

# A novel Mo(V) oligophosphate built up of di- and triphosphate groups: $\text{Cs}(\text{MoO})_4(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$

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## Abstract

A Mo(V) oligophosphate, built up of di and triphosphate groups,  $\text{Cs}(\text{MoO})_4(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  has been synthesized for the first time. This compound crystallizes in the triclinic  $P\bar{1}$  space group with  $a = 9.411(1)\text{Å}$ ,  $b = 10.754(1)\text{Å}$ ,  $c = 12.517(1)\text{Å}$ ,  $\alpha = 94.534(6)^\circ$ ,  $\beta = 102.520(6)^\circ$ ,  $\gamma = 103.663(4)^\circ$ . This original structure can be described by the association of  $\text{MoO}_6$  octahedra,  $\text{MoP}_2\text{O}_{11}$  units built up of one  $\text{P}_2\text{O}_7$  group sharing two apices with the same  $\text{MoO}_6$  octahedron, and triphosphates groups  $\text{P}_3\text{O}_{10}$ . The resulting tridimensional framework forms large S-shaped tunnels running along  $c$  where the  $\text{Cs}^+$  cations are located.

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## 1. Introduction

The study of the behaviour of caesium as an invited cation in a mixed framework built up of tetrahedra and octahedra, such as the molybdenum phosphates, is of interest for the possible realization of matrices for the storage of radioactive caesium issued from the waste products of nuclear reactions. The great ability of molybdenum to accommodate various oxidation states— $\text{Mo}^{6+}$ ,  $\text{Mo}^{5+}$ ,  $\text{Mo}^{4+}$ ,  $\text{Mo}^{3+}$ —and various coordinations—tetrahedral, octahedral, bipyramidal—makes that, to date, a rather large family of compounds has been discovered in the Cs–Mo–P–O system.

Among the caesium molybdenophosphates that are actually known, two classes of compounds have been mainly synthesized, the monophosphates and the diphosphates. In the caesium monophosphates, molybdenum exhibits either the octahedral coordination as in  $\text{Cs}_3(\text{MoO})_4(\text{PO}_4)_3$  [1] or in  $\text{CsMoO}_2\text{PO}_4$  [2],  $\text{Cs}_6\text{Mo}_7\text{O}_9(\text{PO}_4)_7 \cdot \text{H}_2\text{O}$  [3] and  $\text{Cs}_3\text{Mo}_8\text{O}_{11}(\text{PO}_4)_8$  [4] or both coordinations octahedral and tetrahedral simultaneously as in  $\text{Cs}_{8.34}(\text{MoO}_4)\text{Mo}_{12}\text{O}_{18}(\text{PO}_4)_{10}$  [5], and  $\text{CsMo}_6\text{O}_{10}$

$(\text{Mo}_2\text{O}_7)(\text{PO}_4)_4$  [6]. In the caesium diphosphates, four compounds are actually known:  $\text{CsMoP}_2\text{O}_7$  [7],  $\text{Cs}_3\text{Mo}(\text{Mo}_4\text{O}_3\text{P})(\text{P}_2\text{O}_7)_3$  [8] and  $\text{CsMoOP}_2\text{O}_7$  [9] involving  $\text{MoO}_6$  octahedra and the diphosphate  $\text{Cs}_3\text{Mo}(\text{MoO})_4(\text{P}_2\text{O}_7)_3$  [10] where  $\text{MoO}_6$  octahedra and  $\text{MoO}_4$  tetrahedra coexist in the same matrix. Beside these two classes, a series of caesium oligophosphates, containing both isolated  $\text{PO}_4$  groups and  $\text{P}_2\text{O}_7$  groups was discovered by Lii and Haushalter: three forms of  $\text{Cs}(\text{MoO})_2(\text{PO}_4)(\text{P}_2\text{O}_7)$  [11,12],  $\text{Cs}_2\text{Mo}_2\text{MoO}(\text{PO}_4)(\text{P}_2\text{O}_7)_2 \cdot \text{H}_2\text{O}$  [13] and,  $\text{Cs}_3\text{Mo}_2(\text{Mo}_2\text{O})_2(\text{PO}_4)_2(\text{P}_2\text{O}_7)_4$  [14]. The phosphate  $\text{Li}_{3.2}\text{Cs}_{0.8}(\text{MoO})_3(\text{PO}_4)_3(\text{P}_2\text{O}_7)$  [15] belongs also to this series.

