

A Mixed-Valent Molybdenotungsten Monophosphate with a Tunnel Structure: $\text{Na}_x(\text{Mo}, \text{W})_2\text{O}_3(\text{PO}_4)_2$

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A mixed-valent molybdenotungstophosphate, $\text{Na}_x(\text{Mo}, \text{W})_2\text{O}_3(\text{PO}_4)_2$ ($x \sim 0.75$) has been isolated for the first time. It crystallizes in the space group $P2_1/m$ with $a = 7.200(1) \text{ \AA}$, $b = 6.369(1) \text{ \AA}$, $c = 9.123(1) \text{ \AA}$, and $\beta = 106.29(1)^\circ$. Its structure consists of M_2PO_{13} units built up of two MO_6 octahedra ($M = \text{Mo}, \text{W}$) and one PO_4 tetrahedron sharing their apices as already observed in several molybdenum phosphates. These units share their apices with PO_4 tetrahedra forming $[\text{M}_2\text{P}_2\text{O}_{15}]_\infty$ chains running along \vec{c} . The host lattice $[(\text{Mo}, \text{W})_2\text{P}_2\text{O}_{11}]_\infty$ can be described by the assemblage of such chains or by the assemblage of $[\text{MPO}_8]_\infty$ chains running along \vec{b} , in which one PO_4 tetrahedron alternates with one MO_6 octahedron. The tridimensional framework $[\text{Mo}, \text{WP}_2\text{O}_{11}]_\infty$ delimits tunnels running along \vec{b} , occupied by sodium with two kinds of coordination, 6 and 5. The distribution of the different species, in the octahedral sites according to the formulation $\text{Na}_{0.75}(\text{Mo}_{0.42}^{\text{VI}} \text{W}_{0.58}^{\text{VI}})_{\text{M1}}(\text{Mo}_{0.75}^{\text{V}} \text{W}_{0.25}^{\text{VI}})_2\text{O}_3(\text{PO}_4)_2$, is discussed. © 1995 Academic Press, Inc.

INTRODUCTION

An extraordinarily large number of tungsten and molybdenum phosphates characterized by a mixed valence of the transition element have been synthesized up to date. In these oxides, the behaviors of molybdenum and tungsten are fundamentally different. The mixed-valence $\text{W(V)}/\text{W(VI)}$ involves generally an electronic delocalization, leading to several series of phosphate tungsten bronzes (see, for review, Refs. (1-3)) that exhibit metallic properties and are actually studied for their wave density charge properties (4). In contrast, the mixed valence $\text{Mo(V)}/\text{Mo(VI)}$ does not imply an electronic delocalization but leads to the formation of molybdenum units that are isolated one from the other, i.e., connected through PO_4 tetrahedra. This different behavior of molybdenum is due to the particular electronic configuration of Mo(V) that favors the formation of numerous phosphates of pentavalent molybdenum (5). Nevertheless Mo(V) and W(V) are sometimes able to form isostructural phases as shown for the tetragonal phases WPO_5 (6) and MoPO_5 (7).

In spite of the great ability of molybdenum and tungsten to be associated to form octahedral suboxides, like in the shear structures $(\text{Mo}, \text{W})_n\text{O}_{3n-1}$ (8), very few phosphates involving Mo and W at an oxidation state smaller than six are known up to date. For this reason we have investigated the system Na-Mo-W-P-O . We report herein on the synthesis and crystal structure of an original monophosphate $\text{Na}_{0.75}\text{Mo}_{1.17}\text{W}_{0.83}\text{O}_3(\text{PO}_4)_2$.

SYNTHESIS AND CRYSTAL GROWTH

Single crystals of the title compound were grown from a mixture of nominal composition $\text{Na}_2\text{MoWP}_3\text{O}_{15}$. The growth was carried out in two steps. First $\text{H}(\text{NH}_4)_2\text{PO}_4$, Na_2CO_3 , WO_3 , and MoO_3 were mixed in an agate mortar in adequate ratios according to the composition $\text{Na}_2\text{Mo}_{0.83}\text{WP}_3\text{O}_{14}$ and heated at 700 K in a platinum crucible to decompose the ammonium phosphate and carbonate. In a second step the resulting mixture was then added to the required amount of molybdenum (0.17 mole) sealed in an evacuated silica ampoule, heated for 1 day at 853 K and cooled at 753 K. The sample was finally quenched to room temperature.

