

$P_8W_{12}O_{52}$: A Mixed-Valence Tungsten Oxide Built up from WO_6 Octahedra and P_2O_7 Groups

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Abstract

$P_8W_{12}O_{52}$ crystallizes in the orthorhombic system, space group $Pnam$, with $a = 11.9866$ (11), $b = 15.5500$ (15) and $c = 5.3197$ (13) Å. The structure was solved by the heavy-atom method and refined to $R = 0.036$ ($R_w = 0.044$) for 1604 observed reflections. The framework of this structure, built up of WO_6 octahedra and P_2O_7 groups, can be described as ReO_3 -type blocks connected through P_2O_7 groups and determining the existence of pseudo-pentagonal and distorted hexagonal tunnels. This opened framework is compared to that of $P_4W_8O_{32}$. The possibility of insertion of cations like Li^+ and Na^+ in the cavities limited by 12, 13, 14 and 15 oxygen atoms is considered.

Introduction

Since the discovery by Magnéli (1953) of the famous tungsten bronzes A_xWO_3 , mixed-valence tungsten oxides have been extensively studied for their electrical properties due to the presence of d electrons. All these compounds are characterized by an octahedral framework over which the conducting electrons are generally delocalized. Unlike octahedral structures, few oxide networks built up from tetrahedra and octahedra and exhibiting a metallic conductivity are known at the present time. The recent studies concerning the adaptability of the PO_4 tetrahedra to an octahedral framework have shown the existence of two series of microphases $A_xP_8W_{8n}O_{24n+16}$ (Giroult, Goreaud, Labbé & Raveau, 1980, 1981*a*) and $P_4W_{4n}O_{12n+8}$ (Giroult, Goreaud, Labbé & Raveau, 1981*b*). Moreover, it has been shown that these compounds, whose host lattice is built up from ReO_3 -type slabs connected respectively through P_2O_7 groups and PO_4 tetrahedra, exhibit metallic properties similar to those of the sodium tungsten bronzes (Giroult, Goreaud, Labbé, Provost & Raveau, 1981). However, among the $P_4W_{4n}O_{12n+8}$ compounds, phosphorus-rich terms ($n <$

2) were not obtained: for this region of the P–W–O system, a new phase appeared which did not seem to be strongly related to the structures previously studied. We describe here the compound $P_8W_{12}O_{52}$ of this new structural type.

Experimental

Sample preparation

A mixture of $H(NH_4)_2PO_4$ and WO_3 in appropriate ratios was first heated in air at 773 K to decompose the phosphate; the resultant product was then mixed with an adequate amount of W and heated in an evacuated silica ampoule at 1373 K.

Among the preparations corresponding to the general composition $P_4W_{4n}O_{12n+8}$ with $n < 2$, a new phase with $n = 1.5$ appeared. The structural study later confirmed its composition as $P_8W_{12}O_{52}$. The crystals looked like prismatic needles, optically transparent and deep red.

Structure determination

The Weissenberg photographs showed the crystal symmetry to be orthorhombic. The observed systematic absences confirmed later by electron-microscopy patterns, $h0l$ $h = 2n + 1$ and $0kl$ $k + l = 2n + 1$, led to the space groups $Pna2_1$ and $Pnam$. The centrosymmetric group was found to be correct during the structure determination.

The intensities were collected on a CAD-4 Enraf–Nonius four-circle diffractometer with graphite-monochromatized $Mo K\alpha$ radiation, from a prismatic crystal ($12 \times 12 \times 340 \mu m$) up to a maximum Bragg angle of 45° . The lattice parameters were refined by least squares from the θ values of 25 reflections. The parameters of the data collection were fixed after a study of several reflection shapes in the plane (θ , ω). 1604 reflections with $\sigma(I)/I < 0.333$ were finally retained in an independent space, then corrected for

Table 1. Positional parameters with e.s.d.'s for $P_8W_{12}O_{52}$

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | B^* (\AA^2) |
|------|-------------|-------------|---------------|--------------------------|
| P(1) | 0.1997 (4) | 0.4382 (3) | $\frac{1}{4}$ | 0.39 (6) |
| P(2) | 0.0176 (4) | 0.6532 (3) | $\frac{3}{4}$ | 0.36 (6) |
| W(1) | 0.86810 (6) | 0.10185 (5) | $\frac{1}{4}$ | 0.20 (1) |
| W(2) | 0.08270 (7) | 0.13543 (5) | $\frac{3}{4}$ | 0.23 (1) |
| W(3) | 0.29710 (6) | 0.16244 (5) | $\frac{1}{4}$ | 0.19 (1) |
| O(1) | 0.3775 (14) | 0.5180 (12) | $\frac{1}{4}$ | 0.81 (22) |
| O(2) | 0.2169 (16) | 0.5334 (12) | $\frac{3}{4}$ | 0.97 (23) |
| O(3) | 0.0695 (16) | 0.4230 (13) | $\frac{1}{4}$ | 1.05 (23) |
| O(4) | 0.2456 (11) | 0.3984 (8) | 0.4849 (28) | 1.14 (16) |
| O(5) | 0.4735 (10) | 0.3831 (8) | 0.5024 (27) | 0.76 (13) |
| O(6) | 0.0842 (11) | 0.6387 (8) | 0.5107 (26) | 1.01 (15) |
| O(7) | 0.3068 (10) | 0.6647 (8) | 0.4976 (27) | 0.88 (15) |
| O(8) | 0.3355 (15) | 0.2735 (11) | $\frac{3}{4}$ | 0.70 (20) |
| O(9) | 0.0444 (17) | 0.2611 (13) | $\frac{1}{4}$ | 1.16 (26) |

