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BRIEF COMMUNICATION

Synthesis and Structure of $Cs_4Mo_{10}P_{18}O_{66}$

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The crystal structure of $Cs_4Mo_{10}P_{18}O_{66}$ was determined from single crystal X-ray diffraction data with the following unit cell parameters: space group $P\bar{1}$ with $a = 14.395(1)$, $b = 15.600(1)$, $c = 6.4571(6)$ Å, $\alpha = 98.316(6)°$, $\beta = 90.824(7)°$, $\gamma = 90.073(6)°$, $V = 1434.6(4)$ Å^3, R (R_w) = 0.054 (0.066). Important features of the structure include nonintersecting, orthogonal Cs^+-filled tunnels and two pairs of corner-sharing MoO_6 octahedron, with Mo in the +4 oxidation state, bridged together by a $P_2O_7^{4-}$ group and a $P_3O_{10}^{5-}$ group coordinated to a Mo^{3+} center.

1. Introduction

Several new structure types in the mixed octahedral–tetrahedral system M–Mo–P–O (M = alkali metal) were recently reported by Leclaire and co-workers such as Mo^{5+} in $K_4Mo_8P_{12}O_{52}$ (*1*) and Mo^{4+} in $TlMo_2P_3O_{12}$ (*2*). We also observed new tunnel or layer structures in compounds like $Cs_2Mo_4P_6O_{26}$ (*3*), $Cs_4Mo_8P_{12}O_{52}$ (*3*), $AgMo_5P_8O_{33}$ (*4*), $Cs_3Mo_6P_{10}O_{38}$ (*5*), $Cs_4Mo_6P_{10}O_{38}$ (*6*), and $CsMoP_2O_7$ (*7*), as well as metal–metal bonded $Mo_4O_4^{6+}$ cubes in $Cs_3Mo_5P_6O_{25}$ (*8*) and $Cs_3Mo_4P_3O_{16}$ (*9*). In this paper we describe the preparation and structure of $Cs_4Mo_{10}P_{18}O_{66}$ which contains nonintersecting, orthogonal Cs^+-filled tunnels and two pairs of corner-sharing MoO_6 octahedron bridged together by a P_2O_7 group and a $P_3O_{10}^{5-}$ group coordinated to a Mo^{3+} center.

2. Experimental

Reaction of Cs_2MoO_4, Mo, MoO_3, and P_2O_5 in a mole ratio of 1 : 1.83 : 2.17 : 4.5 in an evacuated silica tube at 1025°C for 48 hr results in a large number of long, thin, metallic green needles of the title compound. Simulation of the X-ray powder pattern after the single-crystal structure was solved showed that the title compound constitutes approximately 25% of the reaction mixture after being subjected to the above conditions. The structure of $Cs_4Mo_{10}P_{18}O_{66}$ was solved in the space group $P\bar{1}$ with the experimental details given in Table I.

3. Results and Discussion

As shown in Figs. 1a–1d, which includes both polyhedral representations [STRUPLO 84 (*10*)] and ball-and-stick representations (CHEM-X 87)[1] of the structure, the molybdenum phosphate framework in the unit cell of $Cs_4Mo_{10}P_{18}O_{66}$ contains four pairs of corner-sharing MoO_6 octahedra and two "isolated" MoO_6 octa-

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[1] CHEM-X 87 is a copyright of Molecular Design Ltd.

