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$Cs_3Mo_4P_4O_{22}$: A Mixed Valent Monophosphate Isotypic with $K_2Mo_2P_2O_{11}$

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A new mixed valent molybdenum phosphate, $Cs_3Mo_4P_4O_{22}$ has been isolated. The structure determination of this phase from a single crystal shows its isotypy with the pure Mo(V) phosphate $K_2Mo_2P_2O_{11}$. It crystalizes in the space group $P2_1/c$ with a = 10.134(1) Å, b = 10.104(1) Å, c = 9.952(1) Å, β = 100.44(1)°. The $[Mo_2P_2O_{11}]_\infty$ framework consists of "$Mo_2P_2O_{15}$" units built up from two octahedra and two tetrahedra, and delimits large intersecting tunnels where the Cs^+ ions are located. The important difference with $K_2Mo_2P_2O_{11}$ deals with the stoichiometry of the interpolated Cs^+ cations and their distribution in the structure: two sorts of sites are occupied by Cs^+ instead of three by K^+, owing to the larger size of cesium. Another characteristic of this phase concerns the mixed valency of molybdenum Mo(V)–Mo(VI), compared to the only presence of Mo(V) for $K_2Mo_2P_2O_{11}$. The electronic distribution in the two octahedral Mo sites is discussed.

INTRODUCTION

The studies performed these last ten years, have allowed a large series of Mo(V) phosphates to be isolated [1–11]. The common feature to all these compounds deals with the particular geometry of the MoO_6 octahedra, which are characterized by a very short Mo–O bond so that these phosphates can be considered as containing molybdenyl ions. The great ability of these MoO_6 octahedra to adapt to PO_4 tetrahedra allows various tunnel structures to be generated in the presence of alkaline cations such as potassium, rubidium or cesium. Such tunnel structures can be compared to those of bronzes and bronzoids involving pure octahedral framework. Nevertheless, contrary to the latter, one has never observed isotypic structures for potassium and cesium Mo(V) phosphates. Recently, we have isolated a Mo(V) potassium monophosphate $K_2Mo_2P_2O_{11}$ (12) where K–O distances greater than 2.84 Å and abnormally high thermal B factor of potassium suggested that the replacement of potassium by cesium should be possible. For this reason, we have investigated the system Cs–Mo–P–O, which exhibits already four Mo(V) phosphates with a tunnel or a layer structure, $CsMo_2P_3O_{13}$ (11), $CsMoP_2O_8$ (13), $Cs_4Mo_8P_{12}O_{52}$, and $Cs_2Mo_4P_6O_{26}$ (2). We report here on the crystal structure of the mixed valent monophosphate $Cs_3Mo_4P_4O_{22}$, whose structure is similar to the pure Mo(V) phosphate $K_2Mo_2P_2O_{11}$.

EXPERIMENTAL

The growth of single crystals of $Cs_3Mo_4P_4O_{22}$ was performed in two steps starting from a mixture of nominal composition $Cs_3Mo_4P_4O_{22}$. First, an adequate mixture of Cs_2CO_3, $(NH_4)_2HPO_4$, MoO_3 was heated to 673 K in order to eliminate CO_2, H_2O, and NH_3. In the second step, the appropriate amount of molybdenum was added and the finely ground product sealed in an evacuated silica ampoule was heated up to 1123 K for one day and cooled at a rate of 2 K per hour down to 923 K. The sample was finally quenched to room temperature. The resulting product was found to be a mixture of three sorts of crystals in which some brown sticks were isolated. The cationic ratio deduced from the structural refinement was confirmed by microprobe analysis.

Different attempts to synthesize this phosphate in the form of single phase samples were unsuccessful owing to the low stability.

A crystal, with dimensions 0.071 × 0.077 × 0.077 mm, was selected for the structure determination.

