

Two mixed valent molybdenophosphates with a tunnel structure closely related to $K_{0.17}MoP_2O_7$: $Pb_2(PbO)_2Mo_8(P_2O_7)_8$ and $PbK_2Mo_8(P_2O_7)_8$

André Leclaire*, Bernard Raveau

Laboratoire CRISMAT-ENSICAEN, UMR CNRS 6508, 6 boulevard du maréchal Juin, 14050 CAEN cedex, France

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Abstract

Two new mixed valent Mo(III)/Mo(IV) diphosphates containing lead $Pb_2(PbO)_2Mo_8(P_2O_7)_8$ and $PbK_2Mo_8(P_2O_7)_8$ have been synthesized. The $[Mo_8P_{16}O_{56}]_{\infty}$ frameworks of these phosphates are closely related to that of $K_{0.17}MoP_2O_7$: the MoO_6 octahedra and P_2O_7 groups form two sorts of large eight-sided tunnels. They are occupied in an ordered way by PbO chains and Pb^{2+} cations in $Pb_2(PbO)_2Mo_8(P_2O_7)_8$ and by K^+ and Pb^{2+} cations in $PbK_2Mo_8(P_2O_7)_8$. It results in different symmetries of these two structures, which are tetragonal and monoclinic, respectively, showing the great flexibility of these mixed frameworks, susceptible to accommodate various species with different sizes.

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1. Introduction

A huge family of molybdenophosphates has been synthesized showing that molybdenum can exist at various oxidation states. Numerous hexavalent, pentavalent and tetravalent molybdenum phosphates have indeed been isolated (see for a review Refs. [1–3]), and several Mo(III) phosphates such as the diphosphates $AMoP_2O_7$ with $A = Li, Na, K, Rb, Cs$ [4–8] and $BaMo_2(P_2O_7)_2$ [9], the phosphates $Pb_2Mo(P_2O_7)(PO_4)$ [10] and $Mo(PO_3)_3$ [11] are actually known. In contrast, the number of mixed valent molybdenum phosphates that have been isolated to date is rather limited. For instance six mixed valent Mo(V)/Mo(IV) phosphates are actually known: the phosphates $AMo_2P_2O_{10} \cdot xH_2O$ for $A = NH_4, Rb, Cs$ with the leucophosphate structure [12–14] and $Cs_6Mo_7O_9(PO_4)_7 \cdot H_2O$ [15] which all exhibit an ordering of the Mo^{5+} and Mo^{4+} species in the different sites. Nevertheless, considering the mixed valency Mo(IV)/Mo(III), 10 phosphates have been isolated to our knowledge to date, with an average valency

of molybdenum ranging from 3.4 to 3.8. The latter differ from the Mo(IV)/Mo(V) phosphates by their ability to exhibit two sorts of behaviors, i.e. either a perfect ordering of the Mo^{3+} and Mo^{4+} species, or a total or partial disordering. In the phosphates $NaMo_2(P_2O_7)_2$ [16], $Cs_4Mo_{10}P_{18}O_{66}$ [17] and $Cs_4Mo_6P_{10}O_{38}$ [18] the Mo^{4+} and Mo^{3+} species are distributed in an ordered way in different octahedral sites. In contrast, the monophosphates $AMo_2P_3O_{12}$ ($A = Ca, Sr, Ba$) with the Nasicon structure [19] and the diphosphate $K_{0.17}MoP_2O_7$ [20] exhibit a random distribution of the Mo^{4+} and Mo^{3+} species in the different octahedral sites, whereas an electronic delocalization between several edge-sharing octahedra forming cube-like clusters is observed in the phosphates $A_3Mo_4P_3O_{16}$ with $A = NH_4, Cs$ [21,22] and $Cs_3Mo_5P_6O_{25}$ [23]. Finally, two phosphates $Na_xMoP_2O_7$ [24] and $Cs_3Mo_6P_{10}O_{38}$ [25] were found to exhibit a partial ordering of the Mo^{4+} and Mo^{3+} species.

The great ability of coexistence of Mo(III) and Mo(IV) in the same phosphate matrix suggests that many mixed-valent molybdenophosphates remain to be discovered in this area. Curiously, no mixed-valent Mo(III)/Mo(IV) phosphate containing lead has been obtained to date, in

*Corresponding author. Fax: +33 2 31 95 16 00.

E-mail address: andre.leclaire@ensicaen.fr (A. Leclaire).

spite of the existence of several Mo(III) phosphates. We have thus revisited the systems Pb–Mo–P–O and Pb–K–Mo–P–O in reducing conditions. We report herein on two novel mixed-valent Mo(III)/Mo(IV) diphosphates $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$, which exhibit tunnel structures very closely related to that of $\text{K}_{0.17}\text{MoP}_2\text{O}_7$, and are characterized by an ordered distribution of the Pb^{2+} , K^+ cations and “PbO” chains in the tunnels.

