Monophosphate Tungsten Bronzes with Pentagonal Tunnels $(PO_2)_4(WO_3)_{2m}$: Structure of Two Even-m Members $P_4W_{12}O_{44}$ ($m = 6$) and $P_4W_{16}O_{56}$ ($m = 8$)

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Crystals of $P_4W_{12}O_{44}$ and $P_4W_{16}O_{56}$ have been synthesized. They are orthorhombic, space group $P2_12_12_1$ with $a = 5.2927(7)$, $b = 6.5604(7)$, $c = 23.549(3)$ Å for $P_4W_{12}O_{44}$ and $a = 5.2943(5)$, $b = 6.5534(4)$, $c = 29.700(4)$ Å for $P_4W_{16}O_{56}$. Structures were solved by the heavy-atom method and refined to $R = 0.033$ ($R_w = 0.044$) with 2031 independent reflections for $P_4W_{12}O_{44}$ and $R = 0.043$ ($R_w = 0.052$) with 2272 independent reflections for $P_4W_{16}O_{56}$. The structures are related to that of $P_4W_8O_{32}$ and can be described by the association of zig-zag chains of octahedra and tetrahedra. The members of the series $(PO_2)_4(WO_3)_{2m}$ differ from one another by the length of the links in the chains of polyhedra. Pentagonal tunnels and O_{18} cages are formed at the junction between the ReO_3-type slabs and the slices of PO_4 tetrahedra. The surroundings of P and W have been studied and compared with those of other phosphate tungsten bronzes; the relation with the apparent oxidation state of tungsten is discussed.
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Introduction

The monophosphate tungsten bronzes (MPTB) form a large family whose framework is built up from ReO_3-type slabs interconnected through slices of PO_4 tetrahedra. These bronzes can be divided into two series, the monophosphate bronzes with hexagonal tunnels, $A_x(PO_2)_4(WO_3)_{2m}$, called MPTB$_h$ (1–3) and the monophosphate bronzes with pentagonal tunnels $(PO_2)_4$ $(WO_3)_{2m}$ called MPTB$_p$ (4, 5). These two series differ mainly one from the other by the relative orientation of the octahedral chains in the successive ReO_3-type slabs: in the MPTB$_h$'s, the chains of octahedra belonging to two successive slabs are all ori-ented in the same direction, whereas in the MPTB$_p$'s the direction of the octahedral chains of two successive slabs are related through a 2_1 screw axis, so that these chains are in herringbone pattern. The high-resolution electron microscopy study (6) of the MPTB$_p$'s has shown the existence of numerous members, and the possibility of intergrowth of two or several members. The structural study of such a series should allow to determine the influence of the P–O bonds on the ReO_3-type framework. However, in spite of the large number of microphases known in this system, the structure of only two members $P_4W_8O_{32}$ ($m = 4$) and $P_4W_{10}O_{38}$ ($m = 5$) has been determined from single crystals. The present work

deals with the structural study of two even-m members $P_4W_{12}O_{44}$ ($m = 6$) and $P_4W_{16}O_{56}$ ($m = 8$).

Experimental

Mixtures of $(NH_4)_2HPO_4$ and WO_3 in appropriate ratios were first heated in air at 873 K to decompose the phosphate. Then, the necessary amount of metallic tungsten was added and the corresponding mixture heated in an evacuated silica ampoule at 1173 K for several days. Crystals of both compositions are generally red, diamond-shaped plates, limited by orthorhombic forms {110}, {010}, and {001}.

A preliminary X-ray study with Laue and Weissenberg photographs has given unambiguously the orthorhombic symmetry and the space group $P2_12_12_1$ which are the same for the two compounds. The data were collected with a CAD-4 Enraf-Nonius diffractometer using $MoK\alpha$ monochromatized radiation with a measure of the background on both sides of each reflection. The intensities were corrected for Lorentz, polarization, and absorption effects. Most of the experimental data and structure refinement parameters are listed in Table I. In particular, a linear weighting scheme was adjusted according to $\langle w|F_o| - |F_c|\rangle$ in terms of $\sin \theta/\lambda$. For both compounds, the enantiomorphic structure has been tested, exchanging all atoms coordinates xyz into $xy\bar{z}$. The results (Tables II and III) show that the best fit is obtained for $P_4W_{12}O_{44}$ when all the z values are negative. Projections of both structures are drawn in Figs. 1a and b.