The consideration of the caesium molybdenum phosphates shows that in the latter, the presence of oligophosphate groups  $[\text{P}_n\text{O}_{3n+1}]^{(n+2)-}$  with  $n > 2$  is very rare. Indeed, no “pure” caesium molybdenum triphosphate has been observed to date. The only example of phase containing triphosphate groups is the compound  $\text{Cs}_2\text{Mo}_5\text{O}_2(\text{P}_2\text{O}_7)_3(\text{P}_3\text{O}_{10})$  [16], where molybdenum exhibits the mixed valence Mo(III)–Mo(IV) with an octahedral coordination.

Bearing in mind the great flexibility of pentavalent molybdenum for building mixed frameworks with tetrahedral phosphate groups, due to its molybdenyl bond, we have revisited the Cs–Mo(V)–P–O system. We report

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herein on a novel Mo(V) oligophosphate  $\text{Cs}(\text{MoO})_4(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  with an original tunnel structure, containing both diphosphate and triphosphate groups.

## 2. Synthesis and crystal growth

Single crystals of the title compound were obtained from a batch of nominal composition  $\text{CsMo}_5\text{P}_8\text{O}_{33}$ . First  $\text{CsNO}_3$ ,  $\text{H}(\text{NH}_4)_2\text{PO}_4$  and  $\text{MoO}_3$  were mixed in an agate mortar in the molar ratio (1:8:4.166) and heated at 673 K in a platinum crucible to decompose the ammonium phosphate and the nitrate. In a second step the resulting mixture, added to metallic molybdenum powder (0.833) was crushed in an agate mortar and sealed in an evacuated quartz ampoule and then heated for one day at 1123 K, cooled at 5.7 K per hour to 573 K and finally quenched to room temperature. From the resulting dark product, green crystals were extracted whose EDS analysis was in agreement with the ratio 1/4/7 for the Cs, Mo and P elements.

The quantitative synthesis of  $\text{Cs}(\text{MoO})_4(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  in the form of polycrystalline green powder was carried out in the same experimental conditions as described above, but changing the molar ratio of the precursors, i.e. starting from the molar ratios 1:3.333:7 for the mixture  $\text{CsNO}_3$ ,  $\text{MoO}_3$ ,  $\text{H}(\text{NH}_4)_2\text{PO}_4$  in the first step and adding 0.667 mole of metallic Mo and heating at 1073 K in the second step.

## 3. X-ray single crystal structure determination

A green crystal with dimensions  $0.017 \times 0.048 \times 0.072 \text{ mm}^3$  was selected for the X-ray studies. The data were recorded at room temperature on a NONIUS KAPPA CCD diffractometer using the  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) isolated with a graphite monochromator. The triclinic lattice parameters  $a = 9.4112(7) \text{ \AA}$ ,  $b = 10.7540(7) \text{ \AA}$ ,  $c = 12.5171(7) \text{ \AA}$ ,  $\alpha = 94.534(6)^\circ$ ,  $\beta = 102.520(6)^\circ$ ,  $\gamma = 103.663(4)^\circ$ , were refined from the complete data set.

Measurements and refinement parameters and the crystal data are summarized in Table 1.

Absorption corrections applied to the data were computed by the gaussian method taking into consideration the shape and the size of the crystal. The transmission factors so obtained range from 0.86 to 0.93.

The structure was solved by the heavy atom method in the  $P-1$  space group. The full matrix least-squares refinements of the atomic parameters were performed on the  $Fhkl$  values weighted by  $1/\sigma(Fhkl)^2$  using the JANA2000 package [17]. They lead to  $R = 0.0384$  and  $R_w = 0.0299$  and to the coordinates of Table 2. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-mail: [crysdata@fiz.karlsruhe.de](mailto:crysdata@fiz.karlsruhe.de)) on quoting the depository number CSD416483.

