

# Stabilization of a W(V) Diphosphate, $W_2O_3 \cdot P_2O_7$ , with an Empty Tunnel Structure

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A new form of  $WPO_5$  has been synthesized which is to our knowledge the second pentavalent tungsten phosphate actually known. This phase is isotypic to  $CsP_8W_8O_{40}$  and consequently can be described as a tungsten diphosphate,  $W_2O_3 \cdot P_2O_7$ , with large empty eight-sided tunnels. Although it fundamentally differs from the first form, which is a monophosphate,  $WOPO_4$ , the two structures are closely related by the existence of  $ReO_3$ -type chains and slices, interconnected by  $P_2O_7$  or  $PO_4$  groups, respectively. The stabilization of such an opened structure by adducts such as  $PbF_2$  or  $KBr$  is discussed. © 2000 Academic Press

## INTRODUCTION

Previous investigations of tungsten phosphates have shown the existence of large families of oxides, closely related to the perovskite, called phosphate tungsten bronzes (see for a review Ref. 1) and which are actually studied for their charge density wave properties (see for instance Ref. 2). All these compounds are characterized by a mixed valency of tungsten, i.e., W(VI)–W(V), and often exhibit tunnels generally occupied by univalent or divalent cations. A first issue concerns the possibility of synthesizing such bronzes with large empty tunnels in order to obtain microporous materials with metallic properties. A second question which has not been answered, deals with the rare existence of phosphates with a single W(V) valency, as shown for the P–W–O system, for which  $WOPO_4$  (3) is the only W(V) compound that has been synthesized to date.

In this study, the phosphate tungsten oxides have been revisited, with the objective of stabilizing either W(V) phosphates or microporous tungsten phosphates by working at low temperature, i.e., at about 600°C. For this purpose, we have investigated the Pb–W–P–O system, using seeding agents such as  $PbF_2$  or  $KBr$  for crystal growth. We report herein on the synthesis and crystal structure of a new W(V) diphosphate,  $W_2O_3 \cdot P_2O_7$ , which has the same chemical

composition as the monophosphate  $WOPO_4$ , but which is isotopic to  $CsP_8W_8O_{40}$  (4) and consists of large empty octagonal tunnels.

## EXPERIMENTAL

### *Synthesis and Crystal Growth*

In order to understand the possible stabilization of new W(V) phosphates, the  $P_2O_5$ –“ $W_2O_5$ ” system was revisited, using either  $PbF_2$  or  $KBr$  as adducts. Different attempts which were first made starting from the nominal composition “ $WPO_5$ ” (corresponding to the monophosphate  $WOPO_4$  (3)) and using successively  $PbF_2$  and  $KBr$  as adducts. In these conditions a mixture of three phases was systematically obtained:  $WOPO_4$ ,  $W_{12}P_8O_{52}$  (5), and of a new phase isotypic to the tunnel structure,  $CsP_8W_8O_{40}$  (4). The synthesis of the latter tunnel structure, in spite of the absence of cesium, led us to carry further this investigation, suggesting a possible replacement of cesium by lead. Nevertheless, varying the synthesis conditions—temperature, time, and adduct content—always led to a mixture of these three phases. To understand this phenomenon, attempts were made to grow single crystals of the so-called tunnel structure.

The crystal growth of the new phase was carried out from a mixture of  $PbCO_3$ ,  $H(NH_4)_2PO_4$ ,  $WO_3$ , W, with  $PbF_2$  or  $KBr$  adducts. The best results were obtained by heating a mixture of  $PbCO_3$ ,  $H(NH_4)_2PO_4$  and  $WO_3$  in the molar ratio 1:8:1.333 first in air at 400°C to decompose the salts. Then the resulting products were added to 0.666 mol of metallic tungsten and 3% weight of  $PbF_2$ . After thorough grinding, the mixture was heated in an evacuated silica ampule at 580°C for 3 h and at 550°C for 10 h and then was slowly cooled at 3°C h<sup>-1</sup> down to 330°C and finally quenched at room temperature. Under these conditions more than 50% of the batch was found to be composed of well-formed gold copper crystals, besides a blue polycrystalline phase which was not identified.