TABLE I

EXPERIMENTAL DATA AND STRUCTURE REFINEMENT PARAMETERS

	$P_4W_{12}O_{44}$	$P_4W_{16}O_{56}$
Crystal shape and size	Hexagonal plate 192 × 120 × 36 μm limited by {010}, {001}, and {110}	Needle 168 × 84 × 24 μm limited by {010}, {001}, and {110}
Lattice parameters (Å)	$a = 5.2927(7)$ $b = 6.5604(7)$ $c = 23.549(3)$	$a = 5.2943(5)$ $b = 6.5534(4)$ $c = 29.700(4)$
Conditions limiting possible S.G.	$h00, h = 2n; 0k0, k = 2n; 00l, l = 2n$	$h00, h = 2n; 0k0, k = 2n; 00l, l = 2n$
Possible S.G.	$P2_12_12_1$	$P2_12_12_1$
$(\sin \theta/\lambda)$ max.	0.995	0.941
Number of reflections measured	$5511(-10 \le h \le 10, 0 \le k \le 13, 0 \le l \le 46)$	$6649(-9 \le h \le 9, 0 \le k \le 12, 0 \le l \le 56)$
Number of unobserved reflections	1718 $(\sigma(I)/I > 0.33)$	2607 $(\sigma(I)/I > 0.33)$
Absorption correction	Program AGNOSTC (10, 11)	Program AGNOSTC (10, 11)
Secondary extinction	Isotropic	Isotropic
Linear absorption coefficient	450 cm^{-1}	469 cm^{-1}
Max. and min. values of the transmission factor	0.341 and 0.043	0.328 and 0.023
Method used to solve the structure	Heavy atom	Heavy atom
Atomic scattering factors, f' and f'' values	International tables (12)	International tables (12)
R, R_w, S	0.033, 0.044, 1.50	0.043, 0.052, 1.38
Method used to calculate w	Linear weighting scheme	Linear weighting scheme

TABLE II

POSITIONAL AND THERMAL PARAMETERS WITH e.s.d.'s FOR $P_4W_{12}O_{44}$

	x	y	z	B (Å^2)
W(1)	.2439(2)	.58394(9)	−.03053(2)	$B_{eq} = 0.46$
W(2)	.2595(2)	.76049(7)	−.40333(3)	$B_{eq} = 0.38$
W(3)	.2446(2)	.92212(7)	−.15928(2)	$B_{eq} = 0.33$
P	.2682(8)	.1172(4)	−.2952(2)	0.21(4)
O(1)	.748(4)	.258(2)	−.4021(6)	0.9(1)
O(2)	.742(4)	.086(2)	−.0342(5)	0.9(1)
O(3)	.739(5)	.426(2)	−.1669(6)	1.2(2)
O(4)	.522(3)	.068(2)	−.1384(7)	0.8(1)
O(5)	.022(2)	.107(2)	−.1297(6)	0.6(1)
O(6)	.221(3)	.053(2)	−.2338(6)	1.0(2)
O(7)	−.041(3)	.439(2)	−.0618(7)	0.9(1)
O(8)	−.026(2)	.273(2)	−.5039(6)	0.6(1)
O(9)	.054(3)	.261(2)	−.3112(8)	1.0(2)
O(10)	.525(3)	.219(2)	−.3023(7)	1.0(2)
O(11)	.461(2)	.397(2)	−.0710(6)	0.7(1)

U_{ij}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	.0060(2)	.0055(1)	.0053(2)	.0003(3)	.0001(1)	.0003(1)
W(2)	.0050(2)	.0044(1)	.0059(2)	−.0003(2)	−.0001(2)	−.0005(1)
W(3)	.0042(2)	.0040(1)	.0049(2)	−.0004(2)	−.0001(2)	.0000(1)

Note. The values of the thermal coefficients were obtained from $B_{eq} = (\frac{4}{3})\Sigma_i\Sigma_j\beta_{ij}a_ia_j$ and $U_{ij} = (\frac{1}{2}\pi^2)\beta_{ij}a_ia_j$ (Å^2).