Table 1

Summary of crystal data, intensity measurement and structure refinement of  $\text{Cs}(\text{MoO})_4(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$

Chemical formula	$\text{CsMo}_4\text{P}_7\text{O}_{28}$
Structural formula	$\text{Cs}(\text{MoO})_4(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$
Molecular weight	1181.46 Da
Crystal system	Triclinic
Space group	$P-1$
Cell dimensions	$a = 9.4112(7) \text{ \AA}$ $b = 10.7540(7) \text{ \AA}$ $c = 12.5171(7) \text{ \AA}$ $\alpha = 94.534(6)^\circ$ $\beta = 102.520(6)^\circ$ $\gamma = 103.663(4)^\circ$
Cell volume	$1190.3(2) \text{ \AA}^3$
Z	2
Density	$3.295 \text{ g cm}^{-3}$
$\mu$ ( $\text{mm}^{-1}$ )	4.160
T (min)	0.8566
T (max)	0.9377
Measured reflections	17,896
Independent data	10,065
Independent data with $I > 3\sigma(I)$	4581
Temperature of the data collections	$21^\circ \text{C}$
Secondary extinction (Zachariasen)	0.41(2)
GOF	1.07
Number of variables	362
Difference Fourier density max	2.32
Difference Fourier density min	-1.69
R ( $F_o$ )	0.0384
$R_w$	0.0299

## 4. Description of the structure and discussion

The projection of the structure of this new molybdenophosphate along **a** (Fig. 1) and along **c** (Fig. 2) shows that the trimensional framework  $[\text{Mo}_4\text{P}_7\text{O}_{28}]_\infty$  consists of diphosphate and triphosphate groups sharing apices with  $\text{MoO}_6$  octahedra. In this framework, each  $\text{P}_2\text{O}_7$  group shares two apices with the same octahedron, forming  $\text{MoP}_2\text{O}_{11}$  units (Fig. 1) observed in numerous Mo(V) phosphates (see for a review Ref. [18]). Each  $\text{P}_3\text{O}_{10}$  group shares also two apices with the same octahedron, in a similar manner (Fig. 1). This structure appears as an opened framework forming empty five-sided tunnels running along **a** (Fig. 1) and along **c** (Fig. 2), and very large S-shaped tunnels running along **c** (Fig. 2), where the  $\text{Cs}^+$  cations are located. In fact, this framework can be described as built up from  $[\text{Mo}_4\text{P}_4\text{O}_{26}]_\infty$  layers parallel to (100) containing the  $\text{P}_2\text{O}_7$  groups (in pale grey on Fig. 2), interconnected through  $\text{P}_3\text{O}_{10}$  groups (in dark on Fig. 2, but not clearly evidenced from the projection, since oriented along **c**). In those layers (Fig. 3), the  $\text{MoP}_2\text{O}_{11}$  units share their corners to form  $[\text{MoP}_2\text{O}_{10}]_\infty$  chains running along **c** where one octahedron alternates with one  $\text{P}_2\text{O}_7$  group. Two identical chains, rotated by  $180^\circ$  with respect to each other, share the corners of their  $\text{MoP}_2\text{O}_{11}$  units, in order to form double chains  $[\text{Mo}_2\text{P}_4\text{O}_{18}]_\infty$  running along **c**. These double chains are connected via

Table 2  
Atomic parameters in Cs(MoO)<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>)