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TABLE I

EXPERIMENTAL DETAILS

A. Crystal data	
Empirical formula	$Cs_4Mo_{10}P_{18}O_{66}$
Formula weight	3104.51
Crystal color, habit	green-black, needle
Crystal dimensions (mm)	0.300 × 0.100 × 0.100
Crystal system	Triclinic
No. reflections used for unit cell determination (2θ range)	25 (46.9–49.9°)
ω Scan peak width at half-height	0.32
Lattice parameters:	$a =$ 14.395(1) Å $b =$ 15.600(1) Å $c =$ 6.4571(6) Å $\alpha =$ 98.318(6)° $\beta =$ 90.824(7)° $\gamma =$ 90.073(6)° $V =$ 1434.6(4) Å^3
Space group	$P\bar{1}$ (No. 2)
Z value	1
D_{calcd}	3.593 g/cm^3
F_{000}	1438
$\mu_{(MoK\alpha)}$	52.53 cm^{-1}
B. Intensity measurements	
Diffractometer	Rigaku AFC6R
Radiation	Mo$K\alpha$ (λ = 0.71069 Å)
Temperature	23°C
Take-off angle	6.0°
Detector aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to detector distance	40 cm
Scan type	ω-2θ
Scan rate	16.0°/min (in ω) (2 rescans)
Scan width	$(0.94 + 0.30 \tan \theta)°$
$2\theta_{max}$	50.1°
No. of reflections measured	Total: 5306 Unique: 5084 (R_{int} = .004)
Corrections	Lorentz polarization Absorption (trans. factors: 0.89–1.00) Decay (−0.70% decline) Secondary extinction (coefficient: 0.10029E-06)
C. Structure solution and refinement	
Structure solution	Direct methods
Refinement	Full matrix least squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p factor	0.05
Anomalous dispersion	All nonhydrogen atoms
No. observations ($I > 3.00\sigma(I)$)	3376
No. variables	281
Reflection/parameter ratio	12.01
Residuals: R; R_w	0.054; 0.066
Goodness of fit indicator	1.51
Max shift/error in final cycle	0.13

hedra which share oxygens only with phosphorus. The Mo units are bridged together into a three-dimensional array by two $P_3O_{10}^{5-}$ and six $P_2O_7^{4-}$ groups. There are two basic types of Cs^+ cation both of which reside in tunnels. These various structural entities are discussed in more detail below.

The fractional coordinates and the isotropic temperature factors are given in Table II. The Mo–O and P–O bond lengths are in Tables III and IV, respectively.

In the asymmetric unit there five Mo ions: four ions in two pairs of corner-sharing octahedra and one Mo bonded only to oxygen that are bound to phosphorus. The oxidation states of the molybdenum atoms were calculated from the bond strength–bond length formulas of both Brown and Wu (*11*) and Zachariasen (*12*), which gave essentially identical results, and clearly indicated that the Mo ions involved in the corner-sharing octahedra are Mo^{4+} and the Mo ions that are bonded only to phosphate groups are Mo^{3+}. This particular partitioning of the positive charges among the various Mo ions is fully supported by the structural determinations of $Cs_3Mo_6P_{10}O_{38}$ (*5*) and $Cs_4Mo_6P_{10}O_{38}$ (*6*) which also contain corner-sharing MoO_6 octahedra with Mo in the +4 oxidation state and "isolated" octahedra with Mo in the +3 oxidation state.

The two crystallographically independent pairs of corner-sharing octahedra (hereafter referred to as dimer A which contains Mo(2)–O(11)–Mo(4) and dimer B which contains Mo(1)–O(6)–Mo(3)) have Mo–O–Mo bonds that are somewhat bent (166.9(6)° in dimer B and 172.8(6)° in dimer A), display very short Mo–O contacts (1.86(1), 1.84(1), 1.84(1), and 1.80(1) Å), and have relatively small thermal parameters for the bridging oxygen. The Mo–O–Mo bonds in both dimers lie approximately parallel to the [100] direction. These dimers are connected by an eclipsed pyrophosphate group as shown in Fig. 2. This same pyrophosphate group and dimer A alternate along the *c* axis. Dimer A also shares oxide ligands that are trans to the oxygen, O(11), bridging the two Mo ions together, with two separate but symmetry equivalent $P_3O_{10}^{5-}$