2. Crystal growth

Single crystals of $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ were grown from a batch of nominal composition $\text{Pb}_2\text{Cl}_2\text{Mo}_2\text{P}_3\text{O}_{12}$. First PbCO_3 , $\text{H}(\text{NH}_4)_2\text{PO}_4$ and MoO_3 were mixed in an agate mortar with the molar ratio (1:3:1.167) and heated at 673 K in a platinum crucible to decompose the ammonium phosphate and the carbonate. In a second step, the resulting mixture, added to metallic molybdenum powder (0.833) and to PbCl_2 (1.00), was crushed in an agate mortar and sealed in an evacuated quartz ampoule and then heated for 1 day at 1273 K, cooled at 6 K per hour to 673 K and finally quenched to room temperature.

From the resulting dark product, black crystals were extracted. Their EDS analysis (Pb/Mo/P = 14.4/29.2/56.4) allowed the cationic composition “ PbMo_2P_4 ” to be determined.

Single crystals of $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ were obtained in a batch of nominal composition $\text{PbKMo}_4\text{P}_8\text{O}_{28}$. The experimental conditions were the same as described above but with the molar ratio for the precursors K_2CO_3 , PbCO_3 , $\text{H}(\text{NH}_4)_2\text{PO}_4$ and MoO_3 (1:1:16:4.333) in the first step and adding 3.667 mole of metallic molybdenum in the second step.

From the resulting dark product, black crystals were extracted. The EDS analysis (Pb/K/Mo/P = 3.8/7.8/31.6/56.8) of those crystals is in agreement with the ratio 1/2/8/16 for the Pb, K, Mo and P elements.

3. Crystal structure determination

Black needle shaped crystals with dimensions $0.026 \times 0.026 \times 0.510$ mm for $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and $0.009 \times 0.015 \times 0.058$ mm for $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ were selected. The data for both crystals were recorded at room temperature on a NONIUS KAPPA CCD diffractometer using the $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) isolated with a graphite monochromator. The cell parameters were refined from the complete data sets. Absorption corrections were computed by the Gaussian method taking into consideration the shape and the size of the crystals.

$\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ crystallizes in the tetragonal symmetry with the following lattice parameters $a = b = 21.489(1)$ Å, and $c = 4.9507(8)$ Å. The systematic absences $h+k+l = 2n+1$, in the whole space, $h = 2n+1$ and $k = 2n+1$ in $hk0$ and $l \neq 4n$ in $00l$, are characteristic of the $I4_1/a$ (88) space group.

$\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ crystallizes in the monoclinic symmetry with the lattice parameters $a = 30.113(1)$ Å, $b = 4.9315(8)$, $c = 21.257(1)$ and $\beta = 134.30(1)^\circ$. The systematic absences $h+k = 2n+1$ in the whole space, $l = 2n+1$ and $h = 2n+1$ in $h0l$ and $k = 2n+1$ in $0k0$ are consistent with the Cc (9) or $C2/c$ (15) space groups. The Patterson function map of this crystal shows the U0W and U1/2W Harker peaks characteristic of the centro-symmetrical $C2/c$ space group.

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

Both structures were solved by the heavy atom method. The full matrix least-squares refinements of the atomic parameters were performed on the F values weighted by $1/\sigma(F)^2$ using the JANA2000 package [26]. They lead to $R = 0.0363$ and $R_w = 0.0349$ for $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and to $R = 0.0458$ and 0.0439 for $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and to the atomic coordinates of Table 2. Further details of the crystals structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; E-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 418107 for $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and CSD 418108 for $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$.

4. Description of the host lattice $[\text{Mo}_8\text{P}_{16}\text{O}_{56}]_\infty$

The projections of the structure of $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ (Fig. 1a), of $\text{K}_{0.17}\text{MoP}_2\text{O}_7$ (Fig. 1b) along c and

Table 1
Summary of crystal data, intensity measurement, and structure refinement for $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$

| | | |
|-----------------------------------|--|--|
| Chemical formula | $\text{Pb}_2\text{Mo}_8\text{P}_{16}\text{O}_{58}$ | $\text{PbK}_2\text{Mo}_8\text{P}_{16}\text{O}_{56}$ |
| Structural formula | $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ | $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ |
| Molecular weight | 3019.81 | 2444.43 |
| Crystal system | Tetragonal | Monoclinic |
| Space group | $I4_1/a$ (88) | $C2/c$ (15) |
| Cell dimension | $a = 21.489(1)$ Å $b = 21.489(1)$ Å $c = 4.9507(8)$ Å | $a = 30.112(1)$ Å $b = 4.9315(7)$ Å $c = 21.257(1)$ Å $\beta = 134.30(1)^\circ$ |
| Cell volume | 2286.0(6) | 2259.3(5) |
| Z | 2 | 2 |
| Density (g cm^{-3}) | 4.386 | 3.592 |
| μ (mm^{-1}) | 17.501 | 6.761 |
| Transmission min. | 0.1127 | 0.8249 |
| Transmission max. | 0.6635 | 0.9483 |
| No. of measured reflections | 11,520 | 9459 |
| Independent data | 3294 | 3208 |
| Independent data $I > 3\sigma(I)$ | 1984 | 1639 |
| Data collection temperature (K) | 294 | 294 |
| Number of variables | 132 ^a | 191 |
| R | 0.0372 | 0.0458 |
| R _w | 0.0376 | 0.0439 |
| σ/δ | 0.0005 | 0.0004 |

^aAnharmonic components of the thermal displacement of the lead atoms were refined.

