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A Mixed Valent Molybdenotungsten Phosphate $Na_{1+x}(Mo, W)_2O_5PO_4$ Closely Related to the Phosphate Tungsten Bronzes

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A new mixed valent molybdenotungsten phosphate $Na_{1+x}(Mo, W)_2O_5PO_4$ has been synthesized. It crystallizes in the space group $P\,2_12_12_1$ with $a = 4.853(1)$ Å, $b = 8.516(1)$ Å, $c = 16.646(1)$ Å. The host lattice $[Mo_{0.15}W_{1.85}PO_9]_\infty$ consists of corner-sharing MO_6 octahedra (M = Mo, W) and PO_4 tetrahedra forming elliptic tunnels running along a where the sodium ions are located; the latter are distributed over two kinds of sites that are partly occupied. In fact, the $[Mo_{0.15}W_{1.85}PO_9]_\infty$ framework can be described as built up from ReO_3-type ribbons parallel to (0 1 2) and (0 1 $\bar{2}$) alternately, connected through PO_4 tetrahedra forming a fish bone array. Taking into consideration the presence of abnormally short Mo–O and W–O bonds corresponding to the existence of one free corner per octahedron, the distribution of the different species—Mo(V), W(V), and W(VI)—is discussed on the basis of the formula $Na_{1.3}(Mo^V_{0.15}W^V_{0.15}W^{VI}_{1.70})O_5PO_4$. © 1996 Academic Press, Inc.

INTRODUCTION

The crystal chemistry of molybdenum and tungsten oxides shows that these two elements are susceptible to exhibit great analogies due to their similar size and to their various oxidation states, but also striking differences due to their different electronic configurations. This is illustrated for instance by the very different structures of the octahedral bronzes A_xWO_3 and A_xMoO_3, so that the coexistence of molybdenum and tungsten in the same framework may induce original structures, as shown from the existence of many molybdenotungsten suboxides with a tunnel structure or related to the shear structures $(Mo, W)_nO_{3n}$ (for a review see Refs. (1, 2)). This difference between molybdenum and tungsten is also evidenced in mixed frameworks involving phosphate groups, especially when these transition elements exhibit an oxidation state intermediate between six and five. One indeed observes that tungsten forms a huge structural series of phosphate tungsten bronzes closely related to the perovskite (3, 4), whereas Mo(V)–Mo(VI) phosphates exhibit very different original structures involving either isolated MoO_6 octahedra, or isolated octahedral units of two or three octahedra, perhaps due to the particular electronic configuration of Mo(V), which favors the electron localization (see for review Ref. (5)).

This great difference between molybdenum and tungsten phosphates suggests that besides the numerous phosphates of these transition elements that have been synthesized in the last 15 years, it should be possible to generate new phosphates with original structures by associating these two transition elements in the same framework. The recent synthesis of the polyoxometallate $K_6Mo_3W_9PO_{40}\cdot 13H_2O$ built up of Keggin units (6) and of the monophosphate $Na_x(Mo, W)_2O_3(PO_4)_2$ (7) supports this viewpoint. For this reason a systematic study of the Na–Mo–W–P–O system is being performed varying the Na:Mo:W:P:O ratios. We report herein on a new phosphate $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$, with a structure built up from infinite ReO_3-type ribbons, i.e. closely related to the phosphate tungsten bronzes.

EXPERIMENTAL

Crystal Growth

Single crystals of the title compound were grown from a mixture of nominal composition $Na_4Mo_{3.5}W_{3.5}P_9O_{42}$. The growth was carried out in two steps: first $H(NH_4)_2)PO_4$, MoO_3, WO_3, and Na_2CO_3 were mixed in an agate mortar in adequate ratios according to the composition $Na_4Mo_{2.33}W_{3.5}P_9O_{42}$ and heated in air at 700 K in a platinum crucible to decompose the ammonium phosphate and carbonate. In a second step the resulting mixture was added to the required amount of molybdenum (1.17 mole), sealed in an evacuated silica ampoule, heated for 1 day at 903 K, cooled at 6.5 K/h to 673 K, and then quenched to room temperature. Some black crystals were extracted from this resulting mixture. The microprobe analysis of the black

