

## CsP<sub>8</sub>W<sub>8</sub>O<sub>40</sub>: A Diphosphate Tungsten Bronze with Octagonal Tunnels

M. GOREAUD, PH. LABBÉ, AND B. RAVEAU

*Laboratoire de Cristallographie, Chimie et Physique des Solides, L.A. 251  
ISMRA-Université de Caen, 14032 Caen Cedex, France*

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Reddish maroon crystals of a new bronze CsP<sub>8</sub>W<sub>8</sub>O<sub>40</sub> have been synthesized. They are orthorhombic, space group *Pcmn*, with  $a = 13.061(1)$ ,  $b = 12.319(1)$ , and  $c = 5.2960(5)$  Å. The structure, solved by the heavy-atom method was refined to  $R = 0.022$  ( $R_w = 0.025$ ) for 1646 observed reflections. The framework can be described as  $2 \times 2$  WO<sub>6</sub> octahedra wide ReO<sub>3</sub>-type columns extending indefinitely along [001] and connected through P<sub>2</sub>O<sub>7</sub> groups. These groups delimit octagonal tunnels running along [001] and built up from communicating cages limited by 17 oxygen atoms. Cs<sup>+</sup> ions are distributed at random, off-centered in the cages. The relationships between this original structure and those of P<sub>8</sub>W<sub>12</sub>O<sub>52</sub>, of the monophosphate tungsten bronzes with hexagonal tunnels A<sub>x</sub>(PO<sub>2</sub>)<sub>4</sub>(WO<sub>3</sub>)<sub>2m</sub> and of the diphosphate tungsten bronzes A<sub>x</sub>(P<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(WO<sub>3</sub>)<sub>2m</sub> are discussed. CsP<sub>8</sub>W<sub>8</sub>O<sub>40</sub> appears as the first potential unidimensional conductor which has been synthesized in the field of the phosphate tungsten bronzes. © 1985 Academic Press, Inc.

### Introduction

The recent studies of the P-W-O and A-P-W-O systems (A = Na, K, Rb, Tl, Ba) have shown the great adaptability of the PO<sub>4</sub> tetrahedra and P<sub>2</sub>O<sub>7</sub> groups to an octahedral WO<sub>3</sub> framework. Three series of mixed-valence oxides, whose tunnel structures are closely related in that they exhibit ReO<sub>3</sub>-type slabs, were synthesized. However, the arrangement of these slabs and of the PO<sub>4</sub> tetrahedra, i.e., the nature of the tunnels, depends on the presence and on the nature of the univalent A ions. In the absence of A ions, a first series of monophosphate tungsten bronzes (PO<sub>2</sub>)<sub>4</sub>(WO<sub>3</sub>)<sub>2m</sub> characterized by pentagonal tunnels (1) and related to  $\gamma$ -Mo<sub>4</sub>O<sub>11</sub> (2) was obtained. For large A ions such as Rb<sup>+</sup>, Tl<sup>+</sup>, diphosphate

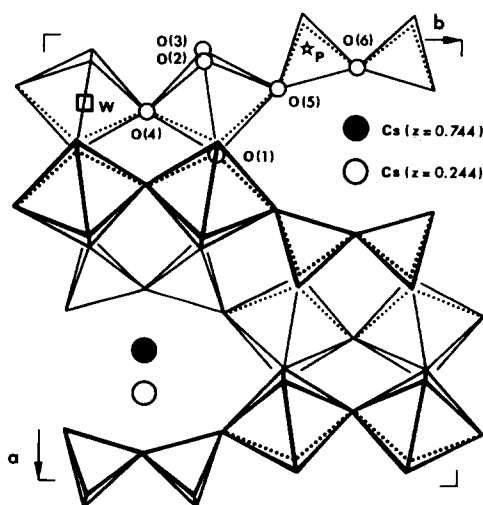


FIG. 1. CsP<sub>8</sub>W<sub>8</sub>O<sub>40</sub>: projection of the structure onto the (001). The polyhedra with dark and light outlines lie at the levels  $z = \frac{3}{4}$  and  $\frac{1}{4}$ , respectively. Cs sites are partially occupied.