Table 2
Atomic coordinates for $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$

| Atom | X | Y | Z | U_{eq} | Site | Occup. |
|------|------------|------------|------------|-----------------|------|--------|
| Pb1 | 0 | 0.25 | 0.0977(3) | 0.0536(4) | 8e | 0.5 |
| Pb2 | 0.2406(1) | 0.9919(2) | 0.302(2) | 0.056(2) | 16f | 0.25 |
| Mo | 0.38617(1) | 0.39315(1) | 0.18458(5) | 0.00796(7) | 16f | 1 |
| P1 | 0.35458(4) | 0.29256(4) | 0.6558(2) | 0.0095(2) | 16f | 1 |
| P2 | 0.24817(4) | 0.35578(4) | 0.4332(2) | 0.0104(2) | 16f | 1 |
| O1 | 0.3526(1) | 0.3325(1) | -0.0950(5) | 0.0166(7) | 16f | 1 |
| O2 | 0.4181(1) | 0.4534(1) | 0.4754(5) | 0.0211(8) | 16f | 1 |
| O3 | 0.4756(1) | 0.3825(1) | 0.0371(5) | 0.0205(8) | 16f | 1 |
| O4 | 0.3658(1) | 0.4671(1) | -0.0696(5) | 0.0205(8) | 16f | 1 |
| O5 | 0.4011(1) | 0.3173(1) | 0.4432(5) | 0.0176(7) | 16f | 1 |
| O6 | 0.2946(1) | 0.4043(1) | 0.3279(5) | 0.0151(7) | 16f | 1 |
| O7 | 0.2867(1) | 0.2962(1) | 0.5228(5) | 0.0147(7) | 16f | 1 |
| O8 | 0 | 0.25 | 0.625 | 0.044(1) | 4b | 1 |
| Mo1 | 0.35666(3) | 0.0606(1) | 0.22110(5) | 0.0075(5) | 8f | 1 |
| Mo2 | 0.11257(3) | 0.1979(1) | 0.50496(5) | 0.0077(5) | 8f | 1 |
| Pb | 0.75931(6) | 0.0421(3) | 0.27058(9) | 0.0245(9) | 8f | 0.25 |
| K | 0 | 0.515(1) | 0.75 | 0.079(3) | 4e | 1 |
| P1 | 0.25149(9) | 0.5616(4) | 0.1096(1) | 0.011(1) | 8f | 1 |
| P2 | 0.14835(9) | 0.3245(4) | -0.0588(1) | 0.010(1) | 8f | 1 |
| P3 | 0.04254(9) | 0.9132(4) | 0.6501(1) | 0.009(1) | 8f | 1 |
| P4 | 0.10257(9) | 0.6875(4) | 0.6011(1) | 0.008(1) | 8f | 1 |
| O1 | 0.4222(3) | 0.324(1) | 0.3177(4) | 0.017(4) | 8f | 1 |
| O2 | 0.2923(3) | -0.219(1) | 0.1268(4) | 0.018(4) | 8f | 1 |
| O3 | 0.2855(3) | 0.329(1) | 0.1728(3) | 0.019(4) | 8f | 1 |
| O4 | 0.4283(3) | -0.206(1) | 0.2762(3) | 0.017(4) | 8f | 1 |
| O5 | 0.3655(3) | 0.219(1) | 0.1399(4) | 0.015(3) | 8f | 1 |
| O6 | 0.3477(3) | -0.097(1) | 0.3034(4) | 0.016(4) | 8f | 1 |
| O7 | 0.1508(2) | -0.061(1) | 0.4798(4) | 0.016(4) | 8f | 1 |
| O8 | 0.0790(3) | 0.470(1) | 0.5353(3) | 0.017(4) | 8f | 1 |
| O9 | 0.1297(3) | -0.071(1) | 0.5921(4) | 0.017(4) | 8f | 1 |
| O10 | 0.1015(2) | 0.474(1) | 0.4236(4) | 0.014(4) | 8f | 1 |
| O11 | 0.2025(2) | 0.343(1) | 0.6085(4) | 0.012(2) | 8f | 1 |
| O12 | 0.0243(2) | 0.046(1) | 0.4002(4) | 0.015(4) | 8f | 1 |
| O13 | 0.2153(2) | 0.457(1) | 0.0130(4) | 0.013(4) | 8f | 1 |
| O14 | 0.0444(2) | 0.790(1) | 0.5828(3) | 0.014(4) | 8f | 1 |

of $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ along b (Fig. 1c) show that the three compounds exhibit a very similar host lattice $[\text{Mo}_8\text{P}_{16}\text{O}_{56}]_{\infty}$ built up of corner sharing MoO_6 octahedra and P_2O_7 diphosphate groups. The isotypism between $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and $\text{K}_{0.17}\text{MoP}_2\text{O}_7$ can be directly deduced from their identical space groups $I4_1/a$ and very similar parameters. In contrast, the space group ($C2/c$) and cell parameters of $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ are very different, but the centered cell built from the shorter diagonal of the $C2/c$ cell and from the c parameter leads to a very similar cell whose symmetry is $I2/a$ and parameters $a \approx b(\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8)$, $c \approx a(\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8)$ and $\beta \approx 90.60^\circ$. Thus the structure of $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ derives from the tetragonal structure of $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ by a simple monoclinic distortion.