Discussion

The determination of the structure of the oxides $P_4W_{12}O_{44}$ and $P_4W_{16}O_{56}$ confirms that these compounds are the $m = 6$ and $m = 8$ members of the series $(PO_2)_4(WO_3)_{2m}$ and have a structure closely related to that of $P_4W_8O_{32}$ which corresponds to the $m = 4$ member (4). Both structures are indeed characterized, like $P_4W_8O_{32}$, by ReO$_3$-type slabs separated by slices of PO$_4$ tetrahedra parallel to (001). They can also be described by the association of zig-zag chains of polyhedra running along **c**. Thus, these different members differ only one from the other by the length of the structural unit which forms the chains of polyhedra: they are formed of $m/2$ octahedra, i.e., three and four octahedra for $P_4W_{12}O_{44}$ and $P_4W_{16}O_{56}$, respectively, and one tetrahedron. The pentago-

nal tunnels, formed at the junction between the ReO$_3$-type slabs and the slices of tetrahedra, as well as the "O$_{18}$" cages belonging to these tunnels are very similar in the three structures and have been previously described for $P_4W_8O_{32}$ (4). It must be noticed that $P_4W_{12}O_{44}$ (Fig. 1a) has a framework similar to that of γ-Mo$_4$O$_{11}$ described by Asbrink and Kihlborg (7) and lately confirmed by Ghedira *et al.* (8), which corresponds also to the sixth member of the series and can be formulated $(MoO_2)_4$ $(MoO_3)_{12}$. However, the latter structure has been refined in a different space group $Pn2_1a$ $(7, 8)$ and exhibits different distortions of the polyhedra owing to the fact that molybdenum is located simultaneously in the octahedra and in the tetrahedra.

It can be noticed that the standard deviations of the atomic positions in the Mo ox-

TABLE III

POSITIONAL AND THERMAL PARAMETERS WITH e.s.d.'s FOR $P_4W_{16}O_{56}$

	x	y	z	B (Å^2)
W(1)	.2567(3)	.4119(1)	.02580(3)	$B_{eq} = 0.75(2)$
W(2)	.2601(3)	.0696(1)	.12794(2)	$B_{eq} = 0.60(2)$
W(3)	.7531(3)	.7440(1)	.07507(2)	$B_{eq} = 0.72(2)$
W(4)	.7548(3)	.4097(1)	.17830(2)	$B_{eq} = 0.40(2)$
P	.734(1)	.2163(6)	.2866(1)	0.36(5)
O(1)	.256(5)	.245(2)	.0797(4)	0.8(2)
O(2)	.240(5)	.075(2)	.3708(5)	0.8(2)
O(3)	.241(5)	.420(2)	.4736(5)	0.8(1)
O(4)	.767(4)	.280(2)	.2378(4)	0.5(2)
O(5)	.754(7)	.409(3)	.3153(6)	1.2(2)
O(6)	.042(3)	.225(3)	−.0038(6)	0.7(2)
O(7)	.480(3)	.264(3)	.1616(6)	0.6(2)
O(8)	−.052(4)	.074(3)	.2995(7)	1.1(2)
O(9)	.456(3)	.440(3)	.3909(5)	0.6(2)
O(10)	.030(4)	.056(3)	.4519(6)	0.7(2)
O(11)	−.026(4)	.222(3)	.1548(6)	0.7(2)
O(12)	.471(4)	.118(3)	.2914(7)	1.0(2)
O(13)	−.041(3)	.386(3)	.3979(6)	0.7(2)
O(14)	.536(4)	.108(3)	.4442(6)	0.7(2)

U_{ij}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	.0106(2)	.0088(2)	.0067(2)	.0007(5)	−.0005(5)	.0024(2)
W(2)	.0071(3)	.0060(2)	.0062(2)	.0018(4)	.0000(4)	.0017(2)
W(3)	.0097(2)	.0080(2)	.0063(2)	.0008(6)	−.0000(6)	.0024(2)
W(4)	.0057(2)	.0047(2)	.0038(2)	.0004(5)	.0001(4)	.0004(2)

Note. For B_{eq} and U_{ij}, see note in Table II.

ides are generally smaller than those of the W oxides and consequently the accuracy for the Mo–O distances is better than for W–O distances. This feature is probably due to the heavy-atom effect.