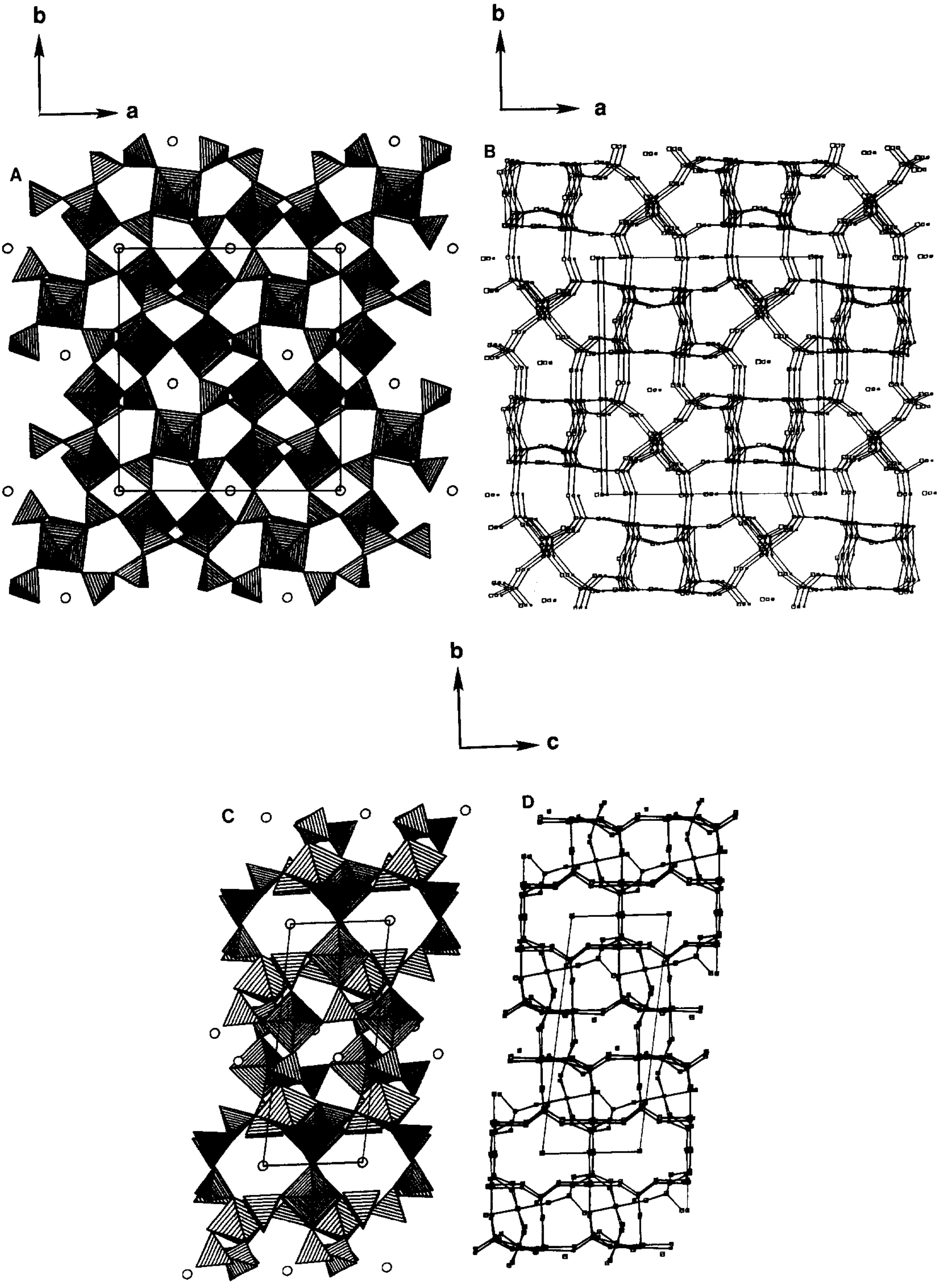

FIG. 1. STRUPLO 84 polyhedral and CHEM-X 87 ball-and-stick representations of the structure of $Cs_4Mo_{10}P_{18}O_{66}$.