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TABLE 1
Interreticular Distances for $Na_2Mo_{0.15}W_{1.85}O_5PO_4$

h k l	d_{calc} (Å)	d_{obs} (Å)	*I*	*h k l*	d_{calc} (Å)	d_{obs} (Å)	*I*
0 1 1	7.569	7.545	10	0 0 8	2.079	2.078	9
0 1 2	5.944	5.940	100	2 1 4	2.033	2.032	9
0 1 3	4.643	4.647	33	0 4 3	1.984	1.985	3
0 2 1	4.118	4.112	14	0 3 6	1.981		
1 1 2	3.757	3.750	48	2 2 4	1.879	1.877	19
1 0 3	3.649	3.645	21	2 3 0	1.842	1.840	8
1 1 3	3.354	3.360	50	2 3 2	1.798	1.794	12
1 2 0	3.196	3.189	50	0 4 5	1.791		
1 2 1	3.139	3.142	15	1 4 4	1.763	1.762	7
0 2 4	2.972	2.965	15	2 3 3	1.748	1.745	6
1 1 4	2.959			1 2 8	1.743		
1 0 5	2.743	2.748	25	1 3 7	1.705	1.707	8
0 1 6	2.635	2.628	44	2 3 4	1.684	1.684	21
0 3 3	2.523	2.524	25	0 5 2	1.666	1.665	12
1 3 1	2.420	2.417	16	2 1 7	1.664		
2 0 1	2.399	2.400	12	0 0 10	1.663		
1 3 2	2.347	2.347	9	0 5 3	1.625	1.625	4
0 3 4	2.342			5 0 4	1.604	1.606	6
2 1 1	2.309	2.306	9	1 4 6	1.593	1.591	18
1 2 5	2.305			2 4 1	1.591		
1 3 3	2.238	2.240	15	0 5 4	1.574	1.573	48
2 0 3	2.221	2.223	3	1 0 10	1.573		
2 1 3	2.149	2.149	4	2 4 2	1.569	1.569	25
0 4 0	2.125	2.121	2				

crystals confirmed the composition $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ in agreement with the structure determination.

Chemical Synthesis

Attempts to prepare the phase in the form of polycrystalline samples, starting from the nominal composition $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$, led to the expected powder X-ray pattern but with always weak extra lines due to impurities. In contrast, a pure phase was systematically synthesized for the compositions $Na_2Mo_yW_{2-y}PO_9$ with $0.15 < y < 0.75$. The powder X-ray pattern can be indexed in an orthorhombic cell as shown for $Na_2Mo_{0.15}W_{1.85}O_5PO_4$ (Table 1) in agreement with the cell parameters deduced from the single crystal study of $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ (Table 2). Note that the parameters of the polycrystalline sample are $a = 4.849(7)$ Å, $b = 8.500(9)$ Å, and $c = 16.63(4)$ Å.

STRUCTURE DETERMINATION

A black crystal with dimensions 0.064 × 0.051 × 0.039 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 $18° < \theta < 22°$. The systematic absences $h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $00l$ are characteristic of the $P2_12_12_1$ space group. The data were collected with an Enraf–Nonius CAD4 diffractometer using the parameters reported in Table 2. The reflections were corrected for Lorentz and polarization effects and for absorption.

The structure was solved with the heavy atom method. The W and Mo atoms were first distributed over the *M*1 site whereas the *M*2 site was filled only with tungsten. The refinement of the parameters of the atoms forming the host lattice and of the population of Mo and W of the *M* sites led to the framework "$Mo_{0.15}W_{1.85}PO_9$." Subsequent difference synthesis allowed sodium to be evidenced and the refinement of the atomic coordinates, population factor, and isotropic thermal factor of the sodium atoms led to the formula $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$.