The cell parameters reported in Table 1 were determined and refined by diffractometric techniques at 294 K with a least square refinement based upon 25 reflections with $18 < \theta < 22°$. The data were collected using a CAD-4 Enraf-Nonius diffractometer with the data collection parameters reported in Table 1. The reflections were corrected for Lorentz and polarization effects. The atoms were located by the heavy atom method. The positional and anisotropic thermal parameters were refined by a full matrix least squares method leading to $R = 0.034$, $R_w = 0.037$ and to the parameters of Table 2. At this stage, the compound was supposed to exhibit a mixed valency Mo(VI)–Mo(V) according to the formula $Cs_3Mo_4P_4O_{22}$, in agreement with the microprobe analysis. However, the

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TABLE 1

Summary of Crystal Data Intensity, Measurements, and Structure Refinement Parameters for $Cs_3Mo_4P_4O_{22}$

1. Crystal data	
Space group	$P2_1/c$
Cell dimensions	a = 10.134(1) Å
	b = 10.104(1) Å β = 100.44(1)°
	c = 9.952(1) Å
Volume	1002(1) $Å^3$
Z	4
ρ_{calc} (g cm^{-3})	4.17
2. Intensity measurements	
$\lambda(MoK\alpha)$	0.71073 Å
Scan mode	ω–$4/3\theta$
Scan width (°)	1.05 + 0.35 tan θ
Slit aperture (mm)	1.10 + 1.0 tan θ
max θ (°)	45
Standard reflections	3 measured every 3000 sec
Reflections with $I > 3\sigma$	2760
μ (mm^{-1})	8.145
3. Structure solution and refinement	
Parameters refined	154
Agreement factors	$R = 0.034$ $R_w = 0.037$
Weighting scheme	$w = f(\sin\theta/\lambda)$
Δ/σ_{max}	<0.005

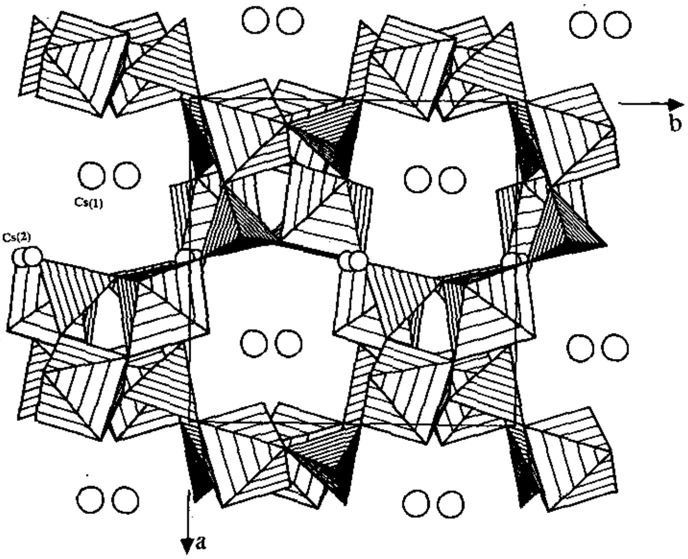

FIG. 1. Projection of the structure of $Cs_3Mo_4P_4O_{22}$ along **c**.

examination of the Mo–O distances, showed that each of the independent Mo atoms exhibited an abnormally short Mo–O distance, characteristic of molybdenyl ions. This suggested that both molybdenum atoms were pentavalent. Subsequent Fourier difference series were then performed in order to detect the eventual presence of hydrogen. No residue could be detected, so that the existence of a mixed valency Mo(V)–Mo(VI) was confirmed.

TABLE 2

Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B ($Å^2$)
Mo(1)	0.33546(5)	0.07135(5)	0.11965(5)	0.413(5)
Mo(2)	0.08735(5)	0.32081(5)	0.13275(5)	0.420(6)
P(1)	0.4057(1)	0.3552(2)	0.3223(2)	0.43(2)
P(2)	0.1184(1)	0.0626(2)	0.3373(2)	0.48(2)
Cs(1)	0.75585(4)	0.19686(5)	0.25889(5)	1.338(6)
Cs(2)	0.5012(2)	0.0161(1)	0.4993(2)	1.87(2)
O(1)	0.2749(5)	−0.0595(5)	0.0258(5)	1.14(7)
O(2)	0.4304(5)	0.1578(5)	−0.0203(5)	0.83(6)
O(3)	0.2480(4)	0.0197(5)	0.2891(5)	0.86(6)
O(4)	0.5023(5)	−0.0318(5)	0.2115(5)	0.95(7)
O(5)	0.1964(4)	0.1900(5)	0.0794(4)	0.71(6)
O(6)	0.4426(4)	0.2239(5)	0.2609(5)	0.85(7)
O(7)	−0.0615(5)	0.2738(5)	0.0408(5)	1.11(7)
O(8)	−0.0008(5)	0.4734(5)	0.2231(5)	0.89(7)
O(9)	0.1451(4)	0.4486(5)	−0.0054(5)	0.73(6)
O(10)	0.0780(5)	0.2062(4)	0.2983(5)	0.80(6)
O(11)	0.2626(4)	0.3961(5)	0.2645(5)	0.76(6)