bronzes  $A_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$  with hexagonal tunnels were synthesized (3–7), whereas for smaller univalent ions like  $\text{Na}^+$ , monophosphate bronzes  $A_x(\text{PO}_2)_4(\text{WO}_3)_{2m}$  related to  $\eta\text{-Mo}_4\text{O}_{11}$  (8) were obtained (9–11). Potassium, owing to its intermediate size, led to both structural series. This effect of the size of the A ions on the structure of these bronzes led us to investigate the Cs–P–W–O system. Moreover, the compounds with phosphorus-rich compositions exhibit a different behavior: the oxide  $\text{P}_8\text{W}_{12}\text{O}_{52}$  (12) does not belong to the three above series since it exhibits no more slabs but  $\text{ReO}_3$ -type columns. The present paper deals with the structure of a new bronze  $\text{CsP}_8\text{W}_8\text{O}_{40}$  characterized by octagonal tunnels and  $\text{ReO}_3$ -type columns.

## Experimental

### Sample Preparation

A mixture of  $\text{Cs}_2\text{CO}_3$ ,  $\text{H}(\text{NH}_4)_2\text{PO}_4$ , and  $\text{WO}_3$  in appropriate ratios was first heated in air at 900 K to decompose the phosphate and the carbonate. Then an adequate amount of W was added to obtain the composition  $\text{CsP}_8\text{W}_8\text{O}_{40}$  and the sample was heated for 15 hr at 1230 K in an evacuated silica ampoule. The crystals look like reddish maroon needles whose composition was confirmed by the structural study.

### Structure Determination

Experimental data and structure refinement parameters are summarized in Table I. After corrections for background, Lorentz, polarization, and absorption effects, 1646 independent reflections were used to solve and refine the structure in the centrosymmetric *Pcmm* group. The final atomic coordinates and interatomic distances are listed in Tables II, III, and IV.

## Description of the Structure and Discussion

The framework of  $\text{CsP}_8\text{W}_8\text{O}_{40}$  is built up

from corner-sharing  $\text{WO}_6$  octahedra and  $\text{P}_2\text{O}_7$  diphosphate groups forming large octagonal tunnels where the  $\text{Cs}^+$  ions are located (Fig. 1).

The geometry of the diphosphate groups has been compared with that observed in the diphosphate bronzes  $\text{Rb}_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$  and in the phase  $\text{P}_8\text{W}_{12}\text{O}_{52}$ . The  $\text{PO}_4$  tetrahedra in the  $\text{P}_2\text{O}_7$  groups have an eclipsed configuration as in  $\text{Rb}_x(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$  (3–7) but the P–O–P angle has a value of  $135.3(3)^\circ$  in  $\text{CsP}_8\text{W}_8\text{O}_{40}$  instead of about  $150^\circ$ . In  $\text{P}_8\text{W}_{12}\text{O}_{52}$  the P–O–P angle is closer— $139.9(9)^\circ$ —but the  $\text{P}_2\text{O}_7$  group is in a staggered configuration. The structure we describe is another example of the adaptability of the diphosphate group. The P–O distances in a tetrahedron, given in Table IV, show that the longest bond is, as usual, between P and the bridging O of the diphosphate group. The phosphorus atom is located at  $0.100(4)$  Å from the center of gravity of O atoms in  $\text{PO}_4$ . The O–O distances in  $\text{P}_2\text{O}_7$  ranges from  $2.412(4)$  to  $2.519(7)$  Å and the mean value,  $2.49$  Å, is a classical value in a  $\text{PO}_4$  tetrahedron.

The  $\text{WO}_6$  octahedra exhibit a rather distorted configuration (Table III) with O–O distances ranging from  $2.661(6)$  to  $2.838(6)$  Å. A 3 + 3 coordination appears for tungsten, due to the fact that each  $\text{WO}_6$  octahedron is linked to three other octahedra and three  $\text{PO}_4$  tetrahedra. Thus, the W atom is off-centered of  $0.120(4)$  Å in its octahedron, in the opposite direction of the three  $\text{PO}_4$  neighbors, forming three longer W–O bonds with the O atoms shared with  $\text{PO}_4$  tetrahedra. This distortion of the  $\text{WO}_6$  octahedra appears as a contrast with respect to the low mean value of the tungsten oxidation state (4.9) which should involve a greater symmetry in the case of a pure octahedral framework. This influence of the P atoms which prevails over the value of the oxidation state of W is in agreement with the results previously observed for  $\text{P}_4\text{W}_8\text{O}_{32}$  (1) in which a type of  $\text{WO}_6$  octahedra linked