### X-ray Structure Determination

A golden crystal with dimensions  $0.17 \times 0.08 \times 0.08$  mm was selected for the structure determination. Its quality was tested by X-ray film technique. The cell parameters (Table 1) were determined with a least squares method using 25 reflections with  $18^\circ < \theta < 22^\circ$ . The data were recorded at room temperature on an Enraf-Nonius CAD4 diffractometer using the  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) isolated with a graphite monochromator. Intensities were checked by monitoring three standard reflections every hour. No significant deviations in intensities were observed. The intensity data were corrected for the Lorentz, polarization, and absorption effects. The systematic absences  $k + l = 2n + 1$  in  $0kl$  and  $h = 2n + 1$  in  $hk0$  are consistent with the  $Pnma$  (62) and the  $Pn2_1a$  (33) space groups. The Harker line  $0V0$  observed on the Patterson function is characteristic of the centrosymmetric space group  $Pnma$  (62).

The structure was solved with the heavy atom method. The full-matrix least squares refinements were performed on  $F$  using a SPARC station with the Xtal 3.4 system (6).

### RESULTS AND DISCUSSION

The atomic parameters (Table 2) of this new phase, obtained for low reliability factors,  $R = 0.023$  and  $R_w = 0.026$ , clearly show that it is isostructural to  $CsP_8W_8O_{40}$  (4) but that there is no cation in the  $Cs^+$  site. Consequently, this phase is a diphosphate and should be formulated  $W_2O_3 \cdot P_2O_7$ . As shown from its projection along  $a$  (Fig. 1), this structure consists of dioctahedral  $W_2O_{11}$  units interconnected with  $P_2O_7$  groups and forms large elliptic tunnels which are empty. Thus, the structure of  $W_2O_3 \cdot P_2O_7$ , like that of  $CsP_8W_8O_{40}$ , is built up of mixed-octahedral-tetrahedral- $[W_2P_2O_{16}]_\infty$  chains running along  $b$  (Figs. 1 and 2), in which one dioctahedral unit  $W_2O_{11}$  alternates with one  $P_2O_7$  groups. The entire structure results from the

**TABLE 1**  
Summary of Crystal Data, Intensity Measurement, and Structure Refinement Parameters for  $W_2O_3P_2O_7$

Chemical formula	$W_2P_2O_{10}$
Molar weight	589.642
Crystal system	Orthorhombic
Space group	$Pnma$ (62)
$\mu$ ( $MoK\alpha$ )	$27.44 \text{ mm}^{-1}$
Agreement factors	$R = 0.0234, R_w = 0.0262$
Cell dimensions	$a = 5.2886(4) \text{ \AA}$ $b = 12.3391(10) \text{ \AA}$ $c = 13.0321(6) \text{ \AA}$
Volume	$850.4(1) \text{ \AA}^3$
Temperature of data collection	$21^\circ\text{C}$
$Z$	4
Reflections with $I > 3\sigma(I)$	1764
No. of variables	68

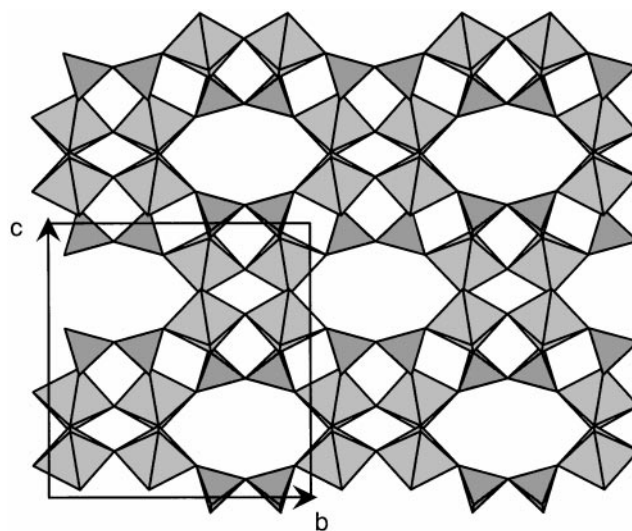
**TABLE 2**  
Atomic Coordinates and Thermal Factors of  $W_2O_3P_2O_7$