Three sorts of crystals were extracted from the resulting product, black needles, black plates that have not been identified owing to their poor quality, and small pale rose crystals of high quality. The latter were studied by X-ray diffraction and microprobe analysis confirmed the composition $\text{Na}_{0.75}\text{Mo}_{1.17}\text{W}_{0.83}\text{P}_2\text{O}_{11}$ deduced from the structure determination.

The synthesis of the corresponding pure phase in the form of powder was carried out under the same experimental conditions but starting with the ideal compositions corresponding to the formula $\text{Na}_x\text{Mo}_{2-y}\text{W}_y\text{P}_2\text{O}_{11}$ with $0.25 \leq x \leq 1$ and $1.75 \leq y \leq 0.25$. From the different attempts two pure phases could be synthesized, $\text{Na}_{0.75}\text{MoWP}_2\text{O}_{11}$ and $\text{Na}_{0.5}\text{Mo}_{0.25}\text{W}_{1.75}\text{P}_2\text{O}_{11}$. Their powder X-ray pattern was indexed in a monoclinic cell in agreement with the cell parameters deduced from the single-crystal study, as shown for $\text{Na}_{0.75}\text{MoWP}_2\text{O}_{11}$ (Table 1).

TABLE 1
Interreticular Distances for $\text{Na}_{0.75}\text{MoWP}_2\text{O}_{11}$

<i>h k l</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)	<i>l</i>	<i>h k l</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)	<i>l</i>
0 0 1	8.754	8.767	5	2 1 -3	2.423	2.422	10
1 0 0	6.911	6.986	10	2 2 -1	2.376	2.377	19
1 0 -1	6.361	6.370	63	1 2 2	2.291	2.292	18
				2 2 -2	2.249	2.248	36
0 1 -1	5.145	5.150	8	2 1 2	2.249		
1 0 1	4.808	4.810	23	3 1 -1	2.245		
1 1 0	4.680	4.685	90	0 0 4	2.188	2.186	38
1 1 -1	4.498	4.498	30	1 2 -3	2.185		
0 0 2	4.377	4.380	62	3 1 0	2.166	2.163	10
1 0 -2	4.280	4.277	9	2 2 1	2.161		
1 1 1	3.835	3.840	18	3 0 -3	2.120	2.119	8
2 0 -1	3.575	3.580	95				
1 0 2	3.303	3.304	81	3 0 1	2.088	2.089	12
2 0 -2	3.181	3.180	100	0 1 4	2.069	2.070	7
0 2 0	3.180			2 1 -4	2.028	2.029	26
2 1 0	3.036	3.041	10	1 3 0	2.027		
1 0 -3	3.007	3.005	60	3 1 -3	2.011	2.011	10
1 2 0	2.889	2.887	5	1 3 -1	2.011		
2 1 -2	2.845	2.840	8	1 3 1	1.939	1.937	6
1 2 -1	2.844			1 0 4	1.936		
1 2 1	2.652	2.651	17	0 3 2	1.908	1.910	9
0 1 -3	2.652			3 0 -4	1.870	1.872	13
2 0 -3	2.621	2.622	14	1 2 -4	1.852	1.853	4
0 2 2	2.573	2.572	12	1 1 4	1.852		

STRUCTURE DETERMINATION

A small plate with dimensions $0.078 \times 0.032 \times 0.07$ mm was selected for the structure determination. The cell parameters reported in Table 2 were determined and refined by diffractometric technique at 294 K with a least-squares refinement based upon 25 reflections with $18 \leq \theta \leq 22^\circ$. The systematic absence $k = 2n + 1$ for $0k0$ is consistent with the space group $P2_1/m$. The data were collected with an Enraf Nonius CAD 4 diffractometer, with the parameters reported in Table 2. The reflections were corrected for Lorentz and polarization effects and for adsorption.

The structure was solved with the heavy atom method. The W and Mo atoms are distributed over two sites $M(1)$ and $M(2)$. The refinement of the occupancy factors of the latter allows a preferential occupation to be evidenced; the $M(1)$ sites are preferentially occupied by tungsten—0.58 W/0.42 Mo—whereas the $M(2)$ sites are essentially occupied by molybdenum, i.e., 0.25 W/0.75 Mo. The sodium sites are characterized by an occupancy factor of 0.185, in agreement with the fact that each site exhibits three closer neighbors located at less than 1.4 Å, so that the four sites cannot be occupied simultaneously.

The refinement of the atomic coordinates, the isotropic thermal factor of sodium, and anisotropic thermal factors of all the other atoms leads to $R = 0.046$ and $R_w = 0.056$. The results are listed on Table 3.

