

Cesium Cation Ordering in the $\text{Mo}_6\text{P}_{10}\text{O}_{38}$ Framework: Synthesis and Structure of $\text{Cs}_4\text{Mo}_6\text{P}_{10}\text{O}_{38}$

ROBERT C. HAUSHALTER

Exxon Research and Engineering Co., Annandale, New Jersey 08801

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Reaction of Cs_2MoO_4 , MoO_3 , P_2O_5 , and Mo at 950°C gives a mixture of the title compound and $\text{Cs}_3\text{Mo}_6\text{P}_{10}\text{O}_{38}$ as the major products. The compound $\text{Cs}_4\text{Mo}_6\text{P}_{10}\text{O}_{38}$ crystallizes in the monoclinic space group $P2_1/m$ with $a = 9.659(2)$, $b = 14.404(2)$, $c = 6.446(2)$ Å, and $\beta = 105.58(2)^\circ$. Important structural features include corner-sharing MoO_6 octahedra containing Mo^{4+} , isolated octahedra containing Mo^{3+} , P_2O_7 , and PO_4 groups, and one-dimensional tunnels filled with Cs^+ cations. © 1990 Academic Press, Inc.

Compared to the tunnel structures found in all-tetrahedral framework materials such as zeolites, there have been relatively few examples of mixed octahedral–tetrahedral lattices. Of these examples, most contain the octahedral transition metal component in a high oxidation state because they were synthesized in air at high temperatures. After the report by Leclaire and coworkers in 1983 (1), we have recently found a large number of new structure types in the reduced molybdenum phosphate system all of which contain Mo in an oxidation state less than $6+$. Examples include new layer or tunnel structures in materials such as $\text{Cs}_2\text{Mo}_4\text{P}_6\text{O}_{26}$ (2), $\text{Cs}_4\text{Mo}_8\text{P}_{12}\text{O}_{52}$ (2), and $\text{AgMo}_5\text{P}_8\text{O}_{33}$ (3) which contain Mo^{5+} , the compounds $\text{Cs}_3\text{Mo}_5\text{P}_6\text{O}_{25}$ (4) and $\text{Cs}_3\text{Mo}_4\text{P}_3\text{O}_{16}$ (5) both of which contain metal–metal bonded $\text{Mo}_4\text{O}_4^{6+}$ cubes with Mo in the $+3.5$ oxidation state, the compound $\text{Cs}_4\text{Mo}_{10}\text{P}_{18}\text{O}_{66}$ (6) which has Mo in both the $+3$ and $+4$ oxidation states, and CsMoP_2O_7 (7)

which contains Mo^{3+} only. In addition to these compounds prepared at high temperatures in the solid state, we have also prepared many reduced molybdenum phosphates via hydrothermal routes in the 100 – 500°C range such as the giant cluster $[\text{Na}_{14}\text{Mo}_{24}\text{P}_{17}\text{O}_{97}(\text{OH})_{31}]^{6-}$ (8), one-dimensional inorganic polymers such as $[(\text{H}_3\text{O})_2\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7]^{2-}$ (9), $\text{Na}_3\text{Mo}_2\text{P}_2\text{O}_{11}(\text{OH}) \cdot 2\text{H}_2\text{O}$ (10) which contains edge-sharing MoO_6 octahedra with molybdenum–molybdenum single bonds, and $(\text{Me}_4\text{N})_{1.3}[(\text{H}_3\text{O})_{0.7}[\text{Mo}_4\text{O}_8(\text{PO}_4)_2] \cdot 2\text{H}_2\text{O}$ (11), the first synthetic oxide with octahedrally coordinated transition metals that is microporous. In this paper the synthesis and structure of $\text{Cs}_4\text{Mo}_6\text{P}_{10}\text{O}_{38}$, (1), are presented and its structure compared to that of $\text{Cs}_3\text{Mo}_6\text{P}_{10}\text{O}_{38}$, (2), which is also formed during the synthesis of (1).