Atom	x	y	z	U <sub>eq</sub>
Mo1	0.27174(4)	0.02219(3)	0.09257(3)	0.0062(1)
Mo2	0.27136(4)	0.48099(3)	0.60085(3)	0.0067(1)
Mo3	0.25353(4)	0.48484(3)	0.12097(4)	0.0069(1)
Mo4	0.27368(4)	0.00804(3)	0.59569(3)	0.0057(1)
Cs	0.01719(4)	0.21955(3)	0.76583(4)	0.0351(2)
P1	0.4557(1)	0.2843(1)	0.7338(1)	0.0069(4)
P2	0.3892(1)	0.0726(1)	0.8625(1)	0.0079(4)
P3	0.4181(1)	0.2851(1)	0.2584(1)	0.0084(4)
P4	0.3716(1)	0.0554(1)	0.3585(1)	0.0069(4)
P5	0.0913(1)	0.7006(1)	0.9761(1)	0.0077(4)
P6	0.0456(1)	0.5859(1)	0.7544(1)	0.0077(4)
P7	0.0593(1)	0.6887(1)	0.5459(1)	0.0073(4)
O1	0.1159(3)	0.0676(3)	0.0951(3)	0.017(1)
O2	0.4195(3)	0.1942(2)	0.1589(3)	0.011(1)
O3	0.3008(3)	−0.0276(3)	0.2464(3)	0.010(1)
O4	0.2857(3)	−0.0643(3)	−0.0598(3)	0.012(1)
O5	0.1572(3)	−0.1640(2)	0.0331(3)	0.015(1)
O6	0.4589(3)	−0.0560(3)	0.0910(3)	0.013(1)
O7	0.3515(3)	0.4510(3)	0.5009(3)	0.019(1)
O8	0.4245(3)	0.6387(3)	0.6857(3)	0.016(1)
O9	0.3496(3)	0.3689(3)	0.7085(3)	0.015(1)
O10	0.1497(3)	0.5944(2)	0.5265(3)	0.011(1)
O11	0.0828(3)	0.3327(2)	0.5449(3)	0.010(1)
O12	0.1572(3)	0.5167(2)	0.7313(3)	0.010(1)
O13	0.3696(4)	0.4609(3)	0.0461(3)	0.023(1)
O14	0.1630(4)	0.6052(3)	0.0308(3)	0.026(1)
O15	0.3818(3)	0.6403(3)	0.2278(3)	0.015(1)
O16	0.3103(3)	0.3681(3)	0.2320(3)	0.017(1)
O17	0.0781(3)	0.3366(2)	0.0354(3)	0.013(1)
O18	0.0925(3)	0.4975(2)	0.2227(3)	0.011(1)
O19	0.1322(3)	0.0752(3)	0.5933(3)	0.019(1)
O20	0.1497(3)	−0.1742(2)	0.5585(3)	0.015(1)
O21	0.3071(3)	−0.0147(3)	0.7553(3)	0.016(1)
O22	0.2719(3)	0.0072(3)	0.4345(3)	0.011(1)
O23	0.4354(3)	0.1788(2)	0.6396(3)	0.010(1)
O24	0.4651(3)	−0.0667(2)	0.5993(3)	0.012(1)
O25	0.4059(3)	0.2189(2)	0.8347(3)	0.014(1)
O26	0.3524(3)	0.1979(2)	0.3431(2)	0.008(1)
O27	0.1205(3)	0.6991(3)	0.8555(3)	0.013(1)
O28	0.0039(3)	0.6661(3)	0.6565(3)	0.013(1)

MoO<sub>6</sub> octahedra leading to the [Mo<sub>4</sub>P<sub>4</sub>O<sub>26</sub>]<sub>∞</sub> layers. Two successive layers are assembled via P<sub>3</sub>O<sub>10</sub> groups oriented along **c** as shown from the projection of the structure along **b** (Fig. 4).

The geometry of the four kinds of MoO<sub>6</sub> octahedra is characteristic of pentavalent molybdenum with one Mo–O short bond (1.636(4)–1.657(3) Å) opposed to a very long one (2.127(4)–2.201(4) Å) and four medium ones (1.990(2)–2.037(2) Å) (Table 3).

The bond valence sums determined from the Brese and O’Keeffe formulation [19], using a more appropriate *R<sub>ij</sub>* values for molybdenum [20] and for caesium, are in agreement with the formal charges deduced from the chemical formula: 5.064, 5.118, 5.131, 5.167 for Mo1–Mo4, respectively; 1.0 for Cs; 5.053, 5.077, 5.041, 5.038, 5.153, 4.946, 5.094 for P1–P7, respectively, and ranging from 1.877 to 2.155 for the oxygen atoms.

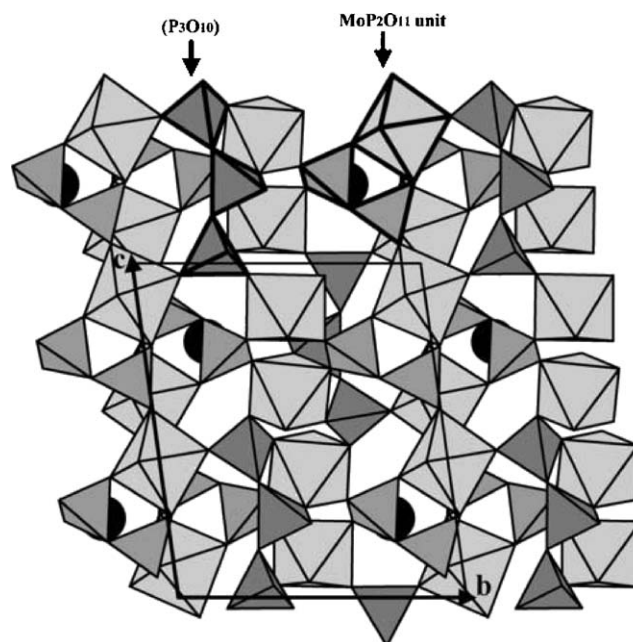


Fig. 1. Projection of the structure of Cs(MoO)<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) along **a**. One P<sub>3</sub>O<sub>10</sub> group and one MoP<sub>2</sub>O<sub>11</sub> unit are emphasised in bold lines.