One remarkable feature which characterizes the two structures with respect to $P_4W_8O_{32}$ is their pseudosymmetry. All the W atoms (Tables II and III) are located close to the (100) plane at the levels $x = 0.25$ and $x = 0.75$. Indeed, in the same ReO$_3$-type slab, the W atoms belonging to the same structural unit of three and four octahedra are located either on one side of this plane (100) or on the other side. Thus W(2), W(1), and W(3), which form the chain of three octahedra (Fig. 1a) are located at the levels

0.2595, 0.2560, and 0.2553 respectively, all slightly greater than 0.25, whereas the three other W atoms of the chain but in the next slab exhibit x values slightly weaker than 0.25. This feature involves numerous anomalies in the Fourier difference synthesis and also in the least-squares procedures, since all the W, which induce the phases of the structure factors are practically situated in the same "mirror-plane." Consequently, some of the oxygen atoms refine in wrong positions, and the O–O distances appear to be untrue. When all the atomic positions are close to the true positions, then the refinement converge quite rapidly. It is worthy of note that such a problem appeared also in the monoclinic phase $P_4W_{10}O_{38}$ (5).

In this latter structure, the resolution in the group $P2_1/m$, involving a localization of the W atoms in the mirror plane led to the splitting of two oxygen positions; the correct positions were then found by using the space group $P2_1$ which does not involve a localization of the W atoms in a mirror plane. These particular features, which occur over all these structures associated with the existence of heavy atoms are probably responsible for the poor precision obtained for the oxygen atoms: the standard deviations in the coordinates correspond always to rather high values.

As shown in Tables IV and V, the P–O distances range from 1.52(2) to 1.54(2) Å while P is located 0.02(2) Å from the center of gravity G of its tetrahedron. So, all the P atoms can be considered at the very center

TABLE IV

$P_4W_{12}O_{44}$: INTERATOMIC DISTANCES (Å)

	P	W(1)	W(2)	W(3)
O(1)		1.96(1)		1.80(1)
O(2)		1.89(1)	1.86(1)	
O(3)	1.54(1)		1.98(1)	
O(4)			1.98(1)	1.82(1)
O(5)			1.96(1)	1.83(1)
O(6)	1.53(2)			1.96(1)
O(7)		1.93(2)	1.84(1)	
O(8)		$\begin{cases} 1.87(1) \\ 1.88(1) \end{cases}$		
O(9)	1.52(2)			2.03(2)
O(10)	1.52(2)			2.02(2)
O(11)		1.93(1)	1.83(1)	
G^a	0.02(2)	0.05(1)	0.10(1)	0.14(2)

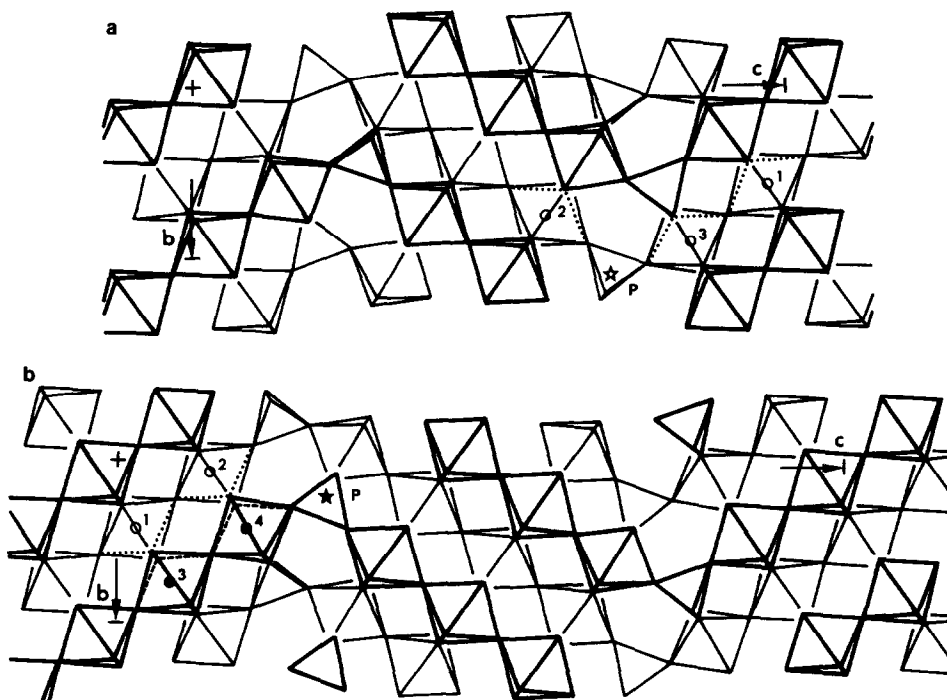^{a} G is the center of gravity of O_4 and O_6 polyhedra.