So the frameworks of the three compounds are very similar, the polyhedra form similar large eight-sided tunnels and small rectangular tunnels running along the direction perpendicular to the above projections (i.e. along c_T for the tetragonal phases or along b_M for the monoclinic one). As in many molybdenum diphosphates, one P_2O_7

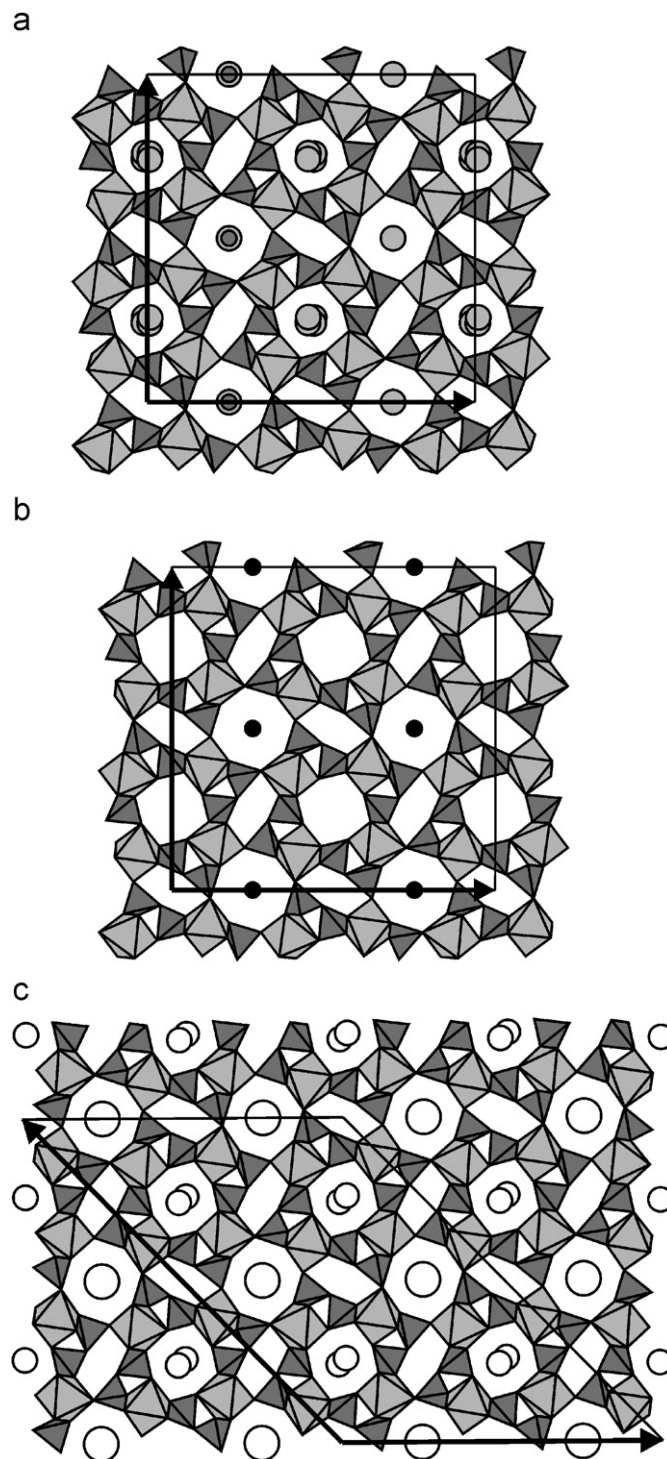


Fig. 1. Projection of the structure of: (a) $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ along $c_{\text{Tetragonal}}$; (b) $\text{K}_{0.17}\text{MoP}_2\text{O}_7$ along $c_{\text{Tetragonal}}$; and (c) $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ along $b_{\text{Monoclinic}}$.

group shares two corners with the same octahedron leading to the well-known $\text{MoP}_2\text{O}_{11}$ unit (Fig. 2a). The projections of these structure along a_T for $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ and $\text{K}_{0.17}\text{MoP}_2\text{O}_7$ (Fig. 3a and b) or along $[101]_M$ for $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ (Fig. 3c) show that the framework $[\text{Mo}_8\text{P}_{16}\text{O}_{56}]_{\infty}$ forms also similar elongated tunnels

