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A New Mo^{5+} Phosphate with a Tunnel Structure: γ-$CsMo_2P_3O_{13}$

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A new Mo^{5+} phosphate, γ-$CsMo_2P_3O_{13}$, was discovered and its crystal structure was determined from single-crystal X-ray diffraction data. γ-$CsMo_2P_3O_{13}$ crystallizes in the triclinic space group $P\bar{1}$ with a = 6.342(1), b = 9.676(1), c = 10.0349(8) Å, α = 83.083(7), β = 97.42(1), γ = 108.30(1)°, V = 577.7(2) Å^3, Z = 2, R = 0.034, R_w = 0.042 for 2927 independent reflections with $I > 2.5\,\sigma(I)$. The structure consists of three different tunnels of which the large and medium ones are occupied by cesium cations. The framework is built up from MoO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. The γ-$CsMo_2P_3O_{13}$ structure is closely related to that of the β-form.

Introduction

The investigation of phases formed in the molybdenum phosphorous oxide system has shown the great ability of PO_4 tetrahedra to form various frameworks with MoO_6 octahedra. Seven different structure types have been characterized in the system Cs–Mo–P–O which contains Mo in oxidation states less than +6. In the system M–Mo^{5+}–P–O there are $Cs_2Mo_4P_6O_{26}$ and $Cs_4Mo_8P_{12}O_{52}$ (*1*). $Cs_4Mo_8P_{12}O_{52}$ has a tunnel structure with various pore sizes in which the cesium cations reside. Interestingly, $Cs_2Mo_4P_6O_{26}$, which has the same chemical composition as $Cs_4Mo_8P_{12}O_{52}$, adopts a layer structure. The compounds containing Mo^{4+} were observed in the mixed-valence compounds, $Cs_3Mo_6P_{10}O_{38}$ and $Cs_4Mo_{10}P_{18}O_{66}$ (*2*). Unusual isolated Mo^{3+} cations in oxygen lattice were discovered in $CsMoP_2O_7$ (*3*). A few remarkable compounds exhibit metal–metal bondings. Cubane-like Mo_4O_4 clusters and Mo_4O_3P clusters were observed in $Cs_3Mo_5P_6O_{25}$ (*4*), $Cs_3Mo_4P_3O_{16}$ (*5*), and $Cs_3Mo_5P_7O_{24}$ (*6*), respectively.

In an attempt to add new members to the family of cesium molybdenum phosphate, a new compound, γ-$CsMo_2P_3O_{13}$, was discovered. $Cs_2Mo_4P_6P_{26}$ and $Cs_4Mo_8P_{12}O_{52}$ are referred to as α- and β-$CsMo_2P_3O_{13}$ because they have the same chemical compositions. The present paper deals with the crystal structure of the γ-form.

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Experimental and Results

Preparation and Characterization

Cs_2MoO_4 (99.9%), MoO_2 (99.9%), MoO_3 (99.9%), and P_2O_5 (99.9%) were obtained from Cerac. The appropriate quantities of powdered Cs_2MoO_4, MoO_2, MoO_3, and P_2O_5 (1 : 2 : 1 : 3 mole ratio) were mixed, pelletized in a nitrogen-filled glove box, heated in an evacuated quartz tube at 950°C for 4 days, slowly cooled to 900°C at a rate of 30°C/hr, and then furnace-cooled to room temperature. Based on visual microscopic examination there were several phases in the product: the major phase occurred as brownish-green plates and the minor phases as green crystalline materials. An X-ray powder pattern of the bulk product suggested the presence of new phases in addition to the diffraction lines which could be indexed based on the structure of α-$CsMo_2P_3O_{13}$ (brownish-green plate). γ-Cs $Mo_2P_3O_{13}$ was present only in a small amount because the strongest reflection for the γ-form was about a tenth of that for the α-form. Single-crystal X-ray structure for the γ-form has been determined (vide infra). However, a product containing the pure γ-form has not been obtained.