	$x$	$y$	$z$	$U_{eq}$
W	0.24398(4)	0.39980(1)	0.15261(1)	0.00624(3)
P	0.2671(4)	0.6305(1)	0.0240(1)	0.0070(2)
O(1)	0.238(1)	0.5607(3)	0.1155(3)	0.0114(8)
O(2)	0.4751(9)	0.3812(4)	0.0276(4)	0.013(1)
O(3)	-0.0541(9)	0.3848(5)	0.0547(4)	0.015(1)
O(4)	0.248(2)	0.25	0.1685(4)	0.011(1)
O(5)	0.5162(9)	0.4190(3)	0.2398(4)	0.009(1)
O(6)	0.249(2)	0.75	0.0666(4)	0.012(1)

Note.  $U_{eq} = \frac{1}{3} \sum_i u_{ii}$ .

assemblage of those chains through the corners of their polyhedra. Each octahedral  $W_2O_{11}$  unit of one  $[010]$  chain shares two apices with a  $W_2O_{11}$  unit of an adjacent chain, and two other apices with a  $P_2O_7$  group of a second adjacent chain (Fig. 1).

One remarkable feature of this new phase concerns its chemical composition, identical to that of the monophosphate  $WOPO_4$  (3). These two forms of  $WPO_5$  are fundamentally different by the fact that they are diphosphate and monophosphate, respectively, and that the first one,  $W_2O_3P_2O_7$ , forms large empty tunnels, whereas the second one is much more compact, forming only small empty five-sided tunnels. Nevertheless, both structures exhibit close relationships, as shown by comparing the projection of the structure of  $W_2O_3 \cdot P_2O_7$  along  $b$  (Fig. 3a) with the projection of a part of the structure of  $WOPO_4$  along  $1\bar{1}0$  (Fig. 3b). One indeed observes the great tendency to form



**FIG. 1.** Projection of the structure of  $W_2O_3P_2O_7$  along  $a$  showing the large empty eight-sided tunnel. The double  $ReO_3$ -type zigzag chains are perpendicular to the projection.

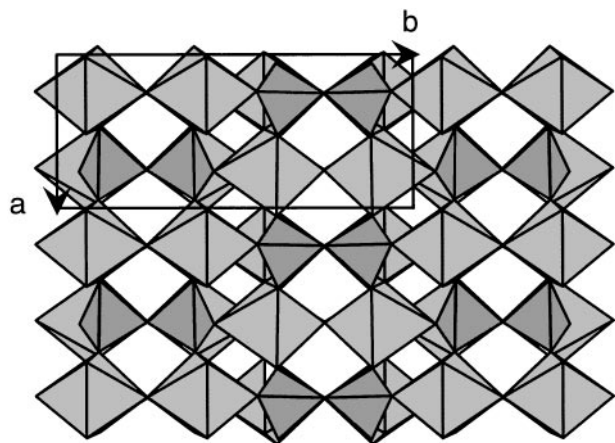


FIG. 2. Projection of the structure of  $W_2O_3P_2O_7$  along  $c$  showing the stacking of the  $[W_2P_2O_{16}]_{\infty}$  chains.

a  $ReO_3$ -type framework in both cases. Both structures form indeed  $ReO_3$ -type zig-zag chains running along  $a$  for  $W_2O_3P_2O_7$  (Fig. 3a) and along  $c$  for  $WOPO_4$  (Fig. 3b), interconnected by rows of  $P_2O_7$  groups and single  $PO_4$  tetrahedra, respectively. Nevertheless double  $ReO_3$ -type zig-zag chains are generated in  $W_2O_3P_2O_7$  (Fig. 1), whereas the  $WOPO_4$  structure consists of single  $ReO_3$ -type zig-zag chains (Fig. 4).