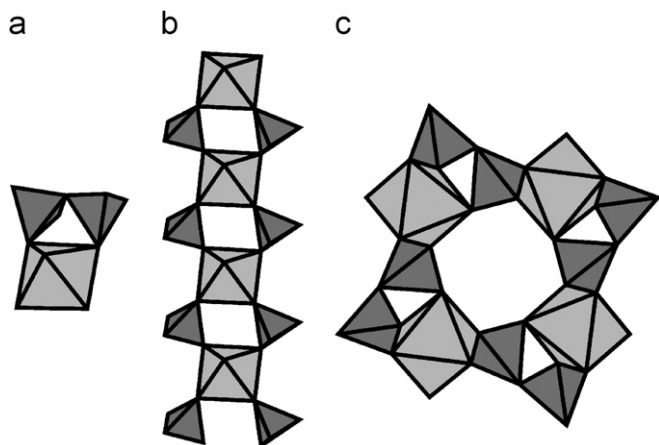


Fig. 2. (a) The MoP₂O₁₁ unit; (b) the [MoP₂O₁₀]_∞ ladder like column; and (c) the [Mo₄P₈O₃₂]_∞ tube made of four [MoP₂O₁₀]_∞ ladders.

intersecting the largest eight-sided tunnels. More importantly, one observes that the PO₄ tetrahedra and the MoO₆ octahedra share their apices forming [MoP₂O₁₀]_∞ ladder-like columns running along *c*_T (or *b*_M) where the MoO₆ octahedra play the role of steps (Fig. 2b). It is the assemblage of four columns that forms [Mo₄P₈O₃₂]_∞ eight-sided tubes parallel to *c*_T (or *b*_M) (Fig. 2c). Note that such tubes are also observed in the pentavalent Mo(V) phosphates *A*(MoO)₁₀(P₂O₇)₈ with *A* = Ba, Sr, Ca, Cd, Pb and *A*(MoO)₅(P₂O₇)₄ with *A* = Ag, Li, Na, K [27]. However for the latter, these tubes are isolated, i.e. are not directly connected to each other (Fig. 4), but linked through MoO₅ pyramids, in contrast to the present Mo(III)/Mo(IV) phosphates whose tubes are directly connected to each other, each phosphate group of one tube sharing one apex with one octahedron of the next tube (Fig. 1). This difference originates from the fact that in Mo(V) phosphates, the MoO₆ octahedra which border the tubes have one free corner, so that the so formed molybdenyl ion hinders a direct connection and forms additional tunnels.

In both compounds, the geometry of the PO₄ tetrahedra is characteristic of the diphosphate units P₂O₇ with one long P–O bond (1.589(2)–1.600(2) Å), whereas the other P–O bonds are significantly shorter (1.479(8)–1.546(2) Å) (Table 3).

The geometry of the MoO₆ octahedra is correlated to the valence of the molybdenum atom.

The unique Mo site in the Pb₂(PbO)₂Mo₈(P₂O₇)₈ phosphate corresponding to an average valence of +3.5 for molybdenum (bond valence sum = 3.20 [28]) shows that the Mo³⁺ and the Mo⁴⁺ species are distributed at random. Similarly PbK₂Mo₈(P₂O₇)₈ exhibits also an average valence of +3.5 for molybdenum, nevertheless in that case two sites are available for molybdenum with average Mo–O distances of 2.067 Å for Mo1 and 2.049 Å for Mo2 (Table 3) suggesting that the distribution of Mo³⁺ and Mo⁴⁺ species is not far being statistic, with a slightly larger content of Mo⁴⁺ on the Mo2 sites (BVS = 3.45)

