related to $Cs_4Mo_8P_{12}O_{52}$ (see, e.g., (*1*)). We report in this paper the synthesis and crystal structure of $Cs_3 Mo_6P_{10}O_{38}$.

Experimental

Preparation

Cs_2MoO_4 (99.9%), MoO_3 (99.9%), Mo (99.9%), and P_2O_5 (99.9%) were obtained

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from Cerac. Golden brown needles of Cs_3 $Mo_6P_{10}O_{38}$ were first discovered in a reaction product by heating a mixture of Cs_2 MoO_4, MoO_3, Mo, and P_2O_5 (mole ratio $3:5:4:9$) in a sealed quartz tube at 900°C for several days. The exact stoichiometry was not known until its single-crystal X-ray structure was solved. Wavelength dispersive spectrometry was used to analyze for Si because the stoichiometry suggested a mixed-valence compound. There was only 240–530 ppm Si in four crystals for an average of 330 ppm Si. Subsequently, a few more reactions to prepare pure Cs_3 $Mo_6P_{10}O_{38}$ were conducted. Reactions at 900, 950, 1000, and 1050°C for several days yielded $Cs_3Mo_6P_{10}O_{38}$ as the major product. The reaction at 1050°C gave large crystals of millimeter dimensions. The reactions at 1000 and 1050°C also produced some green needles of $Cs_4Mo_{10}P_{18}O_{66}$ whose structure has been determined and will be published elsewhere (10). A small amount of black needles also appeared in the reaction products at 1050°C. However, a reaction at 1120°C yielded the black needles as the major product.

Determination of the Structure

Film work on the golden brown needles using a Weissenberg camera indicated that most of them were not single crystals. Many had to be selected before a satisfactory crystal was obtained. Two crystals were selected for indexing and intensity data collection using Mo $K\alpha$ radiation, and the structural analysis results from both data sets were essentially the same. The unit cell parameters, $a = 9.511(3)$, $b = 14.232(4)$, $c = 6.437(5)$ Å, $\alpha = 91.15(5)$, $\beta = 105.92(5)$, $\gamma = 90.04(2)°$, were determined by a least-squares fit of 25 peak maxima with 2θ ranging from 13 to 28°. The intensity data were collected up to $2\theta = 50°$ with a ω-2θ scan. A periodic check of three standard reflections verified the stability of the sample. A total of 1460 reflections with $I >$

2.5 $\sigma(I)$ were corrected for absorption, Lorentz, and polarization effects. Based on the statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The structure was solved by direct methods and refined by full-matrix least-squares refinement based on F values to $R = 0.057$, $R_w = 0.066$, and GOF = 1.97. Due to the limited amount of data, the Cs, Mo, and P atoms

TABLE I
ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $Cs_3Mo_6P_{10}O_{38}$

Atom	x	y	z	B^a
Cs1	0	0	0	2.1(1)
Cs2	−0.3736(2)	−0.2834(1)	−0.419(3)	2.45(8)
Mo1	−0.0402(2)	−0.2495(1)	−0.3804(3)	0.39(7)
Mo2	0.3696(2)	−0.1364(1)	−0.7129(3)	0.40(7)
Mo3	0.3368(2)	−0.3868(1)	−0.7357(3)	0.43(7)
P1	0.0470(6)	−0.2526(4)	−0.842(1)	0.5(2)
P2	0.2826(6)	−0.1130(4)	−0.259(1)	0.5(2)
P3	0.2802(6)	0.0601(4)	−0.490(1)	0.5(2)
P4	0.2956(6)	−0.5752(4)	−0.494(1)	0.5(2)
P5	0.2358(6)	−0.4108(4)	−0.286(1)	0.6(2)
O1	−0.155(2)	−0.123(1)	−0.423(2)	0.8(3)
O2	−0.234(2)	−0.327(1)	−0.464(3)	1.1(3)
O3	−0.055(2)	−0.242(1)	−0.075(3)	1.2(3)
O4	−0.055(2)	−0.250(1)	−0.695(2)	0.8(3)
O5	0.148(2)	−0.171(1)	−0.296(3)	1.2(3)
O6	0.089(2)	−0.367(1)	−0.324(2)	0.9(3)
O7	0.150(2)	−0.166(1)	−0.788(3)	1.2(3)
O8	0.385(2)	−0.145(1)	−0.392(3)	1.0(3)
O9	0.314(2)	0.001(1)	−0.673(2)	0.5(3)
O10	0.588(2)	−0.111(1)	−0.654(3)	1.5(3)
O11	0.392(2)	−0.265(1)	−0.739(2)	0.7(3)
O12	0.362(2)	−0.102(1)	−0.025(2)	0.7(3)
O13	0.226(2)	−0.011(1)	−0.335(2)	0.8(3)
O14	0.127(2)	−0.344(1)	−0.826(2)	0.7(3)
O15	0.335(2)	−0.372(1)	−0.419(2)	1.0(3)
O16	0.282(2)	−0.524(1)	−0.703(2)	0.7(3)
O17	0.552(2)	−0.424(1)	−0.658(2)	0.4(2)
O18	0.325(2)	−0.412(1)	−0.054(2)	0.9(3)
O19	0.202(2)	−0.521(1)	−0.360(2)	0.7(3)