TABLE I  
EXPERIMENTAL DATA AND STRUCTURE REFINEMENT PARAMETERS

Crystal shape and size	Orthorhombic sample (28 × 40 × 144 μm) limited with {100}, {010}, {110}, {201}
Lattice parameters	Measured at 294 K with 25 hkl 2.27° ≤ θ ≤ 32.38°, a = 13.061(1), b = 12.319(1), c = 5.2960(5) Å
Conditions limiting possible reflections	hk0, h + k = 2n; 0kl, l = 2n; h0l, no condition
Possible space groups	Pcmn (No. 62); Pc2 <sub>1</sub> n (No. 33)
Diffractometer and data collection technique	C.A.D. 4 Enraf-Nonius, ω - θ scan
Maximal value of (sin θ)/λ	0.995
Standard reflections and their intensity variation	3 reflections with (ΔI/I) <sub>max</sub> = 0.03
Number of measured reflections	3110
Number of unobserved reflections	1464 with σ(I)/I ≥ 0.333
Absorption correction applied	Based on the crystal morphology
Linear absorption coefficient	μ <sub>MoKα</sub> = 300 cm <sup>-1</sup>
Max. and min. values of the transmission factor	0.359 and 0.218
Method used to solve the structure	Patterson and Fourier methods. Use of F magnitude in least-squares refinement
Atomic scattering factors; f' and f'' values	Source: International Tables for X-ray crystallography (1974), Vol. IV
R, R <sub>w</sub> , and S	0.022, 0.025, and 0.828
Method used to calculate w	Linear weighting scheme: ⟨w ΔF ⟩ in terms of (sin θ)/λ, with a constant value for θ > 23°

TABLE II  
POSITIONAL PARAMETERS WITH E.S.Ds FOR CsP<sub>8</sub>W<sub>8</sub>O<sub>40</sub>

	Position	x	y	z	B (Å <sup>2</sup> )	
Cs	4(c)	0.2982(3)	$\frac{3}{4}$	0.245(1)	4.40(2) <sup>a</sup>	
W	8(d)	0.15299(1)	0.10007(1)	0.25565(4)	0.26(1) <sup>a</sup>	
P	8(d)	0.01971(9)	0.62987(9)	0.2338(3)	0.34(1) <sup>a</sup>	
O(1)	8(d)	0.2600(3)	0.4189(3)	0.4855(8)	0.47(4)	
O(2)	8(d)	0.0538(4)	0.3850(4)	0.552(1)	0.93(5)	
O(3)	8(d)	0.0282(4)	0.3818(4)	0.0250(9)	0.77(5)	
O(4)	4(c)	0.1684(3)	$\frac{1}{4}$	0.255(2)	0.58(5)	
O(5)	8(d)	0.1155(3)	0.5616(3)	0.260(1)	0.60(4)	
O(6)	4(c)	0.0654(4)	$\frac{3}{4}$	0.253(2)	0.67(5)	
	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub> <sup>b</sup>
Cs	0.0158(9)	0.124(5)	0.026(1)	0	0.003(2)	0
W	0.00340(4)	0.00316(4)	0.00336(5)	-0.00021(4)	-0.0002(1)	0.00008(9)
P	0.0045(3)	0.0038(3)	0.0045(5)	0.0007(3)	0.0003(4)	0.0010(4)
O(1)	0.006(2)	0.008(1)	0.006(1)	-0.0007(10)	0.002(1)	0.001(1)
O(2)	0.011(2)	0.012(2)	0.014(2)	-0.0002(13)	-0.008(1)	0.002(1)
O(3)	0.008(1)	0.016(2)	0.008(1)	-0.0001(13)	0.004(1)	-0.002(1)
O(4)	0.008(1)	0.006(1)	0.009(2)	0	-0.003(3)	0
O(5)	0.007(1)	0.006(1)	0.011(1)	0.0021(8)	0.001(1)	0.001(2)
O(6)	0.009(1)	0.005(1)	0.014(2)	0	-0.004(4)	0

<sup>a</sup> B<sub>eq</sub> =  $\frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$ .