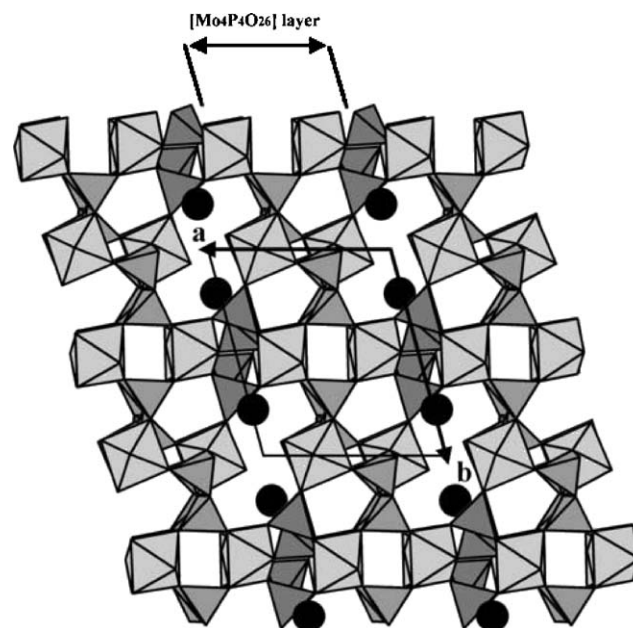


Fig. 2. Projection of the structure of Cs(MoO)<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) along **c** showing the empty five-sided tunnels and the S-shaped tunnels containing the Cs ions. The P<sub>2</sub>O<sub>7</sub> groups in the [Mo<sub>4</sub>P<sub>4</sub>O<sub>26</sub>]<sub>∞</sub> layers are in pale grey while the P<sub>3</sub>O<sub>10</sub> groups connecting the layers are in dark grey.

The geometry of the PO<sub>4</sub> tetrahedra is correlated to the kind of unit in which the tetrahedron is involved and to the rank in the unit. For P1–P4, belonging to diphosphate groups, the P–O bonds corresponding to the bridging oxygen atoms are significantly longer (1.597(4)–1.617(4) Å) than the others (1.480(3)–1.526(3) Å) (Table 3). In the

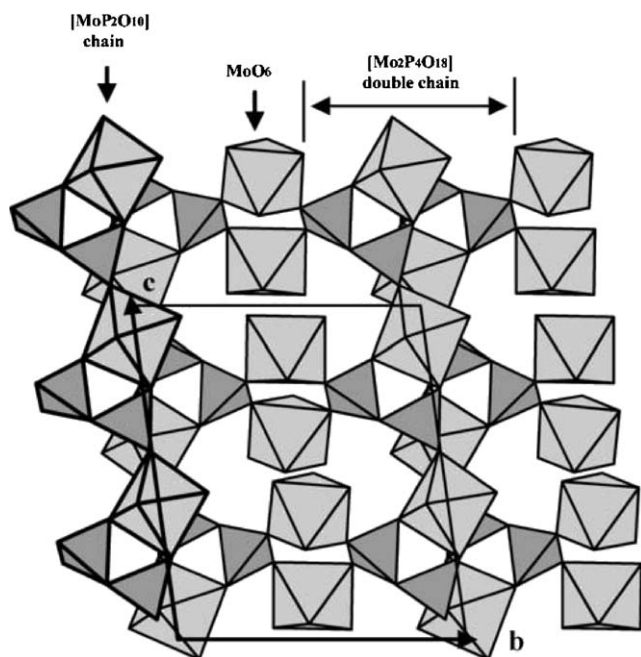


Fig. 3. The  $[\text{Mo}_4\text{P}_4\text{O}_{26}]_\infty$  layer parallel to (100) viewed along *a* showing the  $[\text{Mo}_2\text{P}_4\text{O}_{18}]$  double chains connected through  $\text{MoO}_6$  octahedra.