RESULTS AND DISCUSSION

The final refinement of the structure of $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ led to the reliability factors, $R = 0.036$ and $R_w = 0.033$, for the atomic parameters listed in Table 3. Note that one site M1 is occupied by molybdenum and tungsten, whereas the second site M2 is fully occupied by tungsten.

The projection of the structure along **a** (Fig. 1) shows that the framework $[Mo_{0.15}W_{1.85}PO_9]_\infty$ consists of corner-sharing MO_6 octahedra and PO_4 tetrahedra forming elliptic tunnels running along **a** where the Na^+ ions are located. One observes strings of four corner-sharing MO_6 octahe-

TABLE 2
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$

Crystal data	
Space group	$P2_12_12_1$
Cell dimensions	$a = 4.853(1)$ Å, $b = 8.516(1)$ Å, $c = 16.646(1)$ Å
Volume	688.0(2) Å^3
Z	4
ρ_{calc} (gcm^{-3})	5.40
Intensity measurements	
λ (Mo*K*α)	0.71073 Å
Scan mode	$\omega - 2/3\theta$
Scan width (°)	$1.2 + 0.35 \tan\theta$
Slit aperture (mm)	$1.2 + \tan\theta$
Max θ (°)	45
Standard reflections	3 every hour
Reflections measured	3220
Reflections with $I > 5\sigma$	1128
μ (mm^{-1})	31.52
Structure solution and refinement	
Parameters refined	83
Agreement factors	$R = 0.036$ $Rw = 0.033$
Weighting scheme	$w = 1/\sigma$
Δ/σ max	<0.005