Anisotropically refined atoms are given in the isotropic equivalent displacement parameter defined as: $B = \frac{4}{3}[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

This structure determination, confirms that the phosphate $Cs_3Mo_4P_4O_{22}$ is rigorously isostructural with the pentavalent molybdenum phosphate $K_2Mo_2P_2O_{11}$ (12). Thus the host lattice $[Mo_2P_2O_{11}]_\infty$ consists of octahedral units Mo_2O_{11} and single PO_4 tetrahedra sharing their corners. It can be described by the assemblage of $Mo_2P_2O_{15}$ units along **c** forming $[Mo_2P_2O_{13}]_\infty$ columns running along **c**. Laterally, in the (001) plane, the $[Mo_2P_2O_{13}]_\infty$ columns

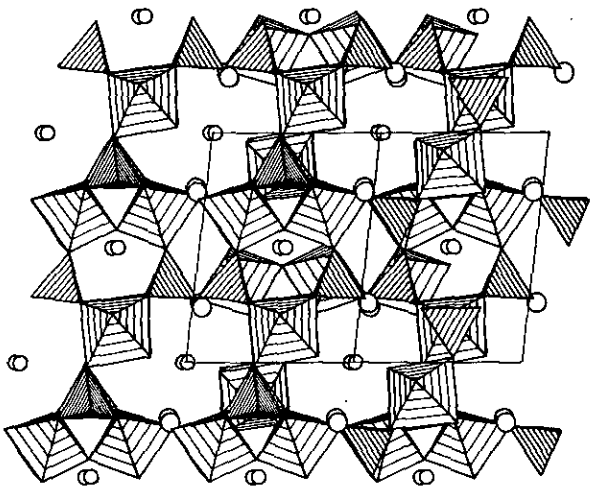

FIG. 2. Projection of the structure of $Cs_3Mo_4P_4O_{22}$ along $[\bar{1}10]$.

TABLE 3

Distances (Å) and Angles (°) in MoO$_6$ and PO$_4$ Polyhedra and Main Cs–O Distances

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.670(5)	2.789(7)	2.800(7)	2.694(7)	2.726(7)	3.89(1)
O(2)	97.4(2)	2.028(5)	4.11(1)	2.986(7)	2.751(6)	2.858(7)
O(3)	94.9(2)	167.5(2)	2.108(5)	2.868(7)	2.682(7)	2.903(7)
O(4)	92.1(2)	94.0(2)	87.1(2)	2.054(5)	3.86(1)	2.719(6)
O(5)	101.8(2)	90.6(2)	85.3(2)	164.7(2)	1.838(4)	2.823(7)
O(6)	170.7(2)	84.1(2)	83.9(2)	78.6(2)	87.3(2)	2.231(5)

Mo(2)	O(5)	O(7)	O(8)	O(9)	O(10)	O(11)
O(5)	1.860(4)	2.708(7)	3.91(1)	2.766(7)	2.675(6)	2.780(7)
O(7)	99.5(2)	1.685(5)	2.708(7)	2.840(7)	2.779(7)	3.82(1)
O(8)	168.4(2)	91.8(2)	2.067(5)	2.939(7)	2.876(6)	2.740(6)
O(9)	89.9(2)	98.6(2)	91.2(2)	2.047(5)	4.04(1)	2.785(7)
O(10)	86.8(2)	96.4(2)	89.1(2)	165.0(2)	2.030(5)	2.743(7)
O(11)	87.6(2)	172.7(2)	81.1(2)	83.2(2)	82.0(2)	2.146(5)