FIG. 1. Projection onto (100) of (a) $P_4W_{12}O_{44}$ (b) $P_4W_{16}O_{56}$. Numbers refer to W atoms of Tables II and III. The polyhedra with light and dark outlines lie at the levels about $x = \frac{1}{4}$ and $\frac{3}{4}$, respectively. Origins are chosen to get the same orientation of the chains of polyhedra and of the tunnels sections. The PO$_4$ tetrahedra are not arranged in the same manner and the WO$_6$ octahedra are tilted in opposite directions due to the fact that the (b) projection is drawn with $-z$ coordinates.

TABLE V

$P_4W_{16}O_{56}$: INTERATOMIC DISTANCES (Å)

	P	W(1)	W(2)	W(3)	W(4)
O(1)		1.94(1)	1.84(1)		
O(2)				1.95(1)	1.82(1)
O(3)			1.90(2)	1.85(2)	
O(4)	1.52(1)				1.97(1)
O(5)	1.53(2)		1.99(2)		
O(6)		{1.89(2) 1.87(2)}			
O(7)			2.00(2)		1.81(2)
O(8)	1.52(2)				2.02(2)
O(9)			1.82(2)	1.97(2)	
O(10)		1.91(2)		1.86(2)	
O(11)			1.98(2)		1.83(2)
O(12)	1.54(2)				2.03(2)
O(13)			1.84(2)	1.96(2)	
O(14)		1.91(2)		1.86(2)	
G^a	0.03(2)	0.02(2)	0.13(2)	0.10(2)	0.14(2)

[a] G is the center of gravity of O_4 and O_6 polyhedra.

of the tetrahedra, as generally pointed out in the other monophosphate tungsten bronzes. On the contrary, the W–O distances are spread over a wide range, with a gradual gap between W and the center of gravity G of its surrounding O neighbors. Table VI gives the W–O distances in $P_4W_{12}O_{44}$ and $P_4W_{16}O_{56}$ compared to the distances in $P_4W_8O_{32}$ and $P_4W_{10}O_{38}$. The dispersion of W–O distances encountered in the four structures and illustrated in Table VI shows the very important influence of the P atom on the distortion of the octahedra. Particularly, for the octahedron linked to three octahedra WO_6 and to three tetrahedra PO_4, a 3 + 3 coordination appears clearly. This phenomenon is not observed in $P_4W_8O_{32}$; however, a great dispersion of the W–O distances is also verified for this compound, close to that observed for the three others.

The determination of the structure of the different members of this series of bronzes brings additional informations about the knowledge of bond lengths and valences in tungsten oxides. Recently, Domengès *et al.*

(9) calculated the apparent oxidation state v_w of the W atoms in eight structures of phosphorus tungsten bronzes $A_x(P_2O_4)_2$ $(WO_3)_{2m}$ (A = Na, K, Rb), $P_8W_{12}O_{52}$, and P_4 W_8O_{32}. The calculation of the valence of tungsten v_w previously described by these authors can be applied also here to these new bronzes: it takes into account the mean oxidation state $\langle v_w \rangle$ for each compound and the relation $v = (R_0/R)^{5.75}$, where R is the interatomic distance W–O and R_0 is an empirical parameter determined for each structure. The values of v_w obtained for P_4 $W_{10}O_{38}$ (5), $P_4W_{12}O_{44}$, and $P_4W_{16}O_{56}$ (Table VI) ranging from 5.28 to 5.84, confirm that in all these mixed valence oxides, the electrons are delocalized rather than forming W^{5+} ions. It is obvious that the standard deviation observed for the W–O distances does not allow to build up a theory with assurance about the oxidation state of the W atoms. Nevertheless, the results obtained for the tungsten oxides are interesting in spite of the rather poor accuracy and can be regarded as a good indication. An original feature which was observed (9) for the DPTB$_h$ $A_x(P_2O_4)_2(WO_3)_{2m}$ and $P_8W_{12}O_{52}$ was that the more distorted octahedra, i.e., those having the most PO_4 tetrahedra neighbors, were those having the higher oxidation state v_w, in contrast to the prediction of Pauling's rule. Moreover, the behavior of $P_4W_8O_{32}$ was pointed out as exceptional since its tungsten atom W(1), bound to one tetrahedron, is close to W(VI) (v_w = 5.82), whereas its atoms W(2) surrounded by three PO_4 tetrahedra tends toward W(V) (v_w = 5.18). The examination of Table VI shows that the general tendency previously observed for the diphosphate tungsten bronzes DPTB$_h$, is also observed for the two members m = 6 ($P_4W_{12}O_{44}$) and m = 8 ($P_4W_{16}O_{56}$) of the monophosphate tungsten bronzes with pentagonal tunnels: for a given oxide, the oxidation state v_w increases with the distortion of the octahedra, i.e., with the number of tetrahedra sur-