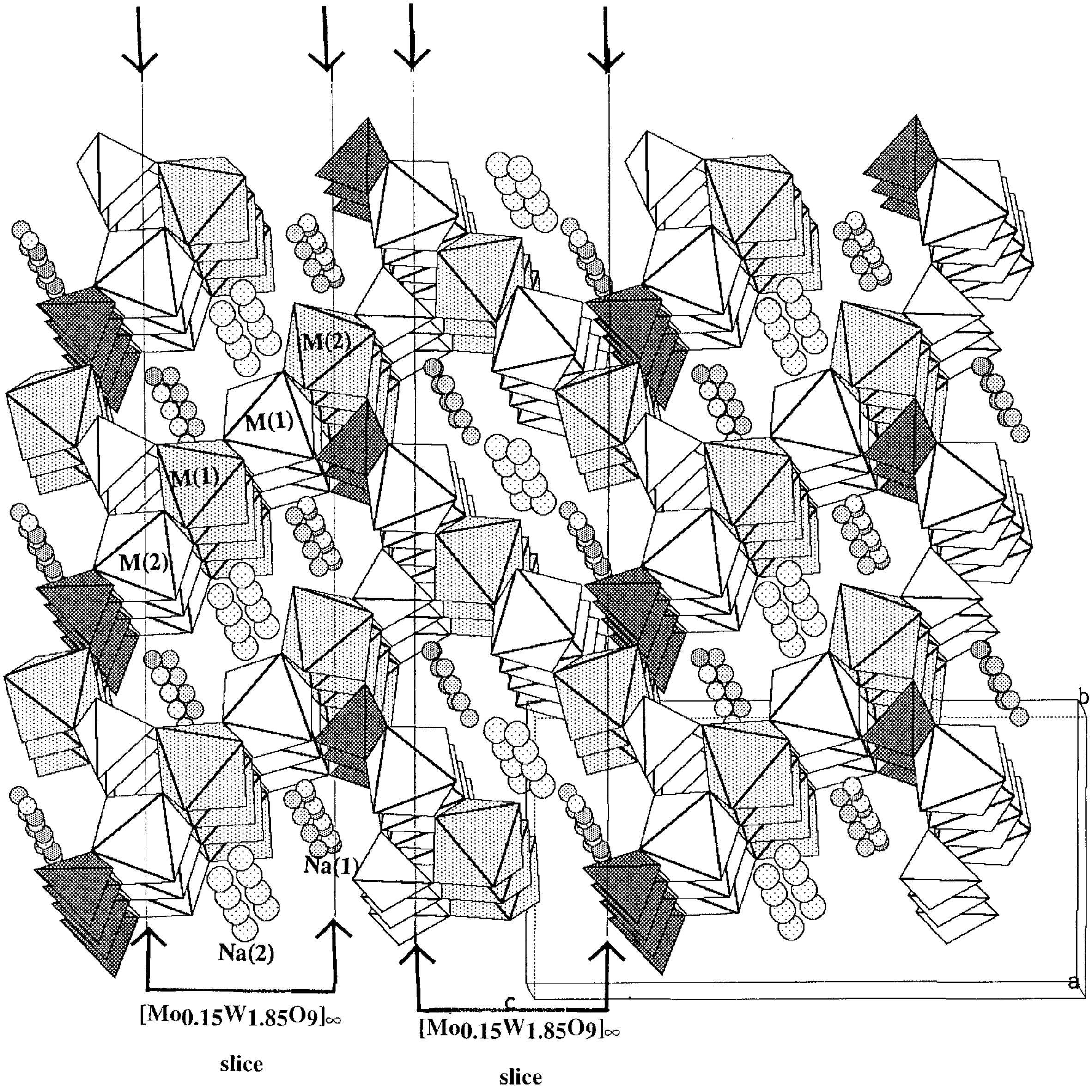

FIG. 1. The projection along **a** slightly tilted of $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ showing the $M_4P_2O_{20}$ ribbons which delimit the elliptic tunnels. In a ribbon the white polyhedra are at the same level or translate of **a**. The hatched polyhedra are at **a**/2 from the white polyhedra.

dra limited at both ends by one PO_4 tetrahedron, and parallel to the $[4\,\bar{2}\,1]$ or $[4\,2\,\bar{1}]$ directions. In fact, the MO_6 octahedra form ReO_3-type ribbons bordered with PO_4 tetrahedra (Fig. 2a), parallel to the 90° oriented (0 1 2) and $(0\,1\,\bar{2})$ planes alternately. The latter that are one octahedron thick, four octahedra wide along $[0\,\bar{2}\,1]$ and $[0\,2\,\bar{2}]$, and infinite along **a** are rather similar to the ribbons observed in the monophosphate tungsten bronzes with pentagonal tunnels (Fig. 2b). The stacking of these ribbons along **b** is different from that observed in the monophosphate tungsten bronzes with pentagonal tunnels. In the present phase, the $[Mo_{0.15}W_{1.85}PO_9]_\infty$ framework can be described as $[Mo_{0.15}W_{1.85}O_9]_\infty$ slices parallel to (001) built up from disconnected ReO_3-type ribbons that are four octahedra wide and interleaved with sodium ions (Fig. 1). In the $m = 4$ member of the monophosphate bronze series $(PO_2)_2(WO_3)_{2m}$ one observes equally similar ReO_3-type ribbons, but the latter share the corners of their octahedra forming ReO_3-type slices that are four octahedra wide (Fig. 3). In both oxides, two successive slices are connected through rows of PO_4 tetrahedra and are about 90° oriented with respect to each other (Fig. 1 and 3).

In this structure, each PO_4 tetrahedron shares its apices with four different MO_6 octahedra, and exhibits the classical geometry of the monophosphate groups with P–O distances ranging from 1.52 to 1.54 Å (Table 4).