TABLE 2
Summary of Crystal Data, Intensity Measurements and Structure Refinement Parameters for $\text{Na}_{0.75}\text{Mo}_{1.13}\text{W}_{0.87}\text{P}_2\text{O}_{11}$

Crystal data	
Space group	$P2_1/m$
Cell dimensions	$a = 7.200(1)$ Å, $b = 6.369(1)$ Å, $c = 9.123(1)$ Å $\alpha = 90.0^\circ$, $\beta = 106.29(1)^\circ$, $\gamma = 90.0^\circ$
Volume	$401.5(1)$ Å ³
<i>Z</i>	2
ρ_{calc} (g cm ⁻³)	4.31
Intensity measurements	
λ (MoK α)	0.71073 Å
Scan mode	ω - θ
Scan width (°)	$1.0 + 0.35 \tan \theta$
Slit aperture (mm)	$1.06 + \tan \theta$
Max θ (°)	45
Standard reflections	3 every hour
Reflections measured	6850
Reflections with $I > 5\sigma$	2011
μ (mm ⁻¹)	14.42
Structure solution and refinement	
Parameters refined	95
Agreement factors	$R = 0.046$, $R_w = 0.053$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	<0.005

TABLE 3
Positional Parameters and Their Estimated
Standard Deviations

Atom	x	y	z	B (\AA^2)
M(1)	0.1099(1)	0.25	0.20000(9)	0.46(2)
M(2)	0.3115(1)	0.25	0.6345(1)	0.56(3)
P(1)	0.4117(5)	0.75	0.6106(4)	0.63(8)
P(2)	0.0167(5)	0.75	0.1738(4)	0.71(8)
Na(1)	0.481(5)	0.594(5)	0.959(4)	3.5(6)
Na(2)	0.391(5)	0.496(5)	0.018(4)	3.2(6)
O(1)	-0.136(1)	0.25	0.128(1)	1.18(2)
O(2)	0.132(1)	0.25	0.394(1)	0.87(2)
O(3)	0.149(1)	0.556(1)	0.184(1)	0.87(2)
O(4)	0.144(1)	0.25	-0.026(1)	1.11(2)
O(5)	0.419(1)	0.25	0.247(1)	0.87(2)
O(6)	0.454(2)	0.25	0.816(1)	1.97(3)
O(7)	0.067(1)	0.25	0.690(1)	0.95(2)
O(8)	0.283(1)	0.557(1)	0.607(1)	1.11(2)
O(9)	0.523(1)	0.25	0.535(1)	0.95(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = \frac{1}{3} \sum_i \sum_j \vec{a}_i \cdot \vec{a}_j \beta_{ij}$. $M(1) = \text{W}_{0.58}\text{Mo}_{0.42}$; $M(2) = \text{W}_{0.25}\text{Mo}_{0.75}$.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the structure of $\text{Na}_{0.75}\text{Mo}_{1.17}\text{W}_{0.83}\text{O}_3(\text{PO}_4)_2$ along \vec{b} (Fig. 1) shows that the host lattice $[\text{Mo}_{1.17}\text{W}_{0.83}\text{P}_2\text{O}_{11}]_\infty$ consists of bioctahedral units connected through PO_4 tetrahedra delimiting large tunnels running along \vec{b} , where the Na^+ cations are located.

The whole structure can in fact be described by the assemblage of $[\text{M}_2\text{P}_2\text{O}_{15}]_\infty$ chains. Such chains are built up

from M_2PO_{13} units already observed in several molybdenum phosphates (8); two corner-shared $M(1)$ and $M(2)$ octahedra share one apex with the same P(1) tetrahedron (circled unit, Fig. 2). In each $[\text{M}_2\text{P}_2\text{O}_{15}]_\infty$ chain two successive M_2PO_{13} units are connected through a P(2) tetrahedron (Fig. 2). At the same y level the different $[\text{M}_2\text{P}_2\text{O}_{15}]_\infty$ chains are disconnected (Fig. 2). In the $[\text{M}_2\text{P}_2\text{O}_{11}]_\infty$ framework each $[\text{M}_2\text{P}_2\text{O}_{15}]_\infty$ chain is linked to two identical chains located above and two others located below them, as shown in Fig. 1. The connection between the different chains is ensured through the apical oxygens of the $M(1)$ and $M(2)$ octahedra that are shared with the P(2) and P(1) tetrahedra, respectively.