Reaction of Cs_2MoO_4 , Mo, MoO_3 , and P_2O_5 in a mole ratio of $2:2.33:1.67:5$ for 48 hr at 925°C in an evacuated silica ampule

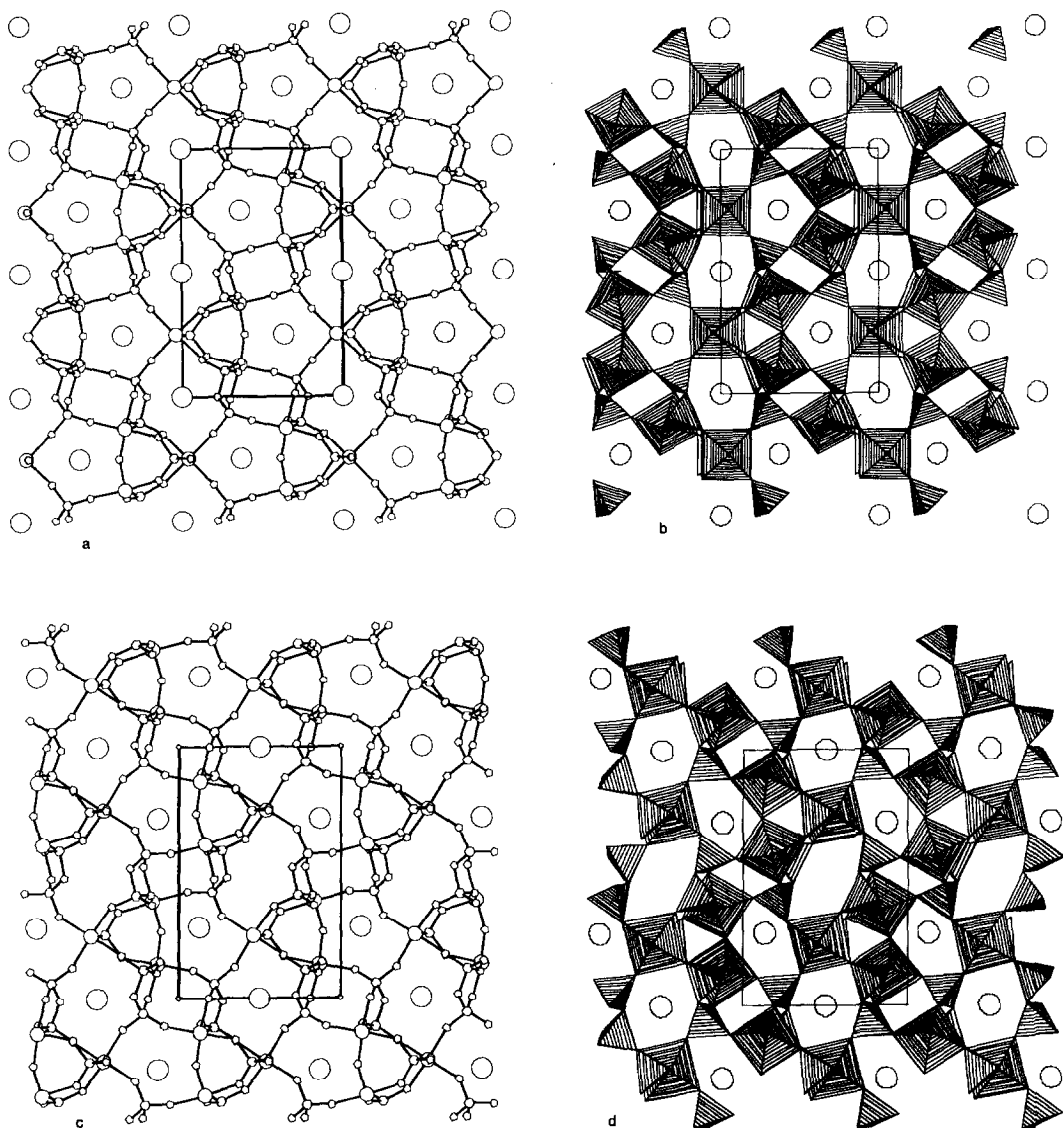


FIG. 1. Ball and stick and polyhedral representations of the structures of (1) (a and b) and (2) (c and d). In all of the structures, [001] is horizontal and [010] is vertical. For a direct comparison of the two frameworks note that a translation of $\frac{1}{2}$ of a unit cell along [001] makes the frameworks "superimposable" within the constraints of the different space groups.

gives a mixture of (1) and (2) as dark needles. Since the stoichiometries of these compounds are so similar, differing by only one atom out of 57, it was not possible to isolate (1) as a single-phase material without contamination by (2).