<sup>b</sup> The anisotropic thermal coefficients were obtained from U<sub>ij</sub> = (1/2π<sup>2</sup>)β<sub>ij</sub>a<sub>i</sub>a<sub>j</sub> (Å<sup>2</sup>).

TABLE III  
THE  $\text{WO}_6$  OCTAHEDRON IN  $\text{CsP}_8\text{W}_8\text{O}_{40}$ :  
INTERATOMIC DISTANCES (Å)

	W	O(1)	O(2)	O(3)
O(1)	{1.842(4) 1.868(4)}	2.661(6)	2.748(6)	
O(2)	2.043(5)			
O(3)	2.049(5)	2.804(6)	2.818(7)	
O(4)	1.858(1)	{2.692(6) 2.693(6)}	2.734(8)	2.734(7)
O(5)	2.051(4)	{2.806(6) 2.838(6)}	2.783(7)	2.790(6)

to three tetrahedra is also rather distorted.

The octagonal tunnels running along [001] are formed by the stacking of cages bounded by 17 oxygen atoms (Fig. 2). Two successive cages communicate through an octagonal ring built up from four  $\text{WO}_6$  octahedra and two  $\text{P}_2\text{O}_7$  groups (Fig. 3). The occupancy factor of the  $\text{Cs}^+$  site obtained after the last refinement is 0.260(9), so that about one  $\text{O}_{17}$  cage out of four is filled by  $\text{Cs}^+$ . This occupation appears to be at random according to the X-ray data. This low occupancy factor is in agreement with the short distance between two crystallographic adjacent positions—2.93(1) Å—which cannot be occupied simultaneously owing to the large size of  $\text{Cs}^+$ . The coordination of  $\text{Cs}^+$  is shown on Figs. 3 and 4.

TABLE IV  
THE DIPHOSPHATE GROUP IN  $\text{CsP}_8\text{W}_8\text{O}_{40}$ :  
INTERATOMIC DISTANCES IN ÅNGSTROMS AND  
ANGLES IN DEGREES

P	O(2)	O(3)	O(5)	O(6)
O(2)	<u>1.498(5)</u>	2.519(7)	2.509(7)	2.495(7)
O(3)	113.7(3)	<u>1.510(5)</u>	2.513(7)	2.518(8)
O(5)	112.8(3)	112.4(3)	<u>1.515(4)</u>	2.412(4)
O(6)	107.3(3)	108.1(3)	101.5(3)	<u>1.599(2)</u>

$\text{P}-\text{O}(6)-\text{P}' = 135.3(3)^\circ$

Note. Underlined values refer to P-O distances.

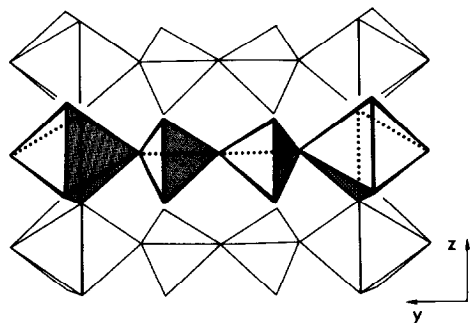


FIG. 2. The " $\text{O}_{17}$ " cage viewed in the  $a$  direction.

One can consider five close oxygen neighbors distant from 3.040(6) to 3.330(4) Å, then six second neighbors at about 3.7 Å. The sum of the ionic radii of  $\text{Cs}^+$  and  $\text{O}^{2-}$  is about 3.10 Å if we consider a regular 6-coordination for Cs. In fact, the coordination of  $\text{Cs}^+$  is often irregular. Koizumi and Nakano (13) describe a 11-coordinated  $\text{Cs}^+$  with six distances ranging from 3.04 to 3.35 Å in  $\text{CsNdP}_4\text{O}_{12}$ . Okada *et al.* (14) describe  $\text{CsO}_{15}$  and  $\text{CsO}_{18}$  polyhedra with five, six, or seven close neighbors (between 2.94 and 3.39 Å) in  $\text{Cs}_6\text{W}_{11}\text{O}_{36}$ . In  $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ , Gasperin (15) notes 4- and 7-coordinated  $\text{Cs}^+$  with the oxygen neighbors on one side. Hussain (16) finds  $\text{Cs}^+$  to be located in the hexagonal tunnels of a cesium intergrowth tungsten bronze  $\text{Cs}_x\text{WO}_3$ , with a coordination of 18 oxygen atoms and distances Cs-