TABLE VI

W Atoms in the Monophosphate Bronzes with Pentagonal Tunnels: Oxidation State (v) and W–O Distances Distribution

$(PO_2)_4(WO_3)_{2m}$	$\langle v_w \rangle$	Atom	W–O distances (Å) in the octahedra	Six neighbors polyhedra	v_w
			1.80 1.90 2.00 2.10		
$P_4W_8O_{32}$	5.50	W(1)		$5\phi + 1T$	5.82
($m = 4$)		W(2)		$3\phi + 3T$	5.18
$P_4W_{10}O_{38}$	5.60	W(3)		6ϕ	5.46[b]
($m = 5$)		W(2)		$5\phi + 1T$	5.78[b]
		W(5)		$5\phi + 1T$	5.28[a]
		W(1)		$3\phi + 3T$	5.82[a]
		W(4)		$3\phi + 3T$	5.66[b]
$P_4W_{12}O_{44}$	5.67	W(1)		6ϕ	5.54
($m = 6$)		W(2)		$5\phi + 1T$	5.66
		W(3)		$3\phi + 3T$	5.80
$P_4W_{16}O_{56}$	5.75	W(1)		6ϕ	5.70
($m = 8$)		W(3)		6ϕ	5.68
		W(2)		$5\phi + 1T$	5.77
		W(4)		$3\phi + 3T$	5.84
			1.80 1.90 2.00 2.10		

Note. $\phi = WO_6$ octahedron; $T = PO_4$ tetrahedron.

[a] These two W build a two-octahedra-long chain.

[b] These three W build a three-octahedra-long chain.

rounding each octahedron. The same is not true for $P_4W_{10}O_{38}$ and $P_4W_8O_{32}$.

However, it must be emphasized that $P_4W_{10}O_{38}$ ($m = 5$) is in fact composed of two sorts of ReO_3-type slabs; two and three octahedra wide, respectively, so that it can be described as a regular intergrowth of the members $m = 4$ ($P_4W_8O_{32}$) and $m = 6$ ($P_4W_{12}O_{44}$). It is worth noting that the mean oxidation state of W(1) + W(5) ($v_w = 5.55$) which form the $m = 4$ ReO_3-type slab is close to that of $P_4W_8O_{32}$ ($v_w = 5.50$) whereas the mean oxidation state of W(3) + W(2) + W(4) ($v_w = 5.63$) which form the $m = 6$ slab is close to that of $P_4W_{12}O_{44}$ ($v_w = 5.67$). Nevertheless, the v_w values of 5.28 and 5.82 found for W(5) and W(1) are inversed with respect to those observed for $P_4W_8O_{32}$ for the same environment of polyhedra (5.82 and 5.18, respectively). In the same way, the oxidation state of tungsten in the $m = 6$ slab W(3), W(2), and W(4) does not increase with the number of connected tetrahedra contrary to the $m = 6$ member $P_4W_{12}O_{44}$. Attention must also be drawn on the fact that the oxidation state v_w cannot really reflect the distortion of the octahedra: for instance, in $P_4W_{16}O_{56}$, W(1) and W(3) are both surrounded by six octahedra and have the same v_w value (5.70–5.68) but not the same distribution of the six W–O distances (Table VI). Thus, it appears that the behavior of the MPTBp's is complex and rather different from that of the DPTB's. It is clear that the distortion of the WO_6 octahedron is correlated to the num-

ber of neighboring PO_4 tetrahedra, but the relation with the apparent oxidation state should be better understood with a good accuracy for the W–O distances.

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