^{a} All of the oxygen atoms were refined isotropically. The thermal parameters for Cs, Mo, and P atoms are given in isotropic equivalent thermal parameter (B_{eq}), which is the mean of the principal axes of the thermal ellipsoid.

were refined anisotropically and all of the oxygen atoms were refined isotropically. The multiplicities of the Cs, Mo, and P atoms were allowed to refine but did not deviate significantly from full occupancy. Therefore all of the atomic sites were considered to be fully occupied in the final cycles of least-squares refinement. The thermal parameters for the cesium atoms in $Cs_3Mo_6P_{10}O_{38}$ are comparable to those in the closely related compound, $Cs_4Mo_8P_{12}O_{52}$. The largest peak on the final difference map was located near the (0, $\frac{1}{2}$, 0)

inversion center and had a height of 5.3 e/$\mathring{A}^3$, which was about a tenth of the peak height for Cs atom on an electron density map. Neutral atom scattering factors and anomalous dispersion terms were taken from "International Tables for X-Ray Crystallography" (*11*). Final positional coordinates and thermal parameters are given in Table I. Selected bond distances are listed in Table II.

Description and Discussion of the Structure

The structure of $Cs_3Mo_6P_{10}O_{38}$, viewed along the *c*-axis, is shown in Fig. 1 and contains various tunnels of which two are occupied by Cs^+. Cs1 is located at the center of the hexagonal tunnel which results from the stacking of rings formed by the edges of two octahedra and four tetrahedra. The pentagonal tunnel, which is filled by Cs2, is formed by the edges of three octahedra and two tetrahedra. The hexagonal tunnel, centered at $x = 0$ and $y = \frac{1}{2}$, is empty. An analogous empty hexagonal tunnel has been observed in the mixed-valence compound $NaMo_2P_4O_{14}$ (*12*).

The framework consists of MoO_6 octahedra, Mo_2O_{11} units, phosphate, and pyrophosphate groups. The structural formula is $Cs_3(Mo)_2(Mo_2O)_2(PO_4)_2(P_2O_7)_4$. The isolated $Mo(1)O_6$ octahedra and $P(1)O_4$ tetrahedra alternate along the *c*-axis. Each $Mo(1)O_6$ octahedron is bonded to two $P(1)O_4$ tetrahedra, two $P(2)P(3)O_7$ groups, and two $P(4)P(5)O_7$ groups. In $Mo(1)O_6$ octahedron the Mo–O bond distances are regular (1.99(2)–2.08(1) Å), excluding the possibilities of Mo^{5+} and Mo^{6+}. $Mo(2)O_6$ and $Mo(3)O_6$ octahedra form units of two octahedra (Mo_2O_{11}) by sharing the common oxygen atom, O11. The MoO_6 octahedra in the Mo_2O_{11} unit has an eclipsed configuration and the Mo(2)–O(11)–Mo(3) bond angle is 154.2(9)° (see Fig. 2). Each Mo_2O_{11} unit shares its 10 corners with three