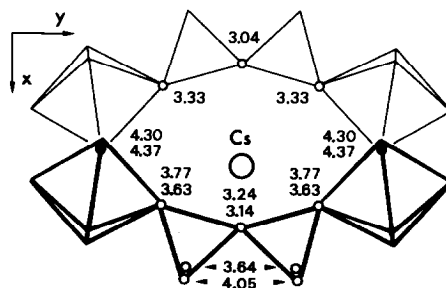


FIG. 3. The octagonal ring viewed in the  $c$  direction. The distances from  $\text{Cs}^+$  are given in Ångstroms for the 17 oxygen atoms forming the cage. The polyhedra with dark outlines lie at levels  $z = \frac{3}{4}$  and  $-\frac{1}{4}$ .

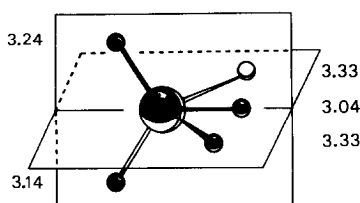


FIG. 4. Coordination of  $\text{Cs}^+$ : idealized representation of the five close oxygen neighbors with  $\text{Cs-O}$  distances in Ångstroms.

O ranging from 3.245 to 3.672 Å. It is worth noting that the  $\text{Cs}^+$  ion exhibits an irregular coordination in  $\text{CsP}_8\text{W}_8\text{O}_{40}$  and is strongly apart from the center of gravity  $G$  of its oxygen neighbors: 0.853(6) Å if we consider the five close atoms and 0.243(6) Å in the  $\text{O}_{17}$  cage. In both cases the displacement of Cs with respect to  $G$  is very close to the [100] direction. The thermal agitation observed for  $\text{Cs}^+$  is very similar to those observed in other structures where this ion has a small coordination number.  $\text{Cs}^+$  takes a high  $B$  value. The displacements given by the anisotropic thermal agitation are  $\sqrt{U_{11}} = 0.13$ ,  $\sqrt{U_{22}} = 0.35$ , and  $\sqrt{U_{33}} = 0.16$  Å. So, the agitation is important along [010] which just corresponds to the elongation direction of the  $\text{O}_{17}$  cage, without any neighbor for  $\text{Cs}^+$  closer than 4.30 Å.

Besides the  $\text{O}_{17}$  cages, the structure of  $\text{CsP}_8\text{W}_8\text{O}_{40}$  encloses only  $\text{O}_{12}$  cages which derive from perovskite cages by replacement of two octahedra by a diphosphate group. Such cages have been already described in the monoclinic diphosphate bronzes: they look like the  $B$  cages in  $\text{Rb}_x\text{P}_8\text{W}_{32}\text{O}_{112}$  (5). In that latter oxide, the  $\text{P}_2\text{O}_7$  groups contribute to the formation of hexagonal tunnels whereas they contribute to the formation of  $\text{O}_{17}$  cages in  $\text{CsP}_8\text{W}_8\text{O}_{40}$ .

The structure of  $\text{CsP}_8\text{W}_8\text{O}_{40}$  is closely related to the  $\text{ReO}_3$ -type structure, like the mixed-valence tungsten phosphate bronzes previously described. However, the closest relationships are observed between this phase and  $\text{P}_8\text{W}_{12}\text{O}_{52}$  (12). Both structures