TABLE II

Positional Parameters and B(eq) for $Cs_4Mo_{10}P_{18}O_{66}$

Atom	x	y	z	B(eq)
Cs(1)	0.7591(1)	0.55921(8)	0.6353(2)	2.58(5)
Cs(2)	½	0	0	9.2(2)
Cs(3)	1.0000	0	0	9.3(2)
Mo(1)	0.62946(9)	0.40577(8)	0.1267(2)	0.41(5)
Mo(2)	0.61533(9)	0.13856(8)	0.5248(2)	0.39(5)
Mo(3)	0.88518(9)	0.39585(8)	0.1325(2)	0.40(5)
Mo(4)	0.86757(8)	0.12620(8)	0.5268(2)	0.32(5)
Mo(5)	0.74378(9)	0.76736(8)	0.1794(2)	0.39(5)
P(1)	0.6398(3)	0.1892(3)	0.0385(6)	0.5(1)
P(2)	0.9188(3)	0.3469(2)	−0.3748(6)	0.5(1)
P(3)	0.8518(3)	0.1801(2)	0.0400(6)	0.6(1)
P(4)	0.9156(3)	0.6104(2)	0.1219(6)	0.5(1)
P(5)	0.5903(3)	0.3622(3)	−0.3809(6)	0.6(1)
P(6)	0.5759(3)	0.6105(2)	0.1199(6)	0.6(1)
P(7)	0.7523(3)	0.8181(3)	0.6705(6)	0.7(1)
P(8)	0.8920(3)	0.9019(3)	0.4591(6)	0.6(1)
P(9)	0.3868(3)	0.0895(3)	0.5368(6)	0.6(1)
O(1)	0.4904(7)	0.4173(7)	0.060(2)	0.8(2)
O(2)	0.6388(7)	0.5370(7)	0.165(2)	0.7(2)
O(3)	0.6444(7)	0.4038(7)	−0.189(2)	1.1(2)
O(4)	0.6043(7)	0.4143(7)	0.441(2)	0.8(2)
O(5)	0.5993(7)	0.2783(7)	0.086(2)	0.9(2)
O(6)	0.7563(6)	0.3952(6)	0.157(1)	0.3(2)
O(7)	0.6250(7)	0.1336(7)	0.208(2)	0.9(2)
O(8)	0.4749(8)	0.1358(7)	0.492(2)	1.2(2)
O(9)	0.6018(7)	0.1400(7)	−0.162(2)	1.0(2)
O(10)	0.6025(7)	0.0055(7)	0.483(2)	1.1(2)
O(11)	0.7432(7)	0.1358(6)	0.543(2)	0.6(2)
O(12)	0.6138(7)	0.2679(7)	−0.442(2)	1.1(2)
O(13)	0.8713(7)	0.3956(7)	−0.185(2)	0.7(2)
O(14)	0.8858(7)	0.5272(7)	0.193(2)	1.1(2)
O(15)	0.9114(7)	0.3990(6)	0.446(2)	0.7(2)
O(16)	0.9014(8)	0.2660(7)	0.084(2)	1.3(2)
O(17)	1.0246(7)	0.4019(6)	0.069(2)	0.7(2)
O(18)	1.0065(7)	0.1028(7)	0.499(2)	1.1(2)
O(19)	0.8606(7)	0.1246(7)	0.209(2)	1.0(2)
O(20)	0.8844(8)	0.2564(7)	0.566(2)	1.2(2)
O(21)	0.8818(8)	0.1270(7)	0.841(2)	1.2(2)
O(22)	0.8574(8)	−0.0058(7)	0.481(2)	1.4(2)
O(23)	0.8332(7)	0.6653(7)	0.090(2)	1.2(2)
O(24)	0.7385(7)	0.7464(7)	0.493(2)	1.0(2)
O(25)	0.6295(7)	0.6889(7)	0.091(2)	1.2(2)
O(26)	0.7466(7)	0.7899(7)	0.877(2)	1.2(2)
O(27)	0.8579(7)	0.8479(7)	0.261(2)	0.9(2)
O(28)	0.3453(7)	0.1259(7)	−0.261(2)	1.0(2)
O(29)	1.0252(7)	0.3376(7)	−0.313(2)	1.2(2)
O(30)	0.6818(8)	0.8954(7)	0.652(2)	1.2(2)
O(31)	0.7457(8)	0.2044(7)	0.009(2)	1.2(2)
O(32)	0.8505(8)	0.8623(7)	0.654(2)	1.3(2)
O(33)	0.4842(8)	0.3663(7)	−0.330(2)	1.5(2)