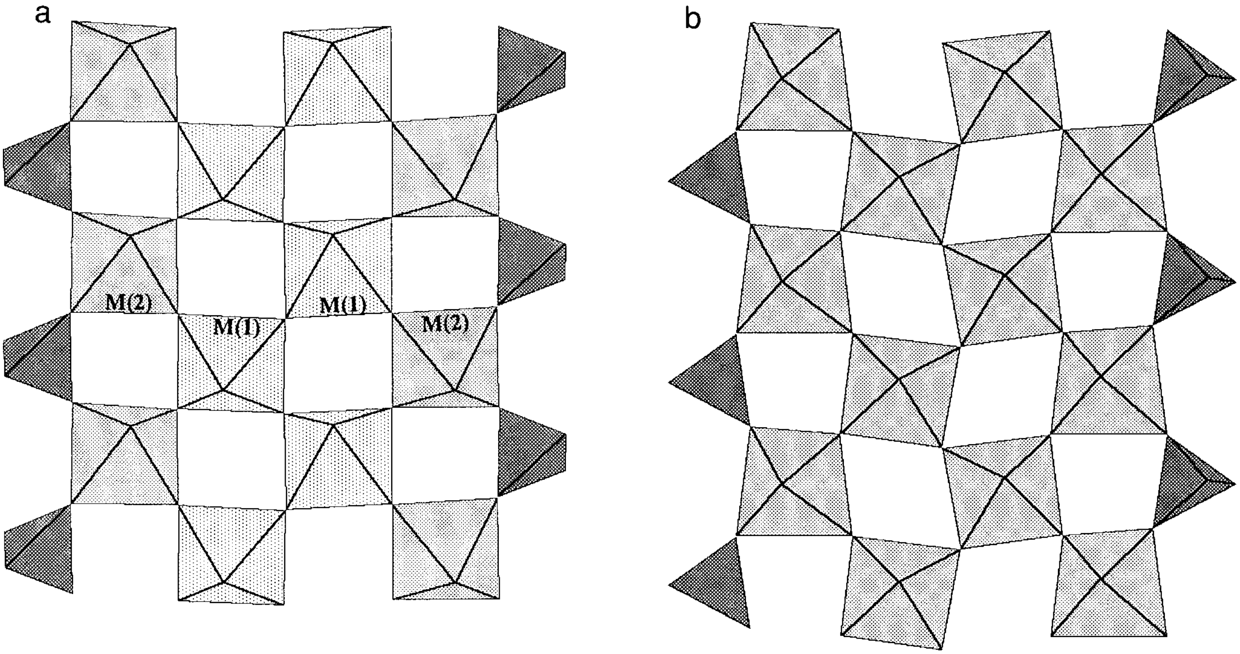

FIG. 2. The $M_4P_2O_{20}$ ribbons in (a) $Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ and (b) $W_8P_4O_{32}$ or $Na_4Nb_8P_4O_{32}$.