can be deduced from a  $\text{ReO}_3$ -type framework by the replacement of one octahedron (Fig. 5a) or two octahedra (Fig. 5b) out of four, by a  $\text{P}_2\text{O}_7$  group, involving a deformation of the resultant host lattice. This operation leads to structures which can be considered as belonging to the same family though they are characterized by very different structural properties. Indeed, as for  $\text{P}_8\text{W}_{12}\text{O}_{52}$  one can describe  $\text{CsP}_8\text{W}_8\text{O}_{40}$  by the coupling of chains running along the [010] direction at levels  $z = \frac{1}{4}$  and  $\frac{3}{4}$  (Fig. 5b). These chains are built up from the periodic succession of two  $\text{WO}_6$  octahedra and one  $\text{P}_2\text{O}_7$  group in  $\text{CsP}_8\text{W}_8\text{O}_{40}$  instead of three  $\text{WO}_6$  and one  $\text{P}_2\text{O}_7$  in  $\text{P}_8\text{W}_{12}\text{O}_{52}$  (Fig. 5a). Different oxides whose structure would be built up from strings  $(\text{WO}_3)_n\text{P}_2\text{O}_4$  of  $n$  octahedra alternating with one  $\text{P}_2\text{O}_7$  group can thus be predicted. These oxides would however exhibit rather different structures as shown by comparing the tunnels formed in  $\text{P}_8\text{W}_{12}\text{O}_{52}$  and  $\text{CsP}_8\text{W}_8\text{O}_{40}$  (Fig. 5). The important difference between these two structures concerns the  $\text{ReO}_3$ -

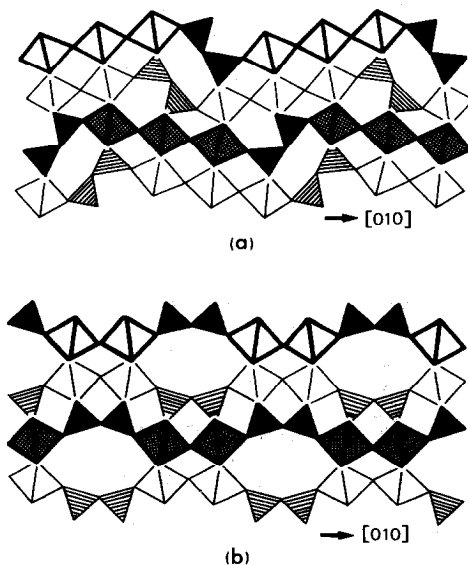


FIG. 5. Schema of the projections along [001] for (a)  $\text{P}_8\text{W}_{12}\text{O}_{52}$  and (b)  $\text{CsP}_8\text{W}_8\text{O}_{40}$ . Stippled octahedra belong to the same chain.

type columns. In  $P_8W_{12}O_{52}$ , the columns running along [001] and characterized by a section of  $2 \times 3$  octahedra, are connected through the  $P_2O_7$  groups, but are also linked directly to one another (Fig. 5a), so that the octahedral framework of  $P_8W_{12}O_{52}$  is three-dimensional. In  $CsP_8W_8O_{40}$ ,  $ReO_3$ -type columns with a  $2 \times 2$   $WO_6$  octahedra section are observed which extend along [001] (Fig. 5b). Contrary to  $P_8W_{12}O_{52}$ , these columns are only linked to one another through  $P_2O_7$  groups so that they are absolutely isolated. Thus this phase should exhibit anisotropic electrical properties:  $CsP_8W_8O_{40}$  represents the first potential unidimensional conductor which has been synthesized in the field of the phosphate tungsten bronzes.

An attractive manner of describing this structure is also to consider the slabs of polyhedra according to the three crystallographic directions of the perovskite framework. The mean plane of the octagonal rings define two of these slabs, which are one-octahedron thick and roughly perpendicular to [103] and  $[10\bar{3}]$ . A projection is drawn on Fig. 6 which shows the  $ReO_3$ -type blocks of four ( $2 \times 2$ )  $WO_6$  octahedra connected through  $P_2O_7$  groups. These groups point alternately an oxygen atom of  $PO_4$  tet-

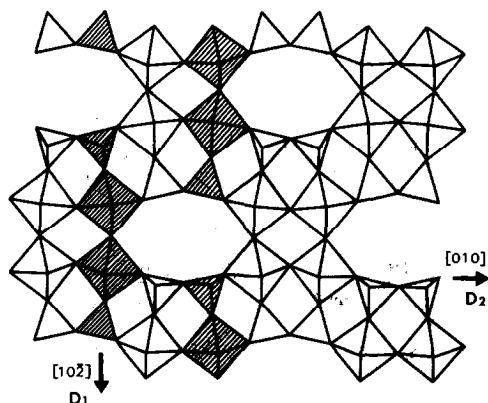


FIG. 6.  $CsP_8W_8O_{40}$ : projection along [103] of the slab corresponding to the mean plane of the octagonal rings.