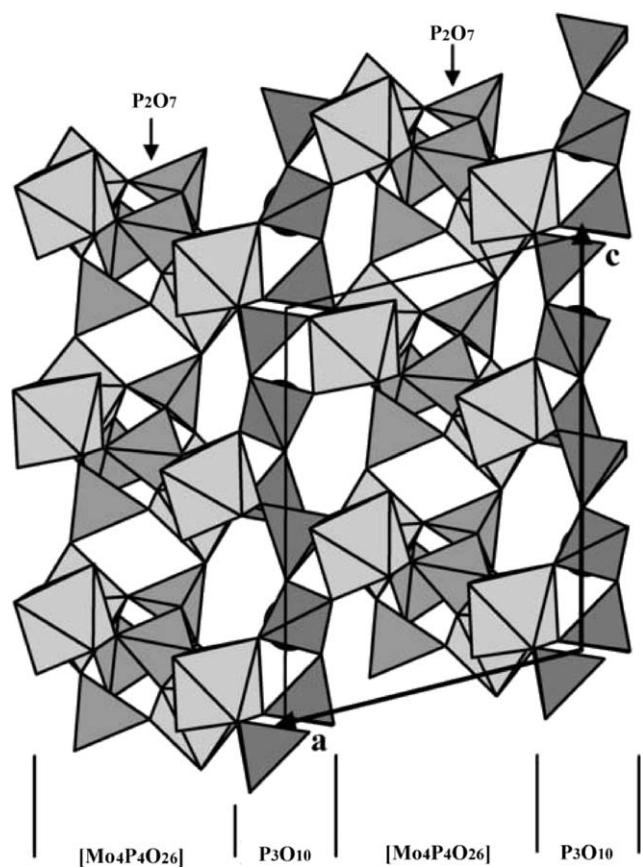


Fig. 4. Projection of the structure of  $\text{Cs}(\text{MoO}_4)(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  along *b*.

triphosphate group (P5–P7), the P–O bonds corresponding to the bridging oxygen atoms are long (1.587(4)–1.598(4) Å), whereas the other bonds are significantly