TABLE II

SOME SELECTED BOND DISTANCES (Å) FOR
$Cs_3Mo_6P_{10}O_{38}$

|			
Mo1–O4	1.99(2)	P5–O6	1.49(2)
Mo1–O3	2.00(2)	P5–O18	1.50(2)
Mo1–O5	2.04(2)	P5–O15	1.55(2)
Mo1–O6	2.05(1)	P5–O19	1.64(1)
Mo1–O2	2.07(2)	Cs1–O7	2.92(2) (2×)
Mo1–O1	2.08(1)	Cs1–O9	3.14(1) (2×)
Mo2–O11	1.85(1)	Cs1–O1	3.20(1) (2×)
Mo2–O10	2.03(2)	Cs1–O13	3.43(1) (2×)
Mo2–O8	2.03(2)	Cs1–O3	3.49(2) (2×)
Mo2–O7	2.05(2)	Cs1–O5	3.58(2) (2×)
Mo2–O12	2.06(2)	Cs2–O3	3.15(2)
Mo2–O9	2.06(1)	Cs2–O4	3.25(1)
Mo3–O11	1.82(1)	Cs2–O11	3.34(1)
Mo3–O14	2.01(1)	Cs2–O15	3.36(2)
Mo3–O17	2.04(1)	Cs2–O2	3.38(2)
Mo3–O18	2.04(2)	Cs2–O18	3.38(1)
Mo3–O15	2.05(2)	Cs2–O8	3.39(2)
Mo3–O16	2.05(1)	Cs2–O16	3.40(1)
P1–O14	1.50(1)	Cs2–O17	3.43(1)
P1–O4	1.52(2)	Cs2–O10	3.55(2)
P1–O7	1.54(2)	Cs2–O12	3.62(1)
P1–O3	1.55(2)	Cs2–O2	3.65(2)
P2–O5	1.48(2)		
P2–O12	1.49(2)		
P2–O8	1.53(2)		
P2–O13	1.59(2)		
P3–O1	1.48(2)		
P3–O10	1.51(2)		
P3–O9	1.53(1)		
P3–O13	1.61(2)		
P4–O2	1.50(2)		
P4–O16	1.51(2)		
P4–O17	1.51(1)		
P4–O19	1.59(1)		
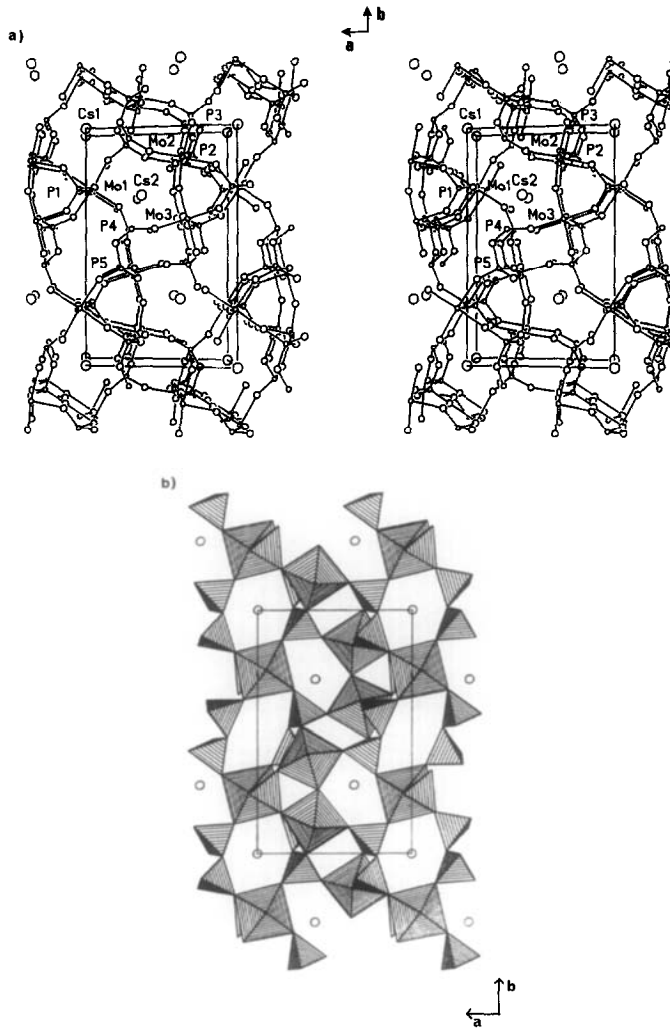
FIG. 1. (a) A stereoscopic view of the $Cs_3Mo_6P_{10}O_{38}$ structure. The Mo and P atoms are represented by smaller circles and the O and Cs atoms are represented by larger circles. (b) A polyhedron representation of the $Cs_3Mo_6P_{10}O_{38}$.