P(1)	O(2^{iv})	O(4^{viii})	O(6)	O(11)
O(2^{iv})	1.546(5)	2.486(7)	2.506(7)	2.541(7)
O(4^{viii})	106.8(3)	1.549(5)	2.534(6)	2.462(7)
O(6)	108.8(3)	110.5(3)	1.535(5)	2.526(6)
O(11)	112.0(3)	106.8(3)	111.6(3)	1.518(5)

P(2)	O(3)	O(8^{v})	O(9^{iv})	O(10)
O(3)	1.540(5)	2.529(7)	2.479(6)	2.566(6)
O(8^{v})	111.1(3)	1.527(5)	2.511(6)	2.476(7)
O(9^{iv})	107.0(3)	109.7(3)	1.544(5)	2.499(6)
O(10)	112.9(3)	107.7(3)	108.3(3)	1.538(5)

Cs(1)–O(1^{ii})	3.119(5)	Cs(2)–O(2^{iv})	3.370(7)
Cs(1)–O(1^{viii})	3.315(6)	Cs(2)–O(3^{iii})	3.01(1)
Cs(1)–O(3)	3.296(5)	Cs(2)–O(3)	3.00(1)
Cs(1)–O(4)	3.424(5)	Cs(2)–O(4)	2.91(1)
Cs(1)–O(6)	3.190(5)	Cs(2)–O(4^{iii})	2.89(1)
Cs(1)–O(7^{i})	3.193(6)	Cs(2)–O(6^{iii})	3.378(8)
Cs(1)–O(7^{ix})	3.083(5)	Cs(2)–O(6)	3.143(8)
Cs(1)–O(8^{vii})	3.337(5)		
Cs(1)–O(10^{i})	3.218(5)		
Cs(1)–O(11^{vii})	3.051(5)		

Symmetry codes

i:	$1 + x$;	y;	z
ii:	$1 - x$;	$-y$;	$-z$
iii:	$1 - x$;	$-y$;	$1 - z$
iv:	x;	$\frac{1}{2} - y$;	$\frac{1}{2} + z$
v:	$-x$;	$-\frac{1}{2} + y$;	$\frac{1}{2} - z$
vi:	x;	$\frac{1}{2} - y$;	$-\frac{1}{2} + z$
vii:	$1 - x$;	$-\frac{1}{2} + y$;	$\frac{1}{2} - z$
viii:	$1 - x$;	$\frac{1}{2} + y$;	$\frac{1}{2} - z$
ix:	$1 + x$;	$\frac{1}{2} - y$;	$\frac{1}{2} + z$

share the corners of their polyhedra, leading to the $[\mathrm{Mo_2P_2O_{11}}]_\infty$ tridimensional framework. The view of the structure along [001] (Fig. 1) and [110] or [1$\bar{1}$0] (Fig. 2) directions respectively shows that this framework delimits large intersecting tunnels running along these directions.

The interatomic distances (Table 3) show that the geometry of the polyhedra is practically identical to that observed in K$_2$Mo$_2$P$_2$O$_{11}$. The PO$_4$ tetrahedra are indeed almost regular; whereas the "O$_6$" octahedra are also almost regular, but with the molybdenum atom significantly off-centered toward the unshared oxygen atom forming an abnormally short Mo–O bond characteristic of the molybdenyl ion, systematically observed for Mo(V).

Nevertheless, the distribution of the Mo–O distances in both octahedra Mo(1) and Mo(2) is very different from that generally observed for pure Mo(V) phosphates. One indeed observes intermediate Mo–O distances of 1.838–1.860 Å which are never observed in pure Mo(V) octahedra except K$_2$Mo$_2^{\mathrm{V}}$P$_2$O$_{11}$ but that exist in Mo(VI) octahedra. This explains the possibility to introduce Mo(VI) species in the $K_2Mo_2^VP_2O_{11}$ structure. It suggests that one electron is delocalised over the two Mo(1) and Mo(2) corner-sharing octahedra of the $Mo_2P_2O_{15}$ units, forming $Mo^V_{(1)}$–$Mo^{VI}_{(2)}$ and $Mo^{VI}_{(1)}$–$Mo^V_{(2)}$ couples. The bond valence calculations using the Brown and Altermatt tables (14) support this view point since they lead to a valency of 5.5 for each of these sites.