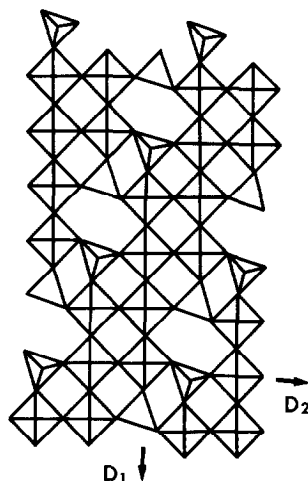


FIG. 7.  $K_xP_2W_4O_{16}$ : schematic representation of a layer of polyhedra parallel to the mean plane of a hexagonal ring.

rahedra on both sides of the slab to realize bonds with other identical slabs. Two successive one-octahedron thick slabs correspond with one another through the  $c$  translation. These slabs are closely related to those observed for the monophosphate tungsten bronzes with hexagonal tunnels  $A_x(PO_2)_4(WO_3)_{2m}$  (9). The structure of  $K_xP_2W_4O_{16}$ ,  $m = 4$  member of this series, can indeed be described by the stacking approximately along  $[2\bar{3}1]$  or  $[23\bar{1}]$  of slabs which exhibit strings built up of four octahedra and bounded by one tetrahedron at both ends in the  $D_1$  direction (Fig. 7) (to be compared to the  $CsP_8W_8O_{40}$  strings which are two octahedra long in the  $D_1$  direction on Fig. 6). In the  $D_2$  direction, the chains of polyhedra are formed of two octahedra which alternate with one  $PO_4$  tetrahedron in  $K_xP_2W_4O_{16}$  (Fig. 7) whereas they alternate with one  $P_2O_7$  group in  $CsP_8W_8O_{40}$  (Fig. 6). The hypothetical structure corresponding to the second member of the  $A_x(PO_2)_4(WO_3)_{2m}$  series is more closely related to that of  $CsP_8W_8O_{40}$  (Fig. 8). Both frameworks would be formed of identical strings in the  $D_1$  direction. It results that the structure of the hypothetical  $m = 2$  member of

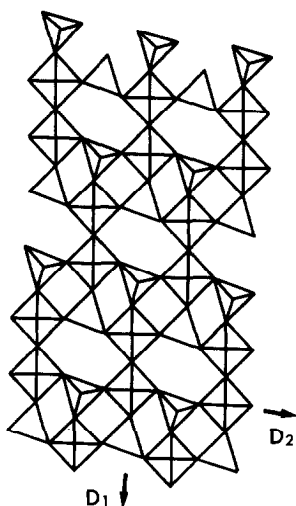


FIG. 8. Schematic representation of a layer in the hypothetical term  $m = 2$  of the monophosphate bronzes series  $A_x(\text{PO}_2)_4(\text{WO}_3)_{2m}$ .

the monophosphate bronzes series can be deduced from the  $\text{CsP}_8\text{W}_8\text{O}_{40}$  bronze by only considering the rows of polyhedra running along the  $D_1$  direction in this latter structure. The simple suppression of one row out of two (like hatched rows in Fig. 6) leads directly from  $\text{CsP}_8\text{W}_8\text{O}_{40}$  to the hypothetical oxide  $A_x(\text{PO}_2)_4(\text{WO}_3)_4$ , forming hexagonal tunnels instead of octagonal tunnels. Thus the intergrowth of the two structures should be possible.

The second type of slabs is parallel to the

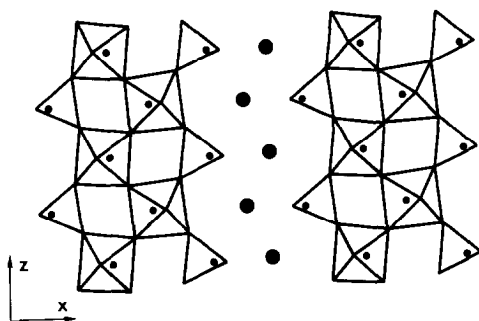


FIG. 9.  $\text{CsP}_8\text{W}_8\text{O}_{40}$ : projection of the structure onto (010). Only one slab is drawn. Small and wide circles are oxygen atoms at  $y = \frac{1}{4}$  and partially occupied Cs sites, respectively.