The connection of the octahedra and tetrahedra along the apical M -O bonds of the octahedra forms, in fact, $[\text{MPO}_8]_\infty$ chains running along \vec{b} . As a result the tridimensional framework $[\text{M}_2\text{P}_2\text{O}_{11}]_\infty$ can also be described by the assemblage of two kinds of chains, $[\text{M}(1)\text{P}(2)\text{O}_8]_\infty$ and $[\text{M}(2)\text{P}(1)\text{O}_8]_\infty$, that share their apices in such a way that one octahedron of one chain can be linked either to one octahedron or to one tetrahedron of another chain (Fig. 3). In this way, each $[\text{M}(1)\text{P}(2)\text{O}_8]_\infty$ chain is linked to one identical $[\text{M}(1)\text{P}(2)\text{O}_8]_\infty$ chain and to three $[\text{M}(2)\text{P}(1)\text{O}_8]_\infty$ chains, and conversely each $[\text{M}(2)\text{P}(1)\text{O}_8]_\infty$ is linked to three $[\text{M}(1)\text{P}(2)\text{O}_8]_\infty$ chains and to one identical $[\text{M}(2)\text{P}(1)\text{O}_8]_\infty$ chain (Fig. 1).

In this framework each PO_4 tetrahedron shares its four apices with four MO_6 octahedra and exhibits the classical geometry of monophosphate groups, as shown in Table 4. Each MO_6 octahedron shares four apices with four PO_4 tetrahedra and one MO_6 octahedron, the sixth apex being free. Note that this free apex is directed toward the center of the tunnel. One observes that the geometry of the O_6

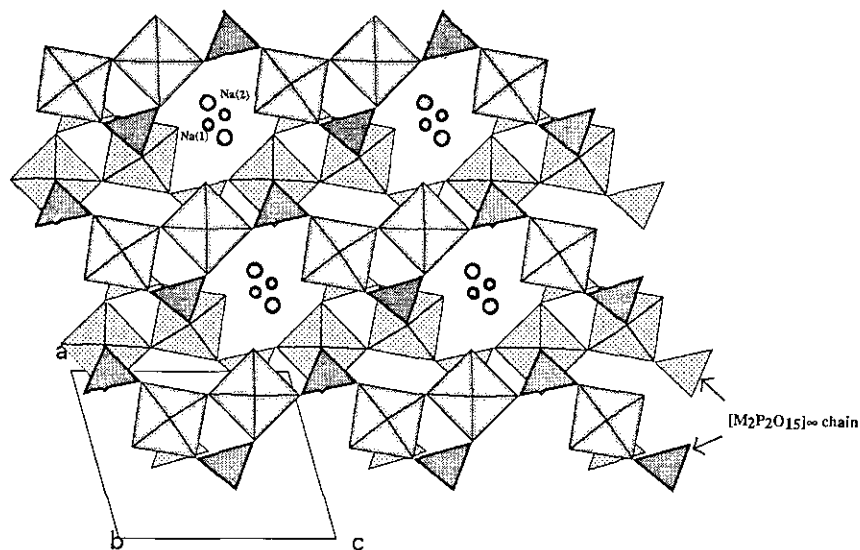


FIG. 1. Projection of the structure of $\text{Na}_{0.75}\text{Mo}_{1.17}\text{W}_{0.83}\text{O}_3(\text{PO}_4)_2$ along \vec{b} .

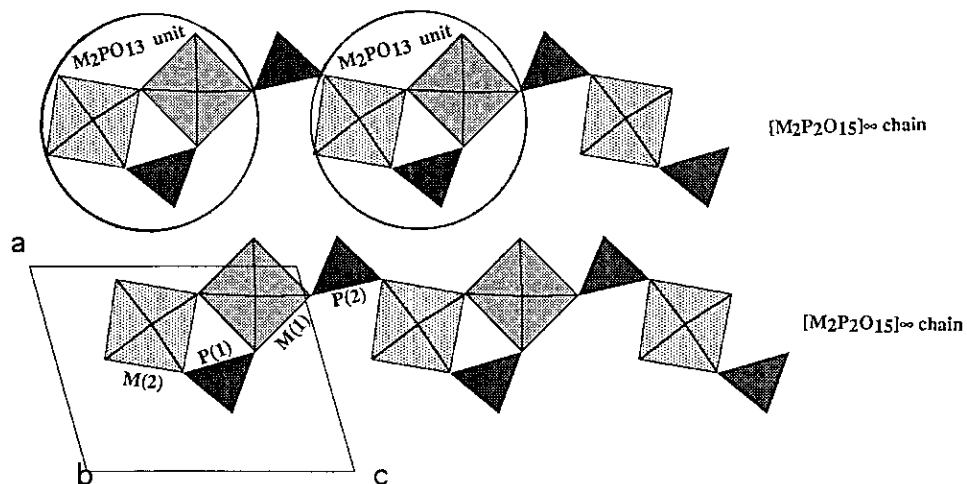


FIG. 2. Chains $[M_2P_2O_{15}]_{\infty}$ running along \vec{c} in the (010) plane.