Single-Crystal X-Ray Structure Determination

A green crystal having the dimensions of 0.35 × 0.07 × 0.03 mm was selected for indexing and intensity data collection on an Enraf–Nonius CAD-4 diffractometer. The unit cell parameters, $a = 6.342(1)$, $b = 9.676(1)$, $c = 10.0349(8)$ Å, $\alpha = 83.083(7)$, $\beta = 97.42(1)$, $\gamma = 108.30(1)°$, were determined by a least-squares fit of 25 peak maxima with 2θ ranging from 20 to 32°. 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 $R = 0.034$, $R_w = 0.042$, and GOF = 0.829. The thermal parameters for both Cs1 and Cs2 are large, suggesting positional disorder. There are two major sites for Cs2 which are related by inversion center and are too closely spaced (1.537(4) Å) to be simultaneously occupied. The occupancy factor for Cs2 was initially refined but the resultant value was very close to 0.5. In the final cycles of refinement, the occupancy factor for Cs2 was fixed at 0.5. The large residual electron density (4.82 e/Å^3) near (1/2, 1/2, 0) on the final difference map is probably related to the incomplete modeling of the disordered Cs atoms. The data were corrected for absorption, Lorentz, and polarization effects. Atomic scattering factors and anomalous dispersion terms were taken from "International Tables for X-ray Crystallography" (*7*). Crystal data, intensity measurements, and structure refinement parameters are collected in Table I. Final positional and anisotropical thermal

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR γ-$CsMo_2P_3O_{13}$

	Crystal data
Space group	$P\bar{1}$ (No. 2)
Cell dimensions	$a = 6.342(1)$, $b = 9.676(1)$, $c = 10.0349(8)$ Å, $\alpha = 83.083(7)$, $\beta = 97.42(1)$, $\gamma = 108.30(1)°$, $V = 577.7(2)$ Å^3
Z	2
Density (calcd)	3.597 g/cm^3
Abs. coeff. (Mo$K\alpha$)	56.8 cm^{-1}
	Intensity measurement
λ(MoKα)	0.70930 Å
Scan mode	$\omega/2\theta$
Scan rate	5.5°/min
Scan width	0.65° + 0.35° tan θ
Max 2θ	60°
Standard reflections	3 measured every 2 hr (no decay)
Reflections measured	3631 total, 3352 unique
	Structure solution and refinement
Reflections included	2927 with $I > 2.5\ \sigma(I)$
Parameter refined	179
Agreement factors[a]	$R = 0.034$, $R_w = 0.042$
GOF[b]	0.829
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	4.82; −3.78 e/Å^3

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma(F_o)$, $R_w = \Sigma(w(F_o - F_c)^2)/\Sigma(w(F_o)^2)$ with $w = 1.0/(\sigma(F_o))^2$.

[b] GOF $= [\Sigma(w(F_o - F_c)^2)/(N_o - N_v)]^{1/2}$.

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR γ-$CsMo_2P_3O_{13}$[a,b,c]

Atom	x	y	z	B(iso)
Cs1	0.5	0	0.5	3.22(3)
Cs2	0.51010(21)	0.57126(17)	0.95471(15)	4.12(6)
Mo1	0.14289(7)	0.63704(5)	0.25290(4)	0.42(2)
Mo2	−0.14807(7)	0.09037(5)	0.18014(4)	0.44(2)
P1	−0.30096(22)	0.72079(15)	0.32152(14)	0.53(5)
P2	0.29835(22)	−0.00032(15)	0.13486(14)	0.50(5)
P3	−0.00958(22)	0.30305(14)	0.44613(13)	0.46(4)
O1	−0.1656(7)	0.6654(5)	0.2367(4)	0.86(15)
O2	0.5358(7)	0.0938(4)	0.1809(4)	0.87(15)
O3	0.4568(6)	0.6284(5)	0.3034(4)	0.88(15)
O4	0.0113(7)	0.4414(5)	0.3573(4)	1.11(15)
O5	0.1650(7)	0.7183(5)	0.4462(4)	0.79(14)
O6	0.1052(8)	0.5575(5)	0.1112(5)	1.49(18)
O7	0.2638(7)	0.1177(4)	0.7011(4)	0.94(15)
O8	0.2493(7)	0.0272(5)	−0.0174(4)	0.92(15)
O9	0.1435(7)	0.0462(5)	0.2127(4)	1.10(16)
O10	0.2328(7)	0.3163(5)	0.5224(4)	0.86(15)
O11	0.0763(7)	0.8314(5)	0.6320(4)	0.96(14)
O12	0.2758(7)	0.8393(5)	0.1754(4)	1.11(16)
O13	0.9513(9)	0.2510(5)	0.0971(5)	1.67(18)