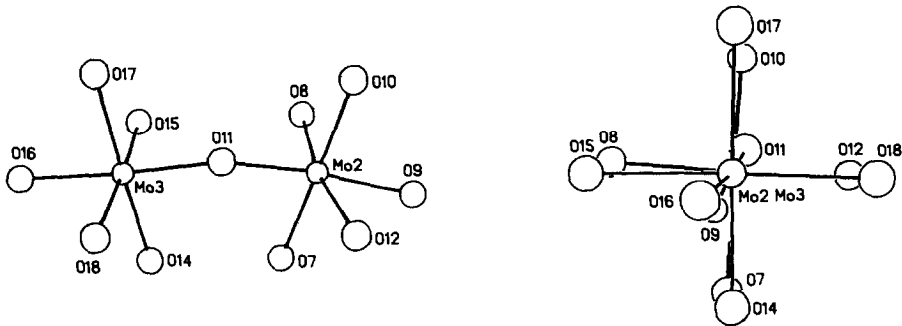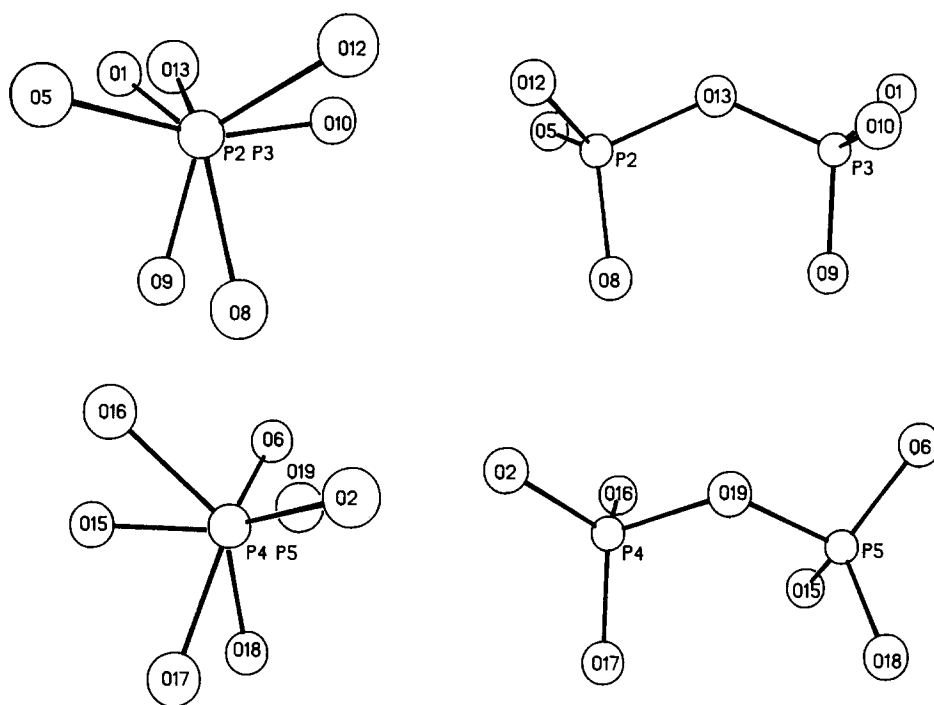FIG. 2. The Mo_2O_{11} unit in $Cs_3Mo_6P_{10}O_{38}$ in two different views.

FIG. 3. Two P_2O_7 groups in $Cs_3Mo_6P_{10}O_{38}$ each in two different views.

$P(2)P(3)O_7$, three $P(4)P(5)O_7$, and one $P(1)O_4$ groups. The two MoO_6 octahedra in a Mo_2O_{11} unit are bridged by a $P(1)O_4$ group, and each are coordinated by a bidentate P_2O_7 ligand. In either octahedron the five Mo–O bond distances, which correspond to the oxygen atoms linked to PO_4 tetrahedra, are rather regular (2.03(2)–2.06(1) Å for MO2; 2.01(1)–2.05(1) Å for Mo3). The Mo–O bond distances involving the bridging oxygen atom are much shorter (Mo2–O11, 1.85(1); Mo3–O11, 1.82(1) Å). The Mo–O bond distances in the Mo_2O_{11} unit are close to those observed in $Tl(Mo^{4+})_2P_3O_{12}$. Each $P(2)P(3)O_7$ group shares six corners with three $Mo(2)O_6$ and two $Mo(1)O_6$ octahedra. Similarly, each $P(4)P(5)O_7$ group shares six corners with three $Mo(3)O_6$ and two $Mo(1)O_6$ octahedra. In the tetrahedra belonging to either pyrophosphate group the P atoms are, as usual, displaced away from the bridging oxygen atoms giving three shorter and one longer P–O bonds. The P–O–P bond angle involving the bridging oxygen atom (O13) in $P(2)P(3)O_7$ is 129(1)°. The corresponding bond angle in $P(4)P(5)O_7$ is smaller (121(1)°), which causes the empty hexagonal tunnel to be a little more elongated than the tunnel occupied by Cs1. The P–O bond distances in $P(1)O_4$ are quite regular. As shown in Fig. 3, the configuration of $P(2)P(3)O_7$ is similar to that in $Cs_4 Mo_8P_{12}O_{52}$. However, the configuration of $P(4)P(5)O_7$ appears rather different. The coordination number of Cs can be determined by the maximum bond distance for Cs–O using the procedure by Donnay and Allmann (13). Accordingly, Cs1 and Cs2 are each surrounded by 12 oxygen atoms at distances ranging from 2.92(2) to 3.58(2) and 3.15(2) to 3.65(2) Å, respectively.