A projection of the structure of monoclinic (1) onto the (001) plane is shown in Fig. 1a and 1b both as a CHEM-X (12) ball-and-stick representation and as a STRUPLO (13) polyhedral representation. Crystallographic data are collected in Table

TABLE I

Empirical Formula	Cs ₄ Mo ₆ P ₁₀ O ₃₈
Formula Weight	2024.98
Crystal Color, Habit	black, plate
Crystal Dimensions (mm)	0.150 × 0.100 × 0.050
Crystal System	Monoclinic
Lattice Parameters	$a = 9.659(2) \text{ \AA}$ $b = 14.404(5) \text{ \AA}$ $c = 6.446(2) \text{ \AA}$ $\beta = 105.58(2)^\circ$ $V = 863.8(8) \text{ \AA}^3$
Space Group	$P2_1/m(\#11)$
Z value	1
D_{calc}	3.89 g cm ⁻³
F000	926
μ (MoK α)	68.79 cm ⁻¹
Diffractometer	Rigaku AFC6
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) Graphite-monochromated
Temperature	23°C
2-theta (max)	50.1 degrees
No. Observations ($I > 3.00(\text{sig}(I))$)	903
No. Variables	93
Residuals: R ; R_w	0.070; 0.081
Goodness of Fit Indicator	2.06
Maximum Shift in Final Cycle	0.02
Largest Peak in Final Diff. Map	2.79 e \AA^{-3}

I while the fractional coordinates and the isotropic temperature factors are given in Table II. (See Fig. 2 for numbering of atoms in (1).) The Cs, Mo, and P atoms were refined anisotropically while the O atoms were refined isotropically. The basic structural units include molybdenum dimers with a single bridging oxygen, that lie on a crystallographic mirror plane, which imparts a corner sharing geometry to these two MoO₆ octahedra. The distance between these two crystallographically equivalent Mo atoms is ca. 3.5 Å indicating that in spite of the relatively low oxidation state there is no Mo–Mo bond as found in many other of our phosphates. The lack of a metal–metal bond in this system is obviously due to the relatively high P:Mo ratio. The calculation of the oxidation state of these two Mo atoms from the bond strength–bond length calculations of either

Zachariassen (14) or Brown and Wu (15) gives the same results and clearly shows that the Mo is in the 4+ oxidation state. These calculations also show that the other unique Mo atom in the asymmetric unit is in the 3+ oxidation state so that the average oxidation state of each molybdenum in the unit cell, based on the observed stoichiometry, that appears to be +22/6 is actually four Mo⁴⁺ and two Mo³⁺. There are two PO₄ tetrahedra and four P₂O₇ groups in the unit cell. Two of the corners of the PO₄ tetrahedra are shared with O atoms that are also part of the Mo⁴⁺ dimer while the other two corners connect the unique Mo³⁺ octahedra into strings that run parallel to the [001] direction. There are two crystallographically independent P₂O₇ groups in the unit cell. In one of these P₂O₇ groups, one PO₃ end bridges together two halves of two crystallographically

TABLE II
POSITIONAL PARAMETERS AND $B(\text{eq})$ FOR (1)

Atom	x	y	z	$B(\text{eq})^a$
Cs1	$\frac{1}{2}$	0	0	2.7(1)
Cs2	0.8651(3)	$\frac{1}{4}$	0.0455(6)	4.5(2)
Mo1	0.5352(3)	$\frac{1}{4}$	0.3767(5)	0.3(1)
Mo2	0.1431(2)	0.1264(2)	0.7201(4)	0.54(8)
P1	0.447(1)	$\frac{1}{4}$	0.834(2)	0.4(3)
P2	0.2361(8)	0.1025(5)	0.268(1)	0.8(3)
P3	0.2105(7)	-0.0672(5)	0.493(1)	0.5(2)
O1	0.551(2)	$\frac{1}{4}$	0.700(4)	0.3(4)
O2	0.352(2)	0.164(1)	0.794(3)	1.1(3)
O3	0.546(3)	$\frac{1}{4}$	1.068(4)	1.0(5)
O4	0.379(2)	0.151(1)	0.300(3)	1.8(4)
O5	0.135(2)	0.138(1)	0.397(3)	1.1(3)
O6	0.154(2)	0.096(1)	0.033(3)	1.1(3)
O7	0.281(2)	-0.001(1)	0.346(3)	0.8(3)
O8	0.203(2)	-0.012(1)	0.686(3)	0.9(3)
O9	0.308(2)	-0.147(2)	0.562(4)	2.5(4)
O10	0.070(2)	-0.096(1)	0.349(3)	1.9(4)
O11	0.108(2)	$\frac{1}{4}$	0.736(4)	0.3(4)