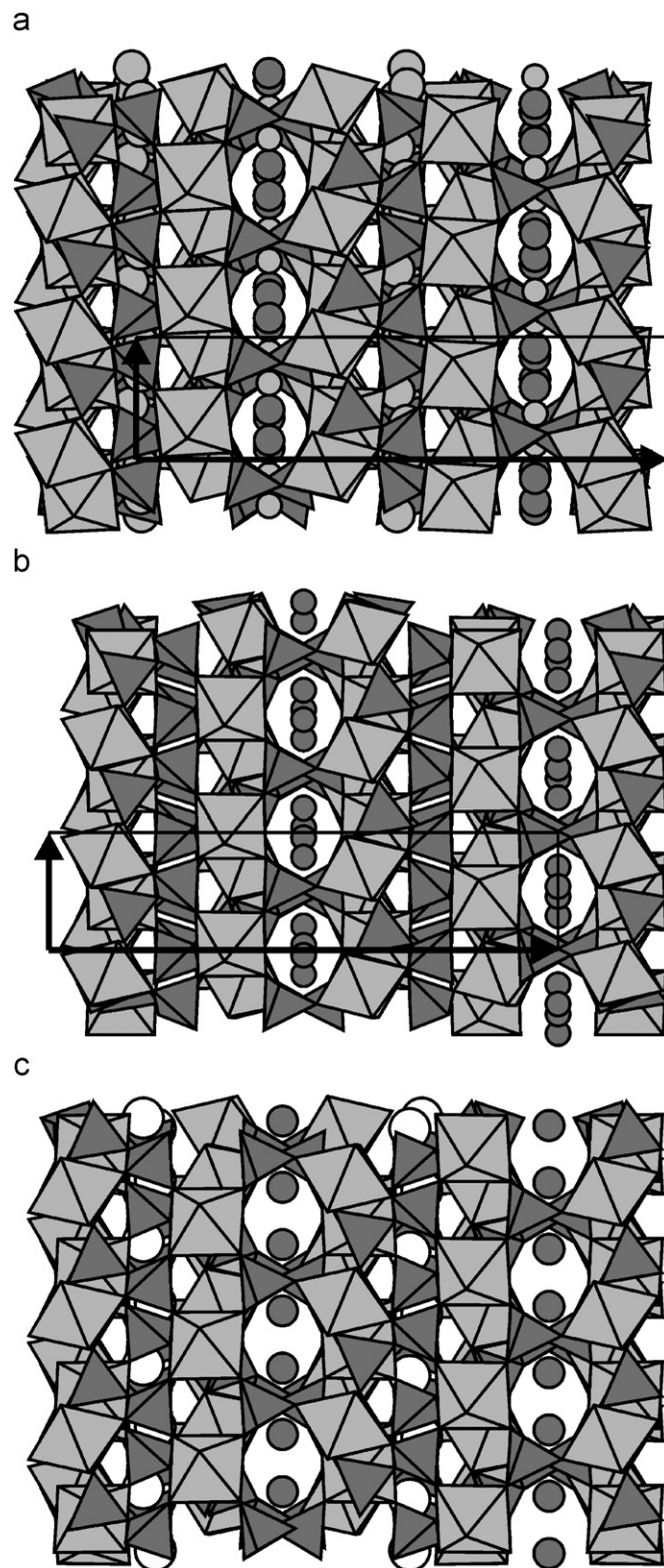


Fig. 3. Projections of the structure of: (a) Pb₂(PbO)₂Mo₈(P₂O₇)₈ along *a*_{Tetragonal}; (b) K_{0.17}MoP₂O₇ along *a*_{Tetragonal}; and (c) PbK₂Mo₈(P₂O₇)₈ along (101)_{Monoclinic}.

than on the Mo1 sites (BVS = 3.25). Note that the average Mo–O distance in Pb₂(PbO)₂Mo₈(P₂O₇)₈ is slightly larger (2.074 Å). Bond valence calculations cannot be here

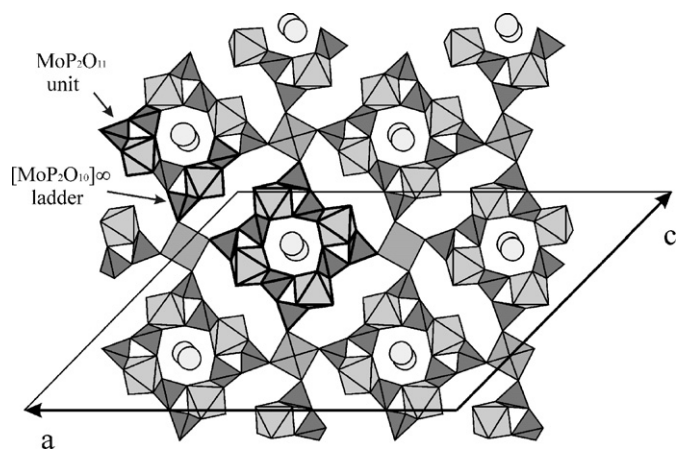


Fig. 4. $[\text{Mo}_4\text{P}_8\text{O}_{32}]_\infty$ tube in the $A^{2+}(\text{MoO})_{10}(\text{P}_2\text{O}_7)_8$ or $A^+(\text{MoO})_5(\text{P}_2\text{O}_7)_4$ structures.

Table 3
Mo–O and P–O distances (Å) in both compounds

| $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ | | $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ | | | |
|--|----------|---|----------|-----------------------|----------|
| Mo–O1 | 2.035(2) | Mo1–O1 | 2.034(5) | Mo2–O7 | 2.025(8) |
| Mo–O2 | 2.058(2) | Mo1–O2 | 2.061(5) | Mo2–O8 | 2.037(9) |
| Mo–O3 | 2.067(2) | Mo1–O3 | 2.080(7) | Mo2–O9 | 2.030(8) |
| Mo–O4 | 2.073(2) | Mo1–O4 | 2.055(7) | Mo2–O10 | 2.037(8) |
| Mo–O5 | 2.097(2) | Mo1–O5 | 2.074(9) | Mo2–O11 | 2.089(4) |
| Mo–O6 | 2.108(2) | Mo1–O6 | 2.097(9) | Mo2–O12 | 2.078(4) |
| P1–O1 ⁱ | 1.499(3) | P1–O2 ^{iv} | 1.479(8) | P3–O1 ^{viii} | 1.503(6) |
| P1–O3 ⁱⁱ | 1.496(2) | P1–O3 | 1.499(6) | P3–O4 ^{ix} | 1.532(7) |
| P1–O5 | 1.546(2) | P1–O11 ^v | 1.533(9) | P3–O12 ^x | 1.493(6) |
| P1–O7 | 1.600(2) | P1–O13 | 1.595(7) | P3–O14 | 1.591(8) |
| P2–O2 ⁱⁱⁱ | 1.492(2) | P2–O5 ^{vi} | 1.480(9) | P4–O6 ^x | 1.522(6) |
| P2–O4 ⁱⁱⁱ | 1.521(3) | P2–O7 ^{vii} | 1.510(7) | P4–O8 | 1.491(7) |
| P2–O6 | 1.538(2) | P2–O10 ^v | 1.542(5) | P4–O9 ^{iv} | 1.529(8) |
| P2–O7 | 1.591(2) | P2–O13 | 1.589(5) | P4–O14 | 1.589(7) |