The geometry of the  $WO_6$  octahedra is distorted and shows two sets of W–O distances, a set of short distances ranging from 1.849(5) to 1.864(5) Å corresponding to the W–O–W bonds and a set of longer ones ranging from 2.036(5) to 2.049(5) Å, corresponding to the W–O–P bonds (Table 3).

The  $PO_4$  tetrahedra exhibit the classical geometry seen in the  $P_2O_7$  groups, i.e., one long bond of 1.597(2) Å corresponding to the oxygen atom bridging the two phosphorous atoms and three shorter ones ranging from 1.504(5) to 1.517(4) Å corresponding to the P–O–W bonds. It is worth pointing out that all the bond distances of  $W_2O_3P_2O_7$  are equal within the experimental errors ( $0 < t_{\text{student}} < 1.4$ ) to the corresponding distances of the  $CsP_8W_8O_{40}$  phosphate bronze (4). This demonstrates that the  $[W_2P_2O_{10}]_{\infty}$  framework, although it is favored by the presence of a big cation like  $Cs^+$ , is very rigid and is not significantly distorted by its presence. The very high thermal factor observed for cesium in  $CsP_8W_8O_{40}$  (4), emphasizes the room left for this cation in the structure and explains why cations smaller than  $Cs^+$  cannot stay in the structure and consequently move out.

The above results raise the issue of the role of the  $Pb^{2+}$  or  $K^+$  cations, combined with halogenides such as  $F^-$  or  $Br^-$ , for the stabilization of the structure of  $W_2O_3 \cdot P_2O_7$ . The EDS analysis of the crystal used for the XRD study shows a high Pb content near the center of the crystal in an area of about the size of the electron beam ( $\approx 1 \mu m$  diameter), whereas the rest of the crystal does not show any Pb trace