^a Ref. (17).

equivalent Mo^{4+} dimers while the other PO_3 end connects one half of the Mo^{4+} dimer to the unique Mo^{3+} as well as bridging this same half of the Mo^{4+} dimer into strings along [001]. The other P_2O_7 group has a very similar coordination environment except that it is coordinated to the

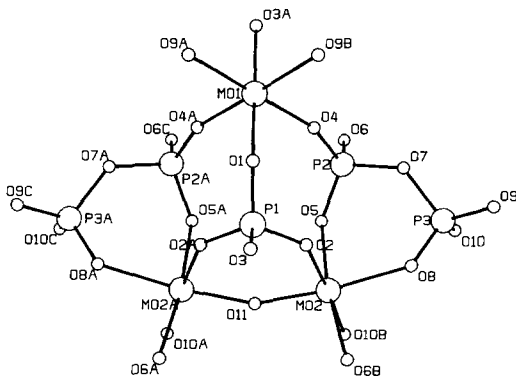


FIG. 2. Number scheme for the atoms in (1).

other half of the Mo^{4+} dimer discussed in connection to the other P_2O_7 group above.

It is interesting to examine the effect on the framework of the removal of the Cs^+ at $(0, 1/2, 0)$ to give the compound $\text{Cs}_3\text{Mo}_6\text{P}_{10}\text{O}_{38}$ (16), (2), which is shown in Figs. 1c and d. The removal of this edge-centered cesium ion causes a general shifting of the atoms as the symmetry of the cell drops from monoclinic to triclinic when the mirror plane and the 2_1 axis disappear. Since (2) is centrosymmetric and contains six Mo atoms in the unit cell and the stoichiometry indicates that the average oxidation state in the structure is $+23/6$, it is not possible to tell on which Mo atom(s) the odd electron resides.

Certain sections of the structure of the title compound are also somewhat related to our recently published structure (6) of $\text{Cs}_4\text{Mo}_{10}\text{P}_{18}\text{O}_{66} = \text{Cs}_4\text{Mo}_6\text{P}_{10}\text{O}_{38} + 4\text{MoP}_2\text{O}_7$.

References

1. A. LECLAIRE, J. C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **48**, 147 (1983).
2. K. H. LII AND R. C. HAUSHALTER, *J. Solid State Chem.* **69**, 320 (1987).
3. K. H. LII, D. J. JOHNSTON, D. P. GOSHORN, AND R. C. HAUSHALTER, *J. Solid State Chem.* **71**, 131 (1987).
4. K.H. LII, R. C. HAUSHALTER, AND C. J. O'CONNOR, *Angew. Chem. Int. Ed. Eng.* **26**, 549 (1987).
5. R. C. HAUSHALTER, *Chem. Commun.* 1566 (1987).
6. R. C. HAUSHALTER AND F. W. LAI, *J. Solid State Chem.* **76**, 218 (1988).
7. K. H. LII AND R. C. HAUSHALTER, *Acta. Crystallogr. C43*, 2038 (1987).
8. R. C. HAUSHALTER AND F. W. LAI, *Angew. Chem.* **101**, 802 (1989).
9. R. C. HAUSHALTER AND F. W. LAI, *Inorg. Chem.* **28**, 2904 (1989).
10. R. C. HAUSHALTER AND L. A. MUNDI, *Inorg. Chem.* **29**, 2879 (1990).
11. R. C. HAUSHALTER, K. G. STROHMAIER, AND F. W. LAI, *Science* **246**, 1289 (1989).
12. CHEM-X is a registered trademark of Chemical Design Ltd., Mahwah, NJ.

13. R. X. FISCHER, *J. Appl. Crystallogr.* **18**, 258 (1985).
14. W. H. ZACHARIASEN, *J. Less Common Metals* **62**, 17 (1978).
15. I. D. BROWN AND K. K. WU, *Acta Crystallogr. Sect. B. Struct. Sci.* **32**, 1957 (1976).
16. This structure was originally solved in 1987, K. H. LIU AND R. C. HAUSHALTER, unpublished results; it was apparently redetermined and published, K. H. LIU AND C. C. WANG, *J. Solid State Chem.* **77**, 117 (1988).
17. R. X. FISCHER AND E. TILLMANN, *Acta Crystallogr. Sect. A: Foundations of Crystal.* **44**, 775 (1988).