considered as giving significant values of the Mo^{3+} and Mo^{4+} distribution, due to the fact that all Pb^{2+} sites are partially occupied.

5. Distribution and coordination of the interpolated species

Due to their small size, the rectangular tunnels are empty. One important feature of these structures deals with the existence of two sorts of eight-sided tunnels which differ mainly by their size. It results in a selective occupation of these tunnels by the different species. $\text{K}_{0.17}\text{MoP}_2\text{O}_7$ possesses the smallest octagonal tunnels characterized by distances between two opposite oxygen atoms ranging from 4.4 to 5.1 Å, consequently those tunnels are empty, and the potassium cations sit in the larger tunnels with O–O distances ranging from 5.3 to 5.6 Å, the occupation level being of 68%. In $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ the smaller tunnels for which O–O distances are comprised between 4.5 and 5.2 Å are occupied by Pb^{2+} cations, whereas the largest tunnels of all the series, with

O–O distances ranging from 5.1 to 5.7 Å are occupied by Pb–O chains. For $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$, the smaller tunnels (O–O distances ranging from 4.6 to 5.0 Å) are occupied by Pb^{2+} cations, whereas the largest ones with O–O distances ranging from 5.3 to 5.6 Å, are occupied by K^+ ions. The positions of the Pb^{2+} and K^+ cations, as well as those of the oxygen atoms vary also from one compound to the other. In $\text{Pb}_2(\text{PbO})_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$ the lead cations Pb2 belonging to the small octagonal tunnels sit on the axis of the latter and are surrounded by seven oxygen atoms. The Pb1 cations belonging to the Pb–O chains running along c_T in the largest tunnels are distributed over split sites (Table 2) with an occupation factor of $\frac{1}{2}$, so that they form linear Pb–O chains running along c , characterized by a longer Pb–O bond (2.608 Å) alternating with a shorter one (2.343 Å); as a consequence the environment of lead in those tunnels can be described as distorted PbO_6 octahedra with distances ranging from 2.343 to 2.613 Å, forming chains running along c (Fig. 5) The chains may have at random the shorter Pb–O bond up side or down side with respect to the oxygen atom in the tunnel. And as the oxygen atoms bridging two lead atoms are always staying at the same position, it results in a splitting of the lead atoms. The K^+ cations of $\text{K}_{0.17}\text{MoP}_2\text{O}_7$ sit on the axis of the largest octagonal tunnels running along c_T (Fig. 1b) but at the intersection with the elongated tunnels running along a_T (Fig. 3b), so that they are surrounded by six oxygen atoms with distances ranging from 2.66 to 3.10 Å. In $\text{PbK}_2\text{Mo}_8(\text{P}_2\text{O}_7)_8$, the K^+ cations are also sitting on the axis of the larger octagonal tunnels, whereas the Pb^{2+} cations sitting in the smaller octagonal tunnels are also distributed over splitted sites with an occupancy factor of $\frac{1}{2}$, so that the K^+ ions are surrounded by six oxygen atoms

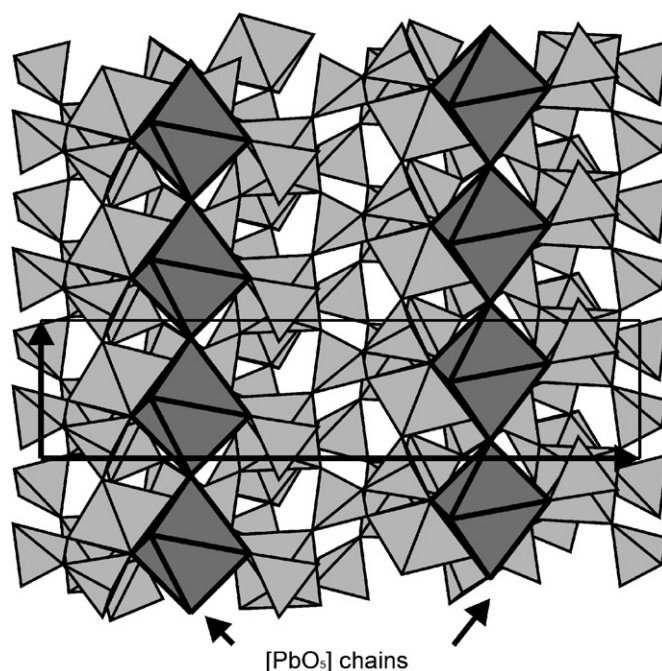


Fig. 5. The $[\text{PbO}_3]_\infty$ chains in the tunnels.