octahedra is rather regular (Table 4). However the $M-O$ distances spread over a rather large range and are different for the $M(1)$ and $M(2)$ octahedra (Table 4). In the $M(1)$ octahedra that are mainly occupied by tungsten, one observes two short $M-O$ bonds (1.71–1.73 Å), two intermediate bonds (1.98 Å), and two larger ones (2.14–2.15 Å). The $M(2)$ octahedra that are preferentially occupied by molybdenum exhibit one short $M-O$ bond (1.69 Å), four intermediate $M-O$ distances (1.96–1.98 Å), and one abnormally long $M-O$ bond (2.21 Å). This geometry of the MO_6 octahedra suggests that the $M(1)$ octahedra are occupied

by W(VI) and Mo(VI), whereas the $M(2)$ octahedra are occupied by Mo(V) and W(VI). In many tungstates and molybdates such as $NaW^{VI}O_2PO_4$ and $NaMo^{VI}O_2PO_4$ (9) the $W-O$ and $Mo-O$ distances spread indeed over a broad range of values, in agreement with the interatomic distances obtained for the $M(1)$ octahedra.

The coordination 1 + 4 + 1 observed for $M(2)$ is in perfect agreement with the preferential occupancy of this site by Mo(V); the inability of W(V) to exhibit an irregular octahedral coordination suggests that this site is partly occupied by W(VI). Consequently, this compound

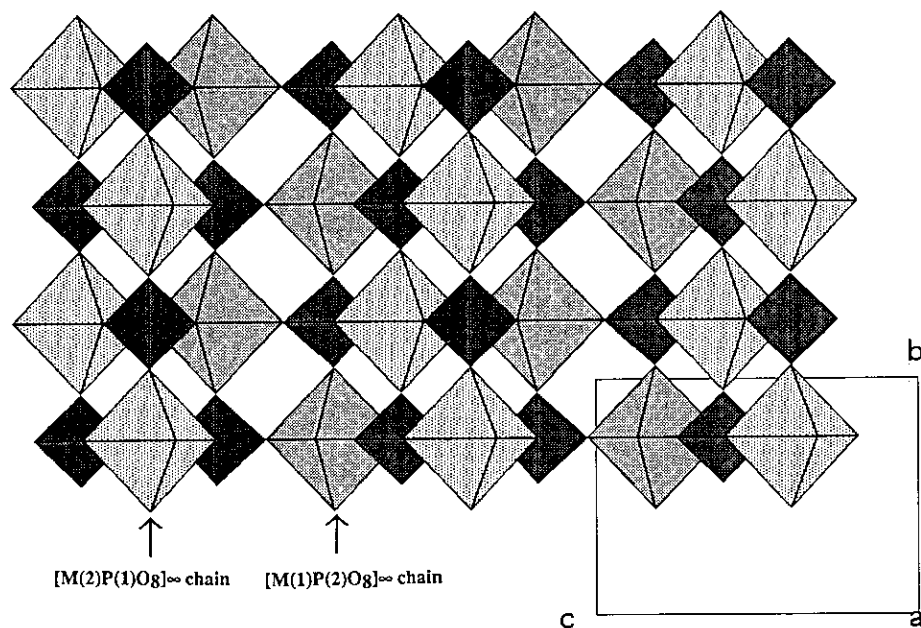


FIG. 3. Projection of $Na_{0.75}Mo_{1.17}W_{0.83}O_3(PO_4)_2$ along \vec{c} showing the $[MPO_8]_{\infty}$ chains.