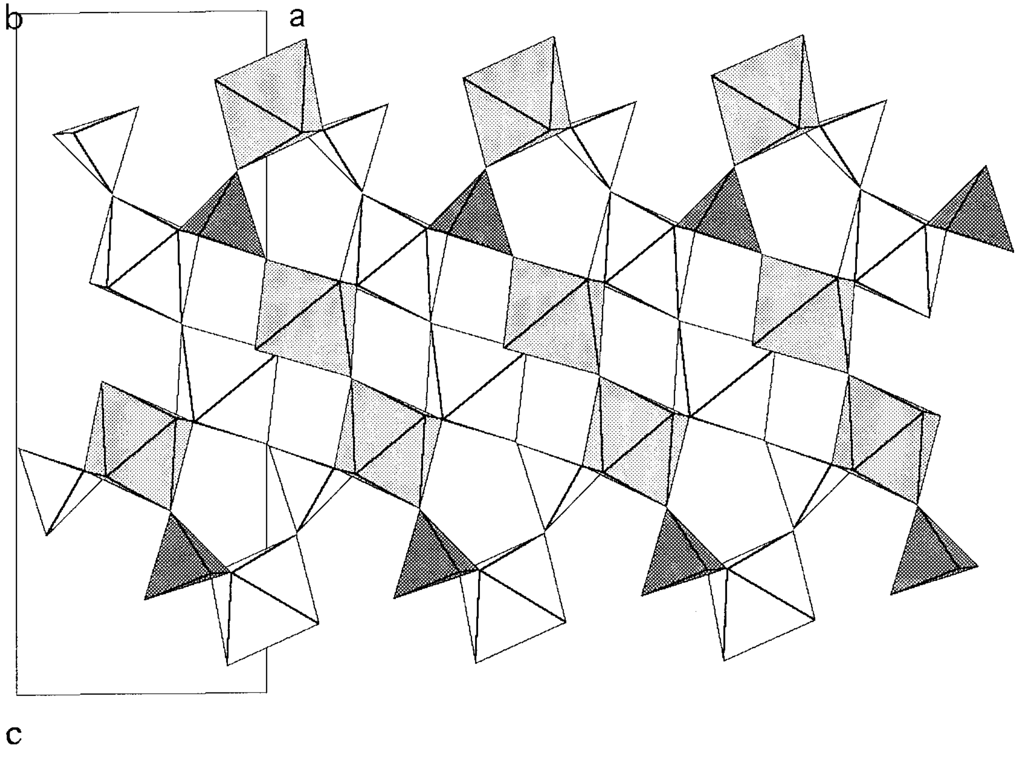

FIG. 3. Projection of $W_8P_4O_{52}$ along **b**.

TABLE 3
$Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å^2)	occupancy
$M$1:(W:Mo)	0.1271(2)	0.3834(1)	0.04377(4)	0.82(1)	0.85(1):0.15(1)
$M$2:W	0.6091(1)	0.6065(1)	0.16022(4)	0.71(1)	1
P(1)	0.133(1)	0.766(5)	0.2740(3)	0.48(1)	1
Na(11)	0.358(7)	0.035(3)	0.136(1)	2.08(4)	0.41(3)
Na(12)	0.816(4)	0.487(2)	0.383(1)	2.08(4)	0.49(3)
Na(13)	0.52(1)	0.027(7)	0.137(4)	2.08(4)	0.16(2)
Na(2)	0.922(7)	0.272(3)	0.477(3)	1.76(8)	0.30(2)
O(1)	0.279(3)	0.505(2)	−0.0236(8)	0.88(3)	1
O(2)	0.367(3)	0.448(1)	0.1319(7)	0.80(2)	1
O(3)	−0.135(3)	0.544(1)	0.0838(7)	0.64(2)	1
O(4)	0.340(3)	0.199(1)	0.0238(7)	0.48(2)	1
O(5)	−0.037(2)	0.238(1)	0.1400(7)	0.40(2)	1
O(6)	0.460(3)	0.761(1)	0.1101(7)	0.72(3)	1
O(7)	0.369(3)	0.653(1)	0.2597(6)	0.72(1)	1
O(8)	0.901(3)	0.740(1)	0.2122(7)	0.88(2)	1
O(9)	0.773(2)	0.437(1)	0.2395(7)	0.48(2)	1

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3 \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \beta_{ij}$.

The "O_6" octahedra that coordinate the molybdenum and tungsten atoms are slightly distorted with O–O distances ranging from 2.66 to 2.80 Å (Table 4). The Mo and W atoms are strongly off-centered in their octahedra, in agreement with the fact that they exhibit one free corner that is directed toward the center of the tunnel. The $M$1 site, where molybdenum and tungsten are sitting, is located in the two central rows in the middle of the ReO_3-type ribbons (Fig. 1) so that each $M$1 octahedron shares four apices with four other octahedra and one apex with one PO_4 tetrahedron (Fig. 2). As a result each $M$1 octahedron exhibits one abnormally short apical M–O bond of 1.69 Å corresponding to the free oxygen, one long opposite M–O bond of 2.17 Å, and four intermediate equatorial M–O bonds ranging from 1.91 to 1.98 Å (Table 4). The $M$2 site that is only occupied by tungsten, is located on the border of the ReO_3-type ribbons (Fig. 1 and 2) so that each WO_6 octahedron is connected to two MO_6 octahedra and three PO_4 tetrahedra. As a result the distribution of the W–O distances is different from that observed for the $M$1 site. One still observes a short W–O apical bond of 1.72 Å corresponding to the free oxygen atom and one opposite long W–O distance of 2.11 Å corresponding to the oxygen shared with a PO_4 tetrahedron; but the intermediate equatorial W–O distances consist of two short W–O distances of 1.85–1.86 Å corresponding to the W–O–M bonds, and two longer distances of 2.01–2.07 Å corresponding to the W–O–P bonds. The strong off-centering of the Mo and W atoms in their octahedra suggests that molybdenum is in the pentavalent state, leading to the formulation $Na_{1.3}(Mo^{V}_{0.15}W^{V}_{0.15}W^{VI}_{1.70})O_5PO_4$. Bond strength calculations performed with the Brown and Altermatt (8) model for W indicate that the $M$2 site contains only W(VI).