Anisotropic thermal parameters ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs1	3.77(4)	3.96(4)	2.81(3)	−2.80(3)	2.43(3)	−2.35(3)
Cs2	3.27(6)	6.97(9)	5.96(8)	1.00(6)	0.55(5)	−4.08(7)
Mo1	0.45(2)	0.59(2)	0.57(2)	0.20(1)	0.03(1)	−0.09(1)
Mo2	0.45(2)	0.64(2)	0.60(2)	0.18(2)	0.05(1)	−0.12(1)
P1	0.44(5)	0.73(6)	0.84(6)	0.21(4)	0.02(4)	−0.05(5)
P2	0.51(5)	0.77(6)	0.67(6)	0.24(5)	0.06(4)	−0.12(4)
P3	0.60(6)	0.58(5)	0.54(5)	0.12(4)	0.04(4)	−0.11(4)
O1	0.64(17)	1.95(20)	1.02(18)	0.83(15)	−0.03(14)	−0.42(15)
O2	0.56(17)	1.06(18)	1.80(20)	0.34(14)	−0.11(14)	−0.48(15)
O3	0.37(16)	1.17(18)	1.71(20)	0.14(14)	−0.09(14)	−0.23(15)
O4	1.65(20)	0.97(18)	1.48(20)	0.34(16)	0.18(16)	0.28(15)
O5	0.82(17)	1.42(19)	0.82(17)	0.23(14)	0.24(14)	−0.46(14)
O6	2.67(24)	1.81(22)	1.24(20)	0.72(19)	−0.19(17)	−0.73(16)
O7	1.28(19)	0.81(17)	1.44(19)	0.31(15)	0.24(15)	0.08(14)
O8	1.59(19)	1.33(19)	0.63(17)	0.56(16)	−0.10(14)	−0.27(14)
O9	0.63(17)	2.76(23)	1.26(19)	0.98(16)	0.11(14)	−0.74(17)
O10	0.64(17)	1.82(20)	0.83(17)	0.49(15)	−0.09(13)	−0.06(15)
O11	1.46(19)	1.20(19)	1.01(18)	0.25(15)	0.12(15)	−0.55(15)
O12	1.48(20)	0.90(18)	1.69(20)	0.29(15)	0.33(16)	0.42(15)
O13	2.50(24)	1.43(21)	1.81(22)	−0.09(18)	0.21(18)	0.26(17)

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[a] B(iso) is the mean of the principal axes of thermal ellipsoid.

[b] The occupancy factor for Cs2 is 0.5.

[c] The anisotropic thermal parameters take the form: $2\pi^2(h^2(a^*)^2U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)$.

parameters are listed in Table II. Selected bond distances are given in Table III.

Description and Discussion of the Structure

Figure 1 shows a stereoscopic view of the γ-$CsMo_2P_3O_{13}$ structure down the *a* axis. It consists of three different tunnels of which the large and medium ones are occupied by Cs^+. Cs1 is located at the center of the medium tunnel. Cs2 is disordered in the large tunnel. The two major sites for Cs2 are so closely spaced that they are not simultaneously occupied. Cs1 and Cs2 are coordinated by 10 and 7 oxygen atoms at distances ranging from 2.942(4) to 3.502(4) Å and 3.139(5) to 3.476(4) Å, respectively. Both Cs atoms exhibit large thermal parameters.