Table 4
Distances (<3.20 Å) between the ions sitting in the tunnels and the oxygen atoms

| Pb ₂ (PbO) ₂ Mo ₈ (P ₂ O ₇) ₈ | | PbK ₂ Mo ₈ (P ₂ O ₇) ₈ | | K _{0.17} Mo(P ₂ O ₇) [20] | |
|--|-----------|--|-----------|--|---------|
| Pb1–O8 ^{xxiv} | 2.343(2) | K–O10 ^x | 2.685(5) | K–O7 ^{xxiv} | 2.66(1) |
| Pb1–O8 | 2.608(2) | K–O10 ^v | 2.685(5) | K–O7 ^{xxv} | 2.66(1) |
| Pb1–O5 ^{xi} | 2.579(2) | K–O4 ^{ix} | 2.746(11) | K–O7 ^{xxvi} | 2.80(2) |
| Pb1–O5 ^{xii} | 2.579(2) | K–O4 ^{xix} | 2.746(11) | K–O7 ^{xxvii} | 2.80(2) |
| Pb1–O5 ^{xiii} | 2.613(2) | K–O5 ^{ix} | 3.158(7) | K–O4 ^{xxvii} | 3.10(2) |
| Pb1–O5 ^{xiii} | 2.613(2) | K–O5 ^{xix} | 3.158(7) | K–O4 ^{xxvi} | 3.10(2) |
| Pb2–O4 ^{xiv} | 2.372(5) | Pb–O9 ^{xx} | 2.467(5) | | |
| Pb2–O6 ^{xv} | 2.437(6) | Pb–O6 ^{xxi} | 2.500(8) | | |
| Pb2–O6 ^{xvi} | 2.589(5) | Pb–O11 ^{xxii} | 2.624(8) | | |
| Pb2–O6 ^{xiv} | 2.753(11) | Pb–O11 ^{xx} | 2.722(7) | | |
| Pb2–O4 ^{xv} | 2.787(8) | Pb–O3 ^{xxi} | 2.746(11) | | |
| Pb2–O6 ^{xviii} | 2.865(10) | Pb–O6 ^{xxiii} | 2.854(8) | | |
| Pb5–O4 ^{xvii} | 2.976(6) | Pb–O3 ^{xxiii} | 2.887(11) | | |

Symmetry codes: (i) $x, y, 1+z$; (ii) $3/4-y, x-1/4, 3/4-z$; (iii) $y-1/4, 3/4-x, z-1/4$; (iv) $x, 1+y, z$; (v) $x, 1-y, z-1/2$; (vi) $1/2-x, 1/2-y, -z$; (vii) $x, -y, z-1/2$; (viii) $1/2-x, 3/2-y, 1-z$; (ix) $1/2-x, 1/2-y, 1-z$; (x) $-x, 1-y, 1-z$; (xi) $1/2-x, 1/2-y, 1/2-z$; (xii) $x-1/2, y, 1/2-z$; (xiii) $1/4-y, x-1/4, z-1/4$; (xiv) $y-1/4, 5/4-x, 1/4-z$; (xv) $1/2-x, 3/2-y, 1/2-z$; (xvi) $3/4-y, 3/4+x, 3/4-z$; (xvii) $x, 1/2+y, -z$; (xviii) $x, 1/2+y, 1-z$; (xix) $x-1/2, 1/2-y, 1/2+z$; (xx) $1-x, -y, 1-z$; (xxi) $1-x, y, 1/2-z$; (xxii) $1/2+x, 1/2-y, z-1/2$; (xxiii) $1/2+x, 1/2+y, z$; (xxiv) $x, y, z-1$; (xxv) $-x, 1/2-y, z-1$; (xxvi) $y-1/4, 1/4-x, 1/4-z$; (xxvii) $1/4-y, x+1/4, z-1/4$.

with distances ranging from 2.685 to 3.158 Å as in K_{0.17}MoP₂O₇, and the Pb²⁺ ions are surrounded by seven oxygen atoms with distances comprised between 2.467 and 2.887 Å (Table 4) similar to that of Pb2 in Pb₂(PbO)₂Mo₈(P₂O₇)₈.

In conclusion, mixed-valent Mo(III)/Mo(IV) phosphates containing lead have been obtained for the first time. The tunnel structures of these new diphosphates, though closely related to that of K_{0.17}MoP₂O₇ exhibit original features. PbK₂Mo₈(P₂O₇)₈, derived from the latter by a monoclinic distortion, which is originated from the ordered distribution of the K⁺ and Pb²⁺ cations in the two sorts of eight-sided tunnels. In contrast, Pb₂(PbO)₂Mo₈(P₂O₇)₈, which keeps the tetragonal symmetry, exhibits also an ordering of the PbO chains and Pb²⁺ cations in these two sorts of tunnels. These results show the great flexibility of the framework [Mo₈P₁₆O₅₆][∞], and suggests the possibility to

generate many other derivatives with various ordering of the interpolated species.

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