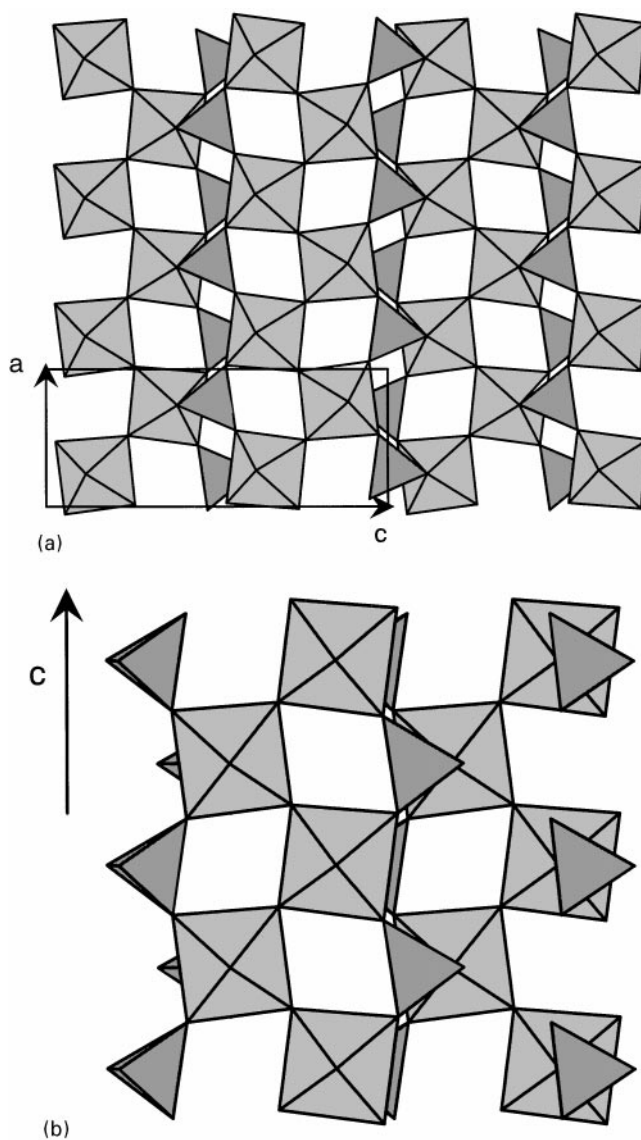


FIG. 3. (a) Projection of the structure of  $W_2O_3P_2O_7$  along  $b$  showing the  $ReO_3$ -type zig-zag chains. The triangles represent  $P_2O_7$  groups projected along  $b$ . (b) Projection a part of the structure of  $WOPO_4$  along  $[1 \bar{1} 0]$ . The triangles correspond to single  $PO_4$  tetrahedra.

from EDS. In contrast no trace of potassium has been detected. This suggests that  $Pb^{2+}$  cations or  $PbF_2$  molecules play the role of seeds for the nucleation of this metastable microporous structure, so that at the beginning of its formation lead cations may be blocked in the structure and then the entire frameworks would grow further from these lead-containing nuclei without needing more adducts, so that the major part of the crystal consists of large empty cages.

In conclusion, a new form of  $WPO_5$  has been grown, using either  $KBr$  or  $PbF_2$  as stabilizers. It is, to our knowledge, the second tungsten phosphate in which tungsten is purely pentavalent. This new form differs from the first one

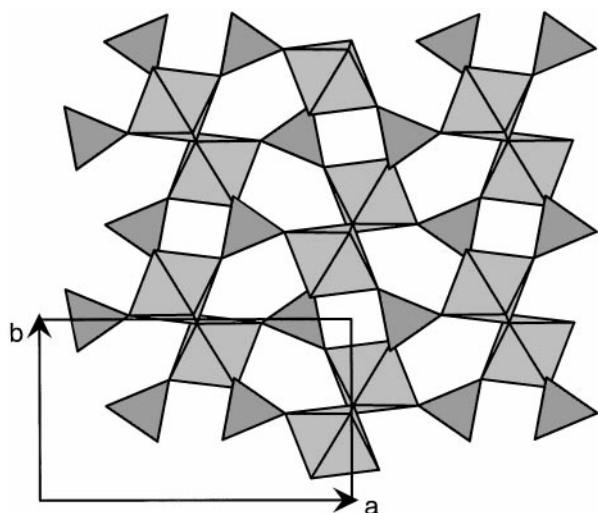


FIG. 4. Projection of the structure of  $WOPO_4$  along  $c$ . The single  $ReO_3$ -type zig-zag chains are perpendicular to the projection.

by the fact that it is built up of diphosphate groups instead of monophosphate groups so that it must be formulated  $W_2O_3 \cdot P_2O_7$  instead of  $WO \cdot PO_4$ . Nevertheless, close relationships between the two structures can be emphasized, showing that  $ReO_3$ -type chains or slices remain the basis of the two frameworks. More importantly, the remarkable feature of  $W_2O_3 \cdot P_2O_7$ , deals with its isotypism with  $CsP_8W_8O_{40}$ , showing large empty tunnels. The stabilization of such an opened framework without any invited cation, by using adducts such as  $PbF_2$  or  $KBr$  suggests that

TABLE 3  
Selected Bond Lengths

W-O(1)	= 2.044(4) Å
W-O(2)	= 2.049(5) Å
W-O(3)	= 2.036(5) Å
W-O(4)	= 1.860(1) Å
W-O(5)	= 1.849(5) Å
W-O(5 <sup>i</sup> )	= 1.864(5) Å
P-O(1)	= 1.517(4) Å
P-O(2 <sup>ii</sup> )	= 1.507(5) Å
P-O(3 <sup>iii</sup> )	= 1.504(5) Å
P-O(6)	= 1.597(2) Å

Note. Symmetry codes: i,  $x - \frac{1}{2}, y, \frac{1}{2} - z$ ; ii,  $1 - x, 1 - y, -z$ ; iii,  $-x, 1 - y, -z$ .

such a method should be applied to the synthesis of many other microporous phosphates.

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