groups. The two Mo–O bonds of dimer A directed parallel to the [010] direction are coordinated to a third $P_3O_{10}^{5-}$ anion. The remaining two Mo–O bonds, which are also parallel to [010], are to $P_2O_7^{4-}$ groups whose other vertices are shared with dimer B, the unique Mo^{3+}, and the symmetry equivalent of dimer B across the inversion center at (0.5, 0.5, 0.5). Dimer B shares oxygens only with pyrophosphate groups. Excluding the short Mo–O contacts involving the oxygens

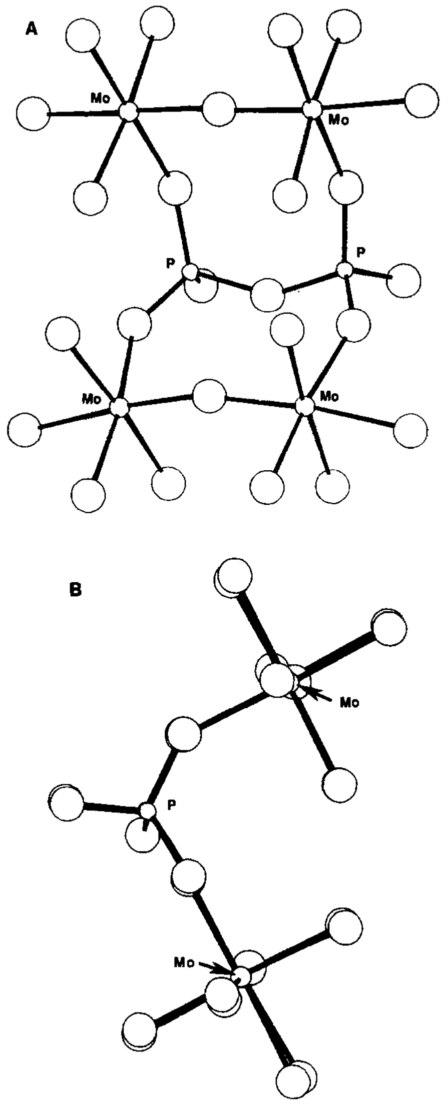

Fig. 2. The two pairs of corner-sharing octahedra and the pyrophosphate group that connects them in $Cs_4Mo_{10}P_{18}O_{66}$.

TABLE III

Mo–O BOND LENGTHS (Å)

Mo(1)		Mo(2)		Mo(3)		Mo(4)		Mo(5)	
O(1)	2.05(1)	O(7)	2.04(1)	O(6)	1.86(1)	O(11)	1.80(1)	O(23)	2.07(1)
O(2)	2.03(1)	O(8)	2.03(1)	O(13)	2.05(1)	O(18)	2.04(1)	O(24)	2.10(1)
O(3)	2.05(1)	O(9)	2.03(1)	O(14)	2.03(1)	O(19)	2.05(1)	O(25)	2.07(1)
O(4)	2.05(1)	O(10)	2.06(1)	O(15)	2.05(1)	O(20)	2.02(1)	O(26)	2.03(1)
O(5)	2.01(1)	O(11)	1.84(1)	O(16)	2.02(1)	O(21)	2.03(1)	O(27)	2.08(1)
O(6)	1.84(1)	O(12)	2.00(1)	O(17)	2.06(1)	O(22)	2.04(1)	O(28)	2.11(1)

connecting the halves of the dimer, the remaining Mo–O distances in the coordination sphere of the dimers all fall in the range of 2.00(1)–2.06(1) Å.