In the tunnels that are built up from the stacking of elliptic crowns of 12 corner-sharing polyhedra (8 octahedra + 4 tetrahedra) the Na^+ ions occupy two kinds of sites labeled Na(1) and Na(2).

The Na(1) cages, although very similar and delimited by six oxygen atoms, correspond to three different crystallographic sites labeled Na(11), Na(12), and Na(13). These sites are too close one from each other, so that they can be only partly occupied with occupancy factors of 0.41, 0.49, and 0.16, respectively (Table 3). Note that this leads to a total occupancy of 1.06 (0.03) Na atom per formula

TABLE 4
$Na_{1.3}Mo_{0.15}W_{1.85}O_5PO_4$ Distances (Å) and Angles (°) in Polyhedra

$M$1:W/Mo	O(1)	O(2)	O(3)	O(4)	O(5)	O(4^{i})
O(1)	**1.69(1)**	2.67(2)	2.71(2)	2.74(2)	3.86(2)	2.74(2)
O(2)	93.7(6)	**1.95(1)**	2.69(2)	2.79(2)	2.66(2)	3.85(2)
O(3)	94.7(6)	86.3(6)	**1.98(1)**	3.87(2)	2.80(2)	2.73(2)
O(4)	98.7(6)	92.4(5)	166.6(5)	**1.91(1)**	2.68(2)	2.70(2)
O(5)	173.7(6)	79.9(5)	84.7(5)	81.9(4)	**2.17(1)**	2.84(2)
O(4^{i})	98.6(6)	167.1(5)	89.0(5)	89.5(5)	87.7(5)	**1.92(1)**

$M$2:W	O(2)	O(6)	O(7)	O(8)	O(9)	O(3^{ii})
O(2)	**1.85(1)**	2.73(2)	2.75(2)	3.83(2)	2.66(2)	2.67(2)
O(6)	99.6(6)	**1.72(1)**	2.69(2)	2.74(2)	3.82(2)	2.74(2)
O(7)	89.2(5)	90.1(5)	**2.07(1)**	2.80(2)	2.71(2)	3.91(2)
O(8)	165.7(5)	94.1(5)	86.8(5)	**2.01(1)**	2.70(2)	2.72(2)
O(9)	84.3(5)	170.4(5)	81.0(5)	81.5(5)	**2.11(1)**	2.78(2)
O(3^{ii})	92.3(6)	99.9(6)	169.5(5)	89.2(6)	88.7(5)	**1.86(1)**

P(1)	O(7)	O(8^{iii})	O(5^{iv})	O(9^{v})
O(7)	**1.52(1)**	2.51(2)	2.43(2)	2.51(2)
O(8^{iii})	110.7(7)	**1.54(2)**	2.55(2)	2.44(2)
O(5^{iv})	106.1(6)	112.4(8)	**1.52(1)**	2.54(2)
O(9^{v})	110.7(7)	104.9(7)	112.1(6)	**1.54(1)**