These results show that the presence of cesium does not influence the geometry of the polyhedra of the $[Mo_2P_2O_{11}]_\infty$ framework.

The important difference with the potassium phosphate $K_2Mo_2P_2O_{11}$ deals with the stoichiometry of the interpolated Cs^+ cations and with their distribution in the tunnels. One indeed observes two kinds of sites, labelled Cs(1) and Cs(2) corresponding to the K(2) and K(3) sites respectively, whereas those corresponding to the K(1) sites are empty.

The Cs(1) atoms are located in the tunnels parallel to **c** and close to the axis of these tunnels, they also sit like K(2) in the tunnels parallel to ⟨110⟩ close to the wall. These cations exhibit a coordination similar to that observed for K(2), and are bond to ten oxygen atoms with Cs–O distances ranging from 3.051 to 3.424 Å (Table 3) to be compared to K–O distances ranging from 2.822 to 3.109 Å. Note that the B factor of Cs(1) (1.33 $Å^2$) is significantly smaller than that of K(2) (4.13 $Å^2$); this is in agreement with the minimum interatomic distances of 3.05 Å for Cs–O which are rather close to the sum of the ionic radii, whereas the minimum value of 2.82 Å observed for K(2) is significantly larger than that usually observed for potassium (2.68 Å).

The Cs(2) atoms, like the K(3) atoms, exhibit a sevenfold coordination and are located near the axis of the ⟨110⟩ tunnels and sit also in the [001] tunnels close to the wall. As the K(3) sites, the Cs(2) sites are splitted over two positions with respect to the symmetry center; the latters are half occupied by cesium owing to their too short distance. Again, the Cs–O distances (Table 3) ranging from 2.89 to 3.37 Å, suggest that Cs(2) is more tightly bonded to the surrounding oxygen atoms than K(3) which in spite of its smaller size exhibits rather similar distances ranging from 2.744 to 3.213 Å. The smaller B factor of Cs(2) of 1.87 $Å^2$, compared to K(3) (2.42 $Å^2$) is in agreement with this view point.

The fact that the K(1) sites for $Cs_3Mo_4P_4O_{22}$ are empty is easily explained by the too large size of cesium. Indeed the very similar assemblage of MoO_6 octahedra and PO_4 tetrahedra in both phosphates, $K_2Mo_2P_2O_{11}$ and $Cs_3Mo_4P_4O_{22}$, leads for K(1) sites to distances ranging from 2.686 to 2.849 Å which are too small for cesium.

CONCLUDING REMARKS

A large possibility of nonstoichiometry in the $K_2Mo_2P_2O_{11}$-type structure has been demonstrated in agreement with the existence of large intersecting tunnels, which may be occupied differently according to the size of the interpolated cations. The structure of the phosphate $Cs_3Mo_4P_4O_{22}$ shows, for the first time the possibility of a mixed valency Mo(V)–Mo(VI) "delocalised" over two corner-sharing MoO_6 octahedra.

REFERENCES

1. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **48,** 147 (1983).
2. H. Lii and R. C. Haushalter, *J. Solid State Chem.* **69,** 320 (1987).
3. D. Riou and M. Goreaud, *J. Solid State Chem.* **79,** 99 (1989).
4. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Z. Kristallogr.* **188,** 77 (1989).
5. J. J. Chen, K. H. Lii, and S. Wang, *J. Solid State Chem.* **79,** 204 (1988).
6. K. H. Lii, D. C. Johnston, D. P. Goshorn, and R. C. Haushalter, *J. Solid State Chem.* **71,** 131 (1987).
7. C. Gueho, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *Z. Anorg. Allg. Chem.* **615,** 104 (1992).
8. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **89,** 10 (1990).
9. G. Costentin, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **89,** 31 (1990).
10. G. Costentin, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **89,** 83 (1990).
11. J. J. Chen, K. H. Lii, and S. L. Wang, *J. Solid State Chem.* **76,** 207 (1988).
12. C. Gueho, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **104,** 202 (1993).
13. A. Guesdon, M. M. Borel, A. Leclaire, A. Grandin, and B. Raveau, *J. Solid State Chem.* **108,** 46 (1994).
14. I. D. Brown, and D. Altermatt, *Acta. Crystallogr. Sect. B* **41,** 244 (1985).