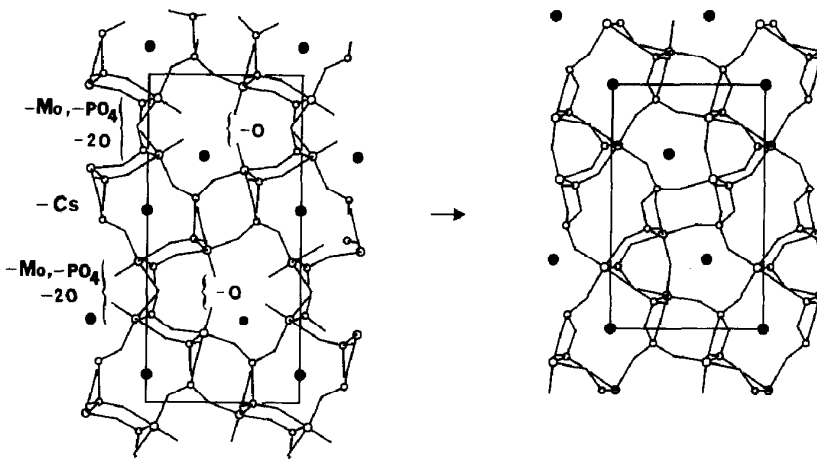Since several phosphates of Mo^{3+} have been structurally characterized, the aver-

FIG. 4. $Cs_4Mo_8P_{12}O_{52}$ (left)–$Cs_3Mo_6P_{10}O_{38}$ (right) transformation. The Cs, Mo, and P atoms are represented by large solid circles, medium, and small open circles, respectively. For clarity, the radii for O atoms are set equal to zero.

age valence of Mo in $Cs_3Mo_6P_{10}O_{38}$ (+3.833) suggests that Mo^{4+} and Mo^{3+} are simultaneously present. Bond strength sums (*14*) show that Mo2 and Mo3 are in a higher oxidation state than Mo1, which has led us to consider the Mo atoms in the Mo_2O_{11} unit to be Mo^{4+}, and equal amounts of Mo^{3+} and Mo^{4+} for Mo1. Interestingly, the $Cs_3Mo_6P_{10}O_{38}$ structure is closely related to $Cs_4Mo_8P_{12}O_{52}$. As shown in Fig. 4, $Cs_4Mo_8P_{12}O_{52}$ consists of tunnels of three different sizes of which the medium and small ones are also found in $Cs_3Mo_6P_{10}O_{38}$. The structural formula for $Cs_4Mo_8P_{12}O_{52}$ is $Cs_4(MoO)_8(PO_4)_4(P_2O_7)_4$. It should be noted that a terminal oxygen atom is only bonded to each Mo atom without being shared with PO_4 tetrahedron. As depicted in Fig. 4, neighboring tunnels in $Cs_4Mo_8P_{12}O_{52}$ are fused together by eliminating six terminal oxygen atoms, two phosphate groups, two Mo atoms, and one Cs atom such that the $Cs_3Mo_6P_{10}O_{38}$ structure is generated. This structural study once again confirms the great ability of PO_4 tetrahedra to form various frameworks with MoO_6 octahedra. The existence of large empty tunnels in Cs_3

$Mo_6P_{10}O_{38}$ suggests the possibility of synthesizing more reduced phases with a similar crystal structure.

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