Na(11)–O(9^{vi}) = 2.33(3)
–O(4) = 2.33(3)
–O(7^{vi} = 2.41(3)
–O(6^{vii}) = 2.42(3)
–O(5) = 2.58(3)
–O(1^{viii}) = 2.79(3)

Na(12)–O(6^{vi}) = 2.34(2)
–O(5^{v}) = 2.43(2)
–O(9) = 2.44(2)
–O(4^{v}) = 2.50(2)
–O(1^{ix}) = 2.51(2)
–O(8^{x}) = 2.97(2)

Na(13)–O(7^{vi}) = 2.11(7)
–O(1^{viii}) = 2.28(7)
–O(6^{vii}) = 2.33(6)
–O(4) = 2.53(7)
–O(9^{vi}) = 2.62(7)
–O(5^{ii}) = 2.81(7)

Na(2)–O(6^{ix}) = 2.30(3)
–O(6^{vi}) = 2.36(3)
–O(1^{ix}) = 2.39(3)
–O(3^{vi}) = 2.43(3)
–O(1^{vi}) = 2.60(3)
–O(3^{xi}) = 2.75(3)

Symmetry codes

i: $x - \frac{1}{2}, \frac{1}{2} - y; -z$
ii: $1 + x, y, z$
iii: $x - 1, y, z$
iv: $-x, \frac{1}{2} + y, \frac{1}{2} - z$
v: $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
vi: $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$
vii: $x, y - 1, z$
viii: $\frac{1}{2} + x, \frac{1}{2} - y, -z$
ix: $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$
x: $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$
xi: $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$

$Na_{1.3}Mo_{0.15}W_{1.85}PO_9$, indicating that the Na(1) cage is fully occupied by sodium. The Na(11)–O and Na(12)–O distances ranging from 2.33 to 2.97 Å (Table 4) and in agreement with those usually observed, whereas the Na(13)–O(7^{vi}) distance (2.11 Å) seems to be abnormally short, the others being normal (Table 4). The Na(2) atom is also surrounded by six oxygen atoms with normal Na(2)–O distances ranging from 2.30 to 2.75 Å. Note that this site exhibits an occupancy factor of 0.3 in agreement with the possible synthesis of the phase $Na_2Mo_{0.15}W_{1.85}O_5PO_4$ with a higher sodium content, observed in the present study.

CONCLUDING REMARKS

The association of molybdenum and tungsten has allowed a new mixed framework involving ReO_3-type ribbons to be synthesized. This suggests that it should be possible to generate many other molybdenum tungsten phosphates with original structures, by varying the Mo/W/O ratios. The electronic configuration of the species and their distribution in the $[MoWPO_9]_\infty$ framework are so far not definitely established. In particular, the issue of the electronic delocalization in these materials has to be considered. The growth of larger crystals is in progress, in order to understand the eventual anisotropic transport properties of this new phosphate.

REFERENCES

1. A. D. Wadsley, *in* ‘Inorganic Nonstochiometric Compounds’’ (L. Mandelcorn, Ed.), p. 98–209. Academic Press, New York, 1964.
2. C. N. R. Rao and B. Raveau, ‘‘Transition Metal Oxides.’’ VCH, New York, 1995.
3. B. Raveau, *Proc. Ind. Acad. Sci.* **96,** 419 (1986).
4. M. M. Borel, M. Goreaud, A. Grandin, Ph. Labbe, A. Leclaire, and B. Raveau, *Eur. J. Solid State Inorg. Chem.* **28,** 93 (1991).
5. G. Costentin, A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Rev. Inorg. Chem.* **13,** 77 (1993).
6. A. Leclaire, M. M. Borel, J. Chardon, and B. Raveau, *Mater. Res. Bull.* **30,** 1075 (1995).
7. A. Leclaire, M. M. Borel, J. Chardon, and R. Raveau, *J. Solid State Chem.* **120,** 353 (1995).
8. I. D. Brown and D. ALtarmatt, *Acta Crystallogr. B* **41,** 244 (1985).