Table 3

Distances (Å) and angles (°) in the polyhedra of  $\text{Cs}(\text{MoO}_4)(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	<b>1.657(3)</b>	2.767(4)	2.717(5)	2.770(5)	2.691(4)	3.779(5)
O(2)	97.1(1)	<b>2.021(2)</b>	2.797(4)	2.846(5)	4.034(3)	2.889(4)
O(3)	94.8(2)	87.6(1)	<b>2.018(4)</b>	4.014(5)	2.826(4)	2.732(5)
O(4)	97.3(2)	89.6(1)	167.8(1)	<b>2.019(4)</b>	2.916(4)	2.818(4)
O(5)	93.2(1)	169.4(1)	88.5(1)	92.1(1)	<b>2.030(2)</b>	2.712(4)
O(6)	173.9(1)	88.3(1)	82.4(1)	85.6(1)	81.4(1)	<b>2.127(3)</b>
Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	<b>1.643(4)</b>	2.795(5)	2.812(5)	2.767(5)	2.741(4)	3.839(5)
O(8)	100.0(1)	<b>1.995(3)</b>	2.872(5)	2.814(4)	3.988(3)	2.749(4)
O(9)	100.0(2)	91.5(1)	<b>2.014(4)</b>	3.972(5)	2.799(4)	2.720(5)
O(10)	98.0(2)	89.3(1)	161.5(2)	<b>2.010(3)</b>	2.775(3)	2.750(5)
O(11)	95.9(1)	164.0(2)	87.5(1)	86.7(1)	<b>2.032(2)</b>	2.785(4)
O(12)	178.1(1)	81.8(1)	80.4(1)	81.5(1)	82.3(1)	<b>2.196(4)</b>
Mo(3)	O(13)	O(14)	O(15)	O(16)	O(17)	O(18)
O(13)	<b>1.636(4)</b>	2.745(6)	2.828(5)	2.718(5)	2.722(4)	3.833(6)
O(14)	97.5(2)	<b>2.003(4)</b>	2.783(5)	3.992(5)	2.818(4)	2.884(5)
O(15)	101.6(1)	87.9(1)	<b>2.008(3)</b>	2.852(5)	4.000(3)	2.777(4)
O(16)	95.7(2)	166.9(2)	90.3(1)	<b>2.016(4)</b>	2.852(4)	2.724(4)
O(17)	95.2(1)	88.6(1)	163.5(1)	89.5(1)	<b>2.033(2)</b>	2.760(5)
O(18)	174.6(1)	89.5(1)	82.4(1)	80.4(1)	81.3(1)	<b>2.201(4)</b>
Mo(4)	O(19)	O(20)	O(21)	O(22)	O(23)	O(24)
O(19)	<b>1.654(3)</b>	2.732(4)	2.715(5)	2.752(5)	2.720(4)	3.785(5)
O(20)	96.7(1)	<b>1.990(2)</b>	2.785(4)	2.780(5)	4.007(3)	2.835(4)
O(21)	95.6(2)	88.6(1)	<b>1.998(4)</b>	3.987(5)	2.817(5)	2.796(5)
O(22)	96.8(2)	88.0(1)	167.5(1)	<b>2.013(4)</b>	2.926(4)	2.740(5)
O(23)	94.4(1)	168.8(1)	88.6(1)	92.5(1)	<b>2.037(2)</b>	2.739(4)
O(24)	172.4(1)	86.8(1)	85.1(1)	82.7(1)	82.1(1)	<b>2.133(3)</b>
P(1)	O(9)	O(15) <sup>i</sup>	O(23)	O(25)		
O(9)	<b>1.504(4)</b>	2.508(4)	2.526(4)	2.413(5)		
O(15) <sup>i</sup>	113.0(2)	<b>1.504(3)</b>	2.484(4)	2.516(4)		
O(23)	113.4(2)	110.6(2)	<b>1.517(3)</b>	2.532(5)		
O(25)	102.1(2)	108.5(2)	108.8(2)	<b>1.597(4)</b>		
P(2)	O(4) <sup>ii</sup>	O(6) <sup>iii</sup>	O(21)	O(25)		
O(4) <sup>ii</sup>	<b>1.512(4)</b>	2.538(5)	2.468(5)	2.428(5)		
O(6) <sup>iii</sup>	116.0(2)	<b>1.480(3)</b>	2.504(4)	2.520(5)		
O(21)	109.4(2)	113.6(2)	<b>1.512(3)</b>	2.503(4)		
O(25)	101.7(2)	108.8(2)	106.2(2)	<b>1.617(4)</b>		
P(3)	O(2)	O(8) <sup>i</sup>	O(16)	O(26)		
O(2)	<b>1.526(3)</b>	2.476(4)	2.537(5)	2.519(5)		
O(8) <sup>i</sup>	110.0(2)	<b>1.497(3)</b>	2.506(4)	2.513(4)		
O(16)	113.7(2)	113.2(2)	<b>1.505(4)</b>	2.439(4)		
O(26)	107.5(2)	108.5(2)	103.6(2)	<b>1.598(3)</b>		
P(4)	O(3)	O(22)	O(24) <sup>iii</sup>	O(26)		
O(3)	<b>1.525(3)</b>	2.438(5)	2.530(4)	2.511(4)		
O(22)	106.8(2)	<b>1.513(4)</b>	2.542(4)	2.470(4)		
O(24) <sup>iii</sup>	114.4(2)	116.0(2)	<b>1.485(4)</b>	2.496(4)		
O(26)	106.6(2)	104.7(2)	107.6(2)	<b>1.606(3)</b>		
P(5)	O(5) <sup>iv</sup>	O(14) <sup>ii</sup>	O(17) <sup>v</sup>	O(27)		
O(5) <sup>iv</sup>	<b>1.494(2)</b>	2.494(4)	2.463(3)	2.478(5)		
O(14) <sup>ii</sup>	113.5(2)	<b>1.488(4)</b>	2.483(5)	2.481(5)		
O(17) <sup>v</sup>	109.6(2)	111.2(2)	<b>1.521(3)</b>	2.521(5)		

Table 3 (continued)

P(5)	O(5) <sup>iv</sup>	O(14) <sup>ii</sup>	O(17) <sup>v</sup>	O(27)
O(27)	106.8(2)	107.3(2)	108.2(2)	<b>1.591(4)</b>
P(6)	O(12)	O(18) <sup>v</sup>	O(27)	O(28)
O(12)	<b>1.486(4)</b>	2.512(5)	2.541(5)	2.507(5)
O(18) <sup>v</sup>	115.0(2)	<b>1.492(3)</b>	2.503(3)	2.543(5)
O(27)	111.1(2)	108.3(2)	<b>1.595(3)</b>	2.455(5)
O(28)	109.3(2)	111.3(2)	101.0(2)	<b>1.587(4)</b>
P(7)	O(10)	O(11) <sup>v</sup>	O(20) <sup>vi</sup>	O(28)
O(10)	<b>1.506(3)</b>	2.505(4)	2.489(3)	2.529(5)
O(11) <sup>v</sup>	112.1(2)	<b>1.512(3)</b>	2.456(3)	2.478(5)
O(20) <sup>vi</sup>	112.1(2)	109.5(2)	<b>1.495(2)</b>	2.507(5)
O(28)	109.1(2)	105.6(2)	108.3(2)	<b>1.598(4)</b>