TABLE III

SELECTED BOND DISTANCES (Å) FOR γ-$CsMo_2P_3O_{13}$

Cs1–O2	3.238(4)	(2×)	P1–O3	1.516(4)
Cs1–O5	2.942(4)	(2×)	P1–O7	1.499(4)
Cs1–O7	3.165(4)	(2×)	P1–O10	1.599(4)
Cs1–O9	3.502(4)	(2×)	P2–O2	1.540(4)
Cs1–O11	3.047(4)	(2×)	P2–O8	1.528(4)
Cs2–O1	3.318(4)		P2–O9	1.529(4)
Cs2–O1	3.247(4)		P2–O12	1.523(4)
Cs2–O2	3.445(4)		P3–O4	1.495(4)
Cs2–O3	3.476(4)		P3–O5	1.508(4)
Cs2–O6	3.139(5)		P3–O10	1.600(4)
Cs2–O6	3.235(5)		P3–O11	1.517(4)
Cs2–O13	3.384(5)			
Mo1–O1	2.043(4)			
Mo1–O3	2.015(4)			
Mo1–O4	2.033(4)			
Mo1–O5	2.151(4)			
Mo1–O6	1.653(4)			
Mo1–O12	1.978(4)			
Mo2–O2	2.017(4)			
Mo2–O7	2.176(4)			
Mo2–O8	2.023(4)			
Mo2–O9	2.004(4)			
Mo2–O11	2.059(4)			
Mo2–O13	1.648(5)			
P1–O1	1.528(4)			

The framework of γ-$CsMo_2P_3O_{13}$ is composed of MoO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. The coordination of either Mo1 or Mo2 is similar to those in the α- and β-forms, i.e., one very short (1.653(4) Å for Mo1, 1.648(5) Å for Mo2) and one very long Mo–O (2.151(4) Å for Mo1, 2.176(4) Å for Mo2) bond distances. Using the bond-length and bond-strength relationship for

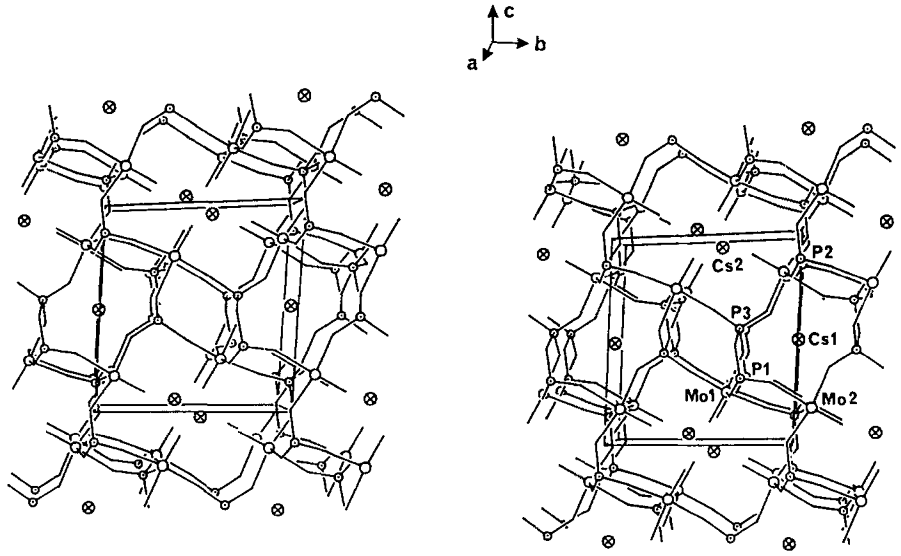

FIG. 1. A stereoscopic view of the γ-$CsMo_2P_3O_{13}$ structure. For clarity, the radii for oxygen atoms are set equal to zero. The P, Cs, and Mo atoms are represented by circles with a dot, circles with a cross, and open circles, respectively.