TABLE 4
Distances (Å) and Angles (°) in Polyhedra

M(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(3 ⁱ)
O(1)	1.71(1)	2.64(2)	2.77(1)	2.76(2)	3.84(2)	2.77(1)
O(2)	100.3(5)	1.73(1)	2.76(1)	3.86(2)	2.76(2)	2.76(1)
O(3)	97.2(2)	95.9(2)	1.977(7)	2.52(1)	2.76(2)	3.89(1)
O(4)	91.1(5)	168.6(4)	82.6(2)	2.14(1)	2.72(1)	2.72(1)
O(5)	169.5(5)	90.2(4)	81.6(2)	78.5(4)	2.15(1)	2.70(1)
O(3 ⁱ)	97.2(2)	95.9(2)	159.5(4)	82.6(3)	81.6(2)	1.977(7)
M(2)	O(2)	O(6)	O(7)	O(8)	O(9)	O(8 ⁱ)
O(2)	2.208(8)	3.90(2)	2.86(2)	2.75(2)	2.75(1)	2.75(1)
O(6)	178.5(5)	1.69(1)	2.70(2)	2.77(1)	2.75(2)	2.77(1)
O(7)	86.5(4)	95.0(5)	1.96(1)	2.73(1)	3.92(2)	2.73(1)
O(8)	82.1(2)	97.9(2)	88.0(3)	1.972(8)	2.80(2)	3.91(1)
O(9)	81.7(4)	96.8(5)	168.2(4)	90.4(3)	1.98(1)	2.80(1)
O(8 ⁱ)	82.1(2)	97.9(2)	88.0(3)	163.9(3)	90.4(3)	1.972(8)
P(1)	O(8)	O(5 ⁱⁱ)	O(9 ⁱⁱ)	O(8 ⁱ)		
O(8)	1.53(1)	2.51(1)	2.48(1)	2.46(1)		
O(5 ⁱⁱ)	110.7(4)	1.51(1)	2.52(2)	2.51(1)		
O(9 ⁱⁱ)	108.1(4)	112.3(6)	1.52(1)	2.48(1)		
O(8 ⁱ)	106.6(5)	110.7(4)	108.1(4)	1.53(1)		
P(2)	O(3)	O(4 ⁱⁱ)	O(7 ⁱⁱ)	O(3 ⁱ)		
O(3)	1.55(1)	2.51(1)	2.51(1)	2.47(1)		
O(4 ⁱⁱ)	110.8(4)	1.51(1)	2.49(2)	2.51(1)		
O(7 ⁱⁱ)	109.3(4)	110.5(6)	1.53(1)	2.51(1)		
O(3 ⁱ)	106.2(5)	110.7(8)	109.3(4)	1.55(1)		

Note. Na(1)–O(6ⁱⁱⁱ) = 2.20(2); Na(2)–O(6^{iv}) = 2.28(2); Na(1)–O(5^v) = 2.41(2); Na(2)–O(4) = 2.32(2); Na(1)–O(6) = 2.43(2); Na(2)–O(1ⁱ) = 2.53(2); Na(1)–O(1^v) = 2.58(2); Na(2)–O(6^{vi}) = 2.55(2); Na(1)–O(4^{iv}) = 2.78(2); Na(2)–O(5) = 2.57(2); Na(2)–O(3) = 2.64(2). Symmetry codes: ⁱ, –x, 1/2 + y, –z; ⁱⁱ, x, 1/2 – y, z; ⁱⁱⁱ, 1 – x, 1/2 + y, 2 – z; ^{iv}, 1 – x, 1/2 + y, 1 – z; ^v, –x, 1/2 + y; 1 – z; ^{vi}, x, y, z.

may be formulated Na_{0.75}(Mo_{0.42}^{VI}W_{0.58}^{VI})_{M1}(Mo_{0.75}^VW_{0.25}^{VI})_{M2}O₃(PO₄)₂.

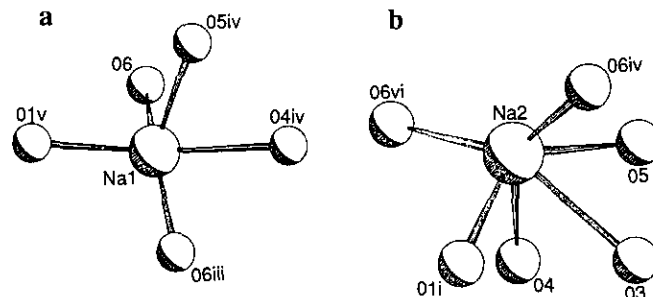


FIG. 4. The Na⁺ surroundings.

In the tunnels, the Na⁺ cations exhibit two kinds of coordination, a square pyramidal for Na(1) (Fig. 4a) and a sixfold one for Na(2) (Fig. 4b).

In conclusion, Na_x(Mo, W)₂O₃(PO₄)₂ represents the first phosphate containing tungsten and molybdenum simultaneously and is characterized by a mixed valence of molybdenum. This study opens the route to the exploration of mixed MoW phosphates with various oxidation states of the transition element.

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