Symmetry codes: (i)  $1-x, 1-y, 1-z$ , (ii)  $x, y, 1+z$ , (iii)  $1-x, -y, 1-z$ , (iv)  $x, 1+y, 1+z$ , (v)  $-x, 1-y, 1-z$ , (vi)  $x, 1+y, z$ , (vii)  $-x, -y, 1-z$ . The Mo–O or P–O distances lie on the diagonal and the O–O distances are above it and the O–Mo–O or O–P–O angles are under it.

Table 4

Caesium coordination in Cs(MoO)<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>)

Cs–O(19)	3.086(4) Å	Cs–O(17) <sup>ii</sup>	3.383(4) Å
Cs–O(3) <sup>vii</sup>	3.174(3) Å	Cs–O(9)	3.415(3) Å
Cs–O(11)	3.229(4) Å	Cs–O(18) <sup>v</sup>	3.439(3) Å
Cs–O(12)	3.257(3) Å	Cs–O(22) <sup>vii</sup>	3.546(3) Å
Cs–O(5) <sup>vii</sup>	3.309(4) Å	Cs–O(25)	3.574(3) Å

shorter (1.486(4)–1.521(4) Å). The two tetrahedra P5 and P7 sitting at the two ends of the triphosphate group, exhibit the same geometry as the tetrahedra of the diphosphate groups, whereas the P6 tetrahedron sitting in the middle of the triphosphate group, exhibits two long bonds and two short ones as usually observed [21].

The caesium cation is surrounded by 10 oxygen atoms, with distances ranging from 3.08 to 3.57 Å (Table 4). But more importantly, it is worth pointing out that all the oxygen atoms are located on the same side of its coordination sphere (Fig. 5), this cations sitting close to the walls of the [001] tunnels (Fig. 2) and not in the middle. So the size of the tunnels and the great bond length allow a high value of the  $U_{eq}$  of the Cs cation but no particular anisotropy of its thermal parameters is observed in spite of its dissymmetric environment.

In conclusion, a caesium Mo(V) oligophosphate containing P<sub>3</sub>O<sub>10</sub> groups has been synthesized for the first time. Regarding the great number of caesium molybdenum phosphates, actually known, this feature is rather rare, since only one molybdenophosphate containing P<sub>3</sub>O<sub>10</sub> groups is actually known Cs<sub>2</sub>Mo<sub>5</sub>O<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>(P<sub>3</sub>O<sub>10</sub>) [16]. The latter is in fact very different, since it exhibits the mixed valence Mo(III)–Mo(IV) and does not show any MoP<sub>2</sub>O<sub>11</sub> unit. More importantly, the two compounds

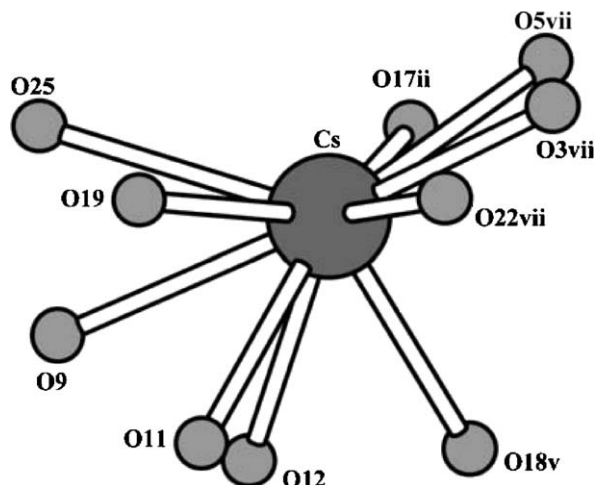


Fig. 5. The dissymmetric surrounding of the caesium ion.

differ also by the geometry of the P<sub>3</sub>O<sub>10</sub> group which is approximately linear in the present phase and exhibits a curved geometry in the previous one, due to the occupation of three coordination sites out of six by the P<sub>3</sub>O<sub>10</sub> group in the same MoO<sub>6</sub> octahedron. Further investigations are in progress in this system in order to understand the chemistry of the oligophosphates with  $n > 2$ .

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