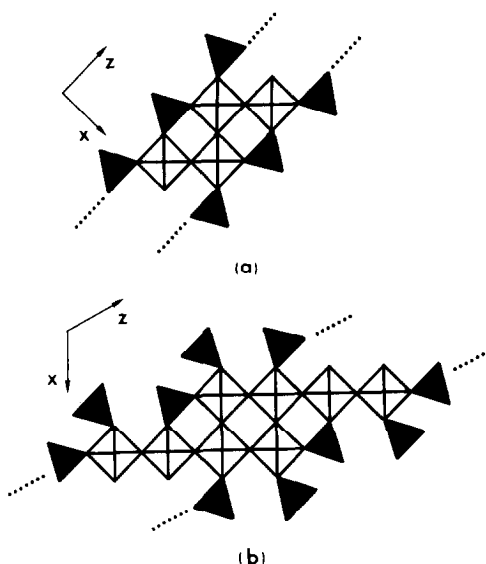


FIG. 10. Constitution of the (010) slabs: (a) in  $\text{CsP}_8\text{W}_8\text{O}_{40}$ , (b) in  $\text{Rb}_2\text{P}_8\text{W}_{16}\text{O}_{64}$ .

(010) plane (Fig. 9). These slabs are built up from two-octahedra thick blocks of the  $\text{ReO}_3$ -type, unlimited in the [001] direction and bounded by the  $\text{P}_2\text{O}_7$  groups which define the tunnels. This arrangement can be compared with that of  $\text{Rb}_2\text{P}_8\text{W}_{16}\text{O}_{64}$  (7) on Fig. 10 where the slabs are projected along [010]. The chains extending between two  $\text{P}_2\text{O}_7$  groups are two-octahedra long in  $\text{CsP}_8\text{W}_8\text{O}_{40}$  whereas in  $\text{Rb}_2\text{P}_8\text{W}_{16}\text{O}_{64}$  they are two-octahedra long in the [100] direction and four-octahedra long in the perpendicular direction. In the latter oxide, the slabs are just superposed, forming hexagonal tunnels which run along [010] whereas they are shifted and form  $\text{O}_{17}$  cages in  $\text{CsP}_8\text{W}_8\text{O}_{40}$ .

## References

1. J. P. GIROULT, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *Acta Crystallogr. Sect. B* **37**, 2139 (1981).
2. A. MAGNÉLI, *Acta Chem. Scand.* **2**, 861 (1948).
3. J. P. GIROULT, M. GOREAUD, PH. LABBÉ, AND B.

- RAVEAU, *Acta Crystallogr. Sect. B* **36**, 2570 (1980).
4. J. P. GIROULT, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *Acta Crystallogr. Sect. B* **37**, 1163 (1981).
  5. J. P. GIROULT, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *Acta Crystallogr. Sect. B* **38**, 2342 (1982).
  6. PH. LABBÉ, D. OUACHÉE, M. GOREAUD, AND B. RAVEAU, *J. Solid State Chem.* **50**, 163 (1983).
  7. J. P. GIROULT, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *Rev. Chim. Miner.* **20**, 829 (1983).
  8. L. KIHNBORG, *Ark. Kemi* **21**(35), 365 (1963).
  9. J. P. GIROULT, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *J. Solid State Chem.* **44**, 407 (1982).
  10. B. DOMENGÈS, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *J. Solid State Chem.* **50**, 173 (1983).
  11. A. BENMOUSSA, D. GROULT, PH. LABBÉ, AND B. RAVEAU, *Acta Crystallogr. Sect. C*, in press.
  12. B. DOMENGÈS, M. GOREAUD, PH. LABBÉ, AND B. RAVEAU, *Acta Crystallogr. Sect. B* **38**, 1724 (1982).
  13. H. KOIZUMI AND J. NAKANO, *Acta Crystallogr. Sect. B* **34**, 3320 (1978).
  14. K. OKADA, F. MARUMO, AND S. IWAI, *Acta Crystallogr. Sect. B* **34**, 50 (1978).
  15. M. GASPERIN, *Acta Crystallogr. Sect. B* **37**, 641 (1981).
  16. A. HUSSAIN, *Chem. Scr.* **11**, 224 (1977).