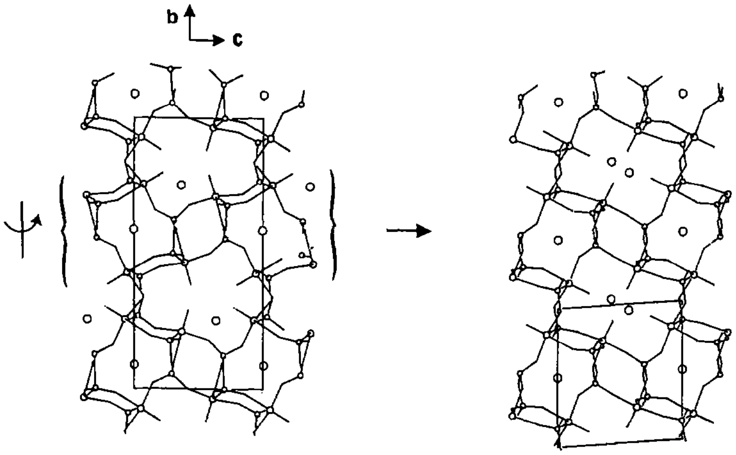

FIG. 2. β-$CsMo_2P_3O_{13}$–γ-$CsMo_2P_3O_{13}$ transformation. The γ-form (right) is generated from the β-form (left) by rotating the neighboring small and medium tunnels around the b axis for 180°. The Cs, Mo, and P atoms are represented by large, medium, and small open circles, respectively. For clarity, the radii for oxygen atoms are set equal to zero.

Mo–O bond ($s = (d/1.882)^{-6}$) (*8*), we have found that the effective charges on Mo1 and Mo2 are 5.27 and 5.21, respectively. The P2–O bond distances (1.523(4)–1.540(4) Å) and O–P2–O bond angles (105.3(2)–111.6(2)°) indicate that P2 is essentially located at the center of the phosphate group. Whereas in the tetrahedra belonging to the pyrophosphate groups each phosphorus atom is displayed away from the bridging oxygen atom giving three shorter (1.499(4)–1.528(4) Å for P1, 1.495(4)–1.517(4) Å for P3) and one longer (1.599(4) Å for P1, 1.600(4) Å for P3) P–O bond distances. The P1–O–P3 bond angle involving the bridging oxygen atom is 129.0(3)°. The configuration of the P_2O_7 group is rather similar to that in the β-form. Each MoO_6 octahedron in the γ-form shares five corners with PO_4 tetrahedra or P_2O_7 groups with the sixth corner being unshared. Mo1 shares its five corners with three P_2O_7 groups and one PO_4 tetrahedron. One of the pyrophosphate groups shares two oxygen atoms with Mo1. Mo2 shares its five corners with two P_2O_7 groups and three PO_4 tetrahedra. Each phosphate group shares its four corners with four MoO_6 octahedra. Each pyrophosphate group shares its six corners with five MoO_6 octahedra.

Based on the above description the structural formula for γ-$CsMo_2P_3O_{13}$ is $Cs(MoO)_2(PO_4)(P_2O_7)$, which is identical with those for the α- and β-forms. In other words, all three forms are composed of the same building units. The structure types of these phases are determined by the arrangements of the building units in the lattice, which in turn appear to be directed by the experimental conditions. Interestingly, the γ-$CsMo_2P_3O_{13}$ structure is closely related to the β-form. The β-form also consists of three different tunnels of which the small and medium ones are essentially the same as those in the γ-form. However, the small and medium tunnels in the β-form are related to the neighboring tunnels by a 2_1-screw axis along the b axis. As depicted in Fig. 2, the γ-form can be generated from the β-form by rotating the neighboring small and medium tunnels around the b axis for 180°. The β-form has a smaller density than the γ-form, which is, however, less dense than the α-form. It would be of great interest to study the possible transformations among the three polymorphs at high pressures. On the other hand, the use of high pressure in the synthesis may produce new phases with higher densities.

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