The oxide ligands proximate to the octahedrally coordinated unique Mo^{3+}, Mo(5), as shown in Fig. 3. All of the Mo(5) to oxygen contacts fall in the range 2.03(1)–2.11(1) Å. An interesting feature of the environment around Mo(5) is the $P_3O_{10}^{5-}$ group that occupies three of the six available coordination sites. The $P_3O_{10}^{5-}$ anion is made by the ton for use in detergents and oil well drilling muds (*13*).

There are three crystallographically independent Cs cations in the unit cell all of which reside in tunnels. The Cs$^+$ ions can be divided into two types. The Cs(1) ion is coordinated to eight oxygens with distances between 3.20(1) and 3.45(1) Å, with no other contacts less than 3.6 Å, and has roughly spherical thermal parameters. This Cs(1) ion is located in tunnels that run parallel to [001]. The other two Cs$^+$ ions, Cs(2) and Cs(3), have very anisotropic thermal parameters and lie in tunnels that run parallel to the [100] direction. There are four short Cs(2)–O contacts in the range 2.92(1)–2.95(1) Å with the next Cs–O contact at 3.42(1) Å. Likewise, Cs(3) has four Cs–O contacts in the range 2.90(1)–2.99(1) Å with the next closest contact at 3.39(1) Å. Thus both Cs(2) and Cs(3) have large thermal parameters in the direction of the long Cs–O contacts possibly indicative of a small positional disorder.

TABLE IV

P–O BOND LENGTHS (Å)

P(1)		P(2)		P(3)		P(4)		P(5)	
O(5)	1.50(1)	O(13)	1.52(1)	O(16)	1.51(1)	O(14)	1.50(1)	O(3)	1.52(1)
O(7)	1.51(1)	O(15)	1.51(1)	O(19)	1.49(1)	O(17)	1.50(1)	O(4)	1.51(1)
O(9)	1.50(1)	O(20)	1.49(1)	O(21)	1.50(1)	O(23)	1.49(1)	O(12)	1.51(1)
O(31)	1.56(1)	O(29)	1.59(1)	O(31)	1.59(1)	O(29)	1.61(1)	O(33)	1.57(1)
P(6)		P(7)		P(8)		P(9)			
O(1)	1.51(1)	O(24)	1.49(1)	O(18)	1.49(1)	O(8)	1.51(1)		
O(2)	1.52(1)	O(26)	1.47(1)	O(22)	1.51(1)	O(10)	1.48(1)		
O(25)	1.48(1)	O(30)	1.59(1)	O(27)	1.50(1)	O(28)	1.48(1)		
O(33)	1.62(1)	O(32)	1.58(1)	O(32)	1.60(1)	O(30)	1.60(1)		

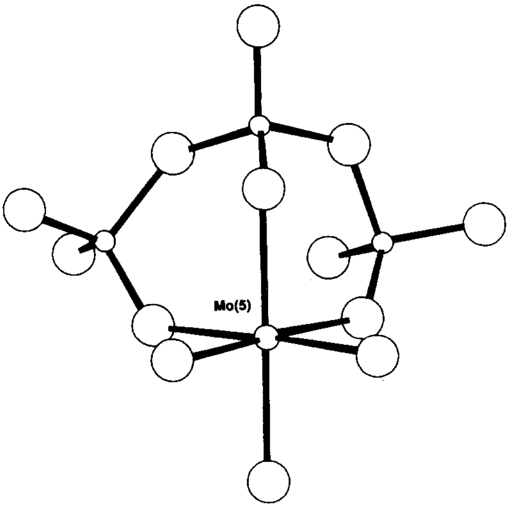

FIG. 3. The coordination environment around trivalent Mo(5) showing the $P_3O_{10}^{5-}$ ligand.

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