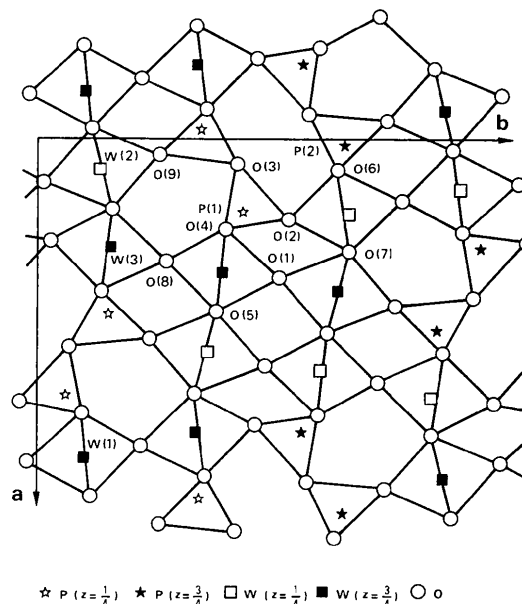
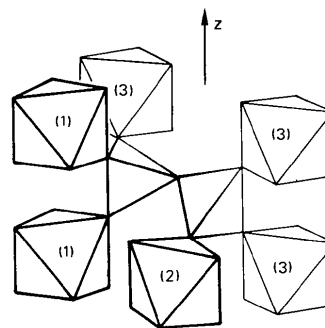
* B_{eq} for W(1), W(2), W(3).

Fig. 1. Projection of the structure on (001).

Lorentz and polarization effects. An absorption correction based on the indexed {110} and {001} forms of the crystal morphology was applied: the maximum and minimum values of the transmission factor were 0.672 and 0.561. The structure was solved by the heavy-atom method. The W positions, given by the Patterson-function study, were refined and the other atoms were located in the subsequent difference synthesis. Using the scattering factors for W^{6+} , P (Cromer & Waber, 1965) and O^{2-} (Suzuki, 1960), and the anomalous-dispersion tables of Cromer (1965), the coordinates were refined by full-matrix least squares. A linear weighting scheme was adjusted according to $\langle w|F_o| - |F_c| \rangle$ in terms of $\sin \theta/\lambda$. An isotropic extinction correction was tested but gave only minor corrections. The final atomic parameters given in Table 1 led to $R = 0.036$ and $R_w = 0.044$.*

Description of the structure and discussion

The structure of $P_8W_{12}O_{52}$ is built up from corner-sharing WO_6 octahedra and P_2O_7 groups (Fig. 1). Each tetrahedron shares its corners with three octahedra and one tetrahedron, forming $P_2W_6O_{37}$ units (Fig. 2) in which a set of three octahedra is approximately rotated by about $\pi/3$ with respect to the other set, owing to the staggered configuration of the pyrophosphate groups. The three symmetrically independent octahedra of the structure are surrounded in a different way: the $W(1)O_6$ octahedron shares its corners with two

Fig. 2. The $P_2W_6O_{37}$ unit in projection on (031). $W(1)O_6$, $W(2)O_6$ and $W(3)O_6$ octahedra are labelled (1), (2) and (3).

tetrahedra and four octahedra, the $W(2)O_6$ octahedron is linked to five octahedra and one tetrahedron, while the $W(3)O_6$ octahedron shares its corners with three octahedra and three tetrahedra. The geometry of the units formed by these groups of six polyhedra is worthy of note: the disposition of the polyhedra around the WO_6 octahedra is similar to that observed in perovskite; the polyhedral groups centred on W(3) are, however, more distorted due to the greater number of tetrahedra.

Comparison of this structure with that of the $Rb_xP_8W_{8n}O_{24n+16}$ family (Giroult *et al.*, 1980) shows that the P_2O_7 groups can accommodate an octahedral framework in different ways. However, one can note here a certain adaptability of the P_2O_7 groups by means of distortion: Table 2 gives classical distances for P—O but the P—O—P angle is not as large as in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36739 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *The P_2O_7 group: interatomic distances (Å) and angles (°)*

| Neighbour <i>N</i> | P(2) | O(2) | O(3) | O(4) | O(6) | O(9) |
|---------------------|-----------|----------|-----------|---------------|---------------|---------------|
| P(1)— <i>N</i> | 2.967 (7) | 1.49 (2) | 1.58 (2) | 2 × 1.50 (1) | | |
| P(1)—O(3)— <i>N</i> | 139.9 (9) | | | | | |
| O(2)—P(1)— <i>N</i> | | | 106.5 (7) | 2 × 111.0 (7) | | |
| O(3)—P(1)— <i>N</i> | | | | 2 × 107.6 (7) | | |
| O(4)—P(1)— <i>N</i> | | | | 112.9 (8) | | |
| P(2)— <i>N</i> | | | 1.58 (2) | | 2 × 1.52 (1) | 1.52 (2) |
| O(3)—P(2)— <i>N</i> | | | | | 2 × 103.6 (7) | 109.5 (7) |
| O(6)—P(2)— <i>N</i> | | | | | 113.8 (7) | 2 × 112.7 (7) |

Table 3. *Coordination of W in $P_8W_{12}O_{52}$: interatomic distances (Å)*

| Neighbour <i>N</i> | W(1)— <i>N</i> | W(2)— <i>N</i> | W(3)— <i>N</i> |
|--------------------|----------------|----------------|----------------|
| O(1) | 1.87 (2) | 1.89 (2) | |
| O(2) | | | 2.01 (2) |
| O(4) | 2 × 2.04 (1) | | |
| O(5) | 2 × 1.84 (1) | 2 × 1.90 (1) | |
| O(6) | | | 2 × 2.02 (1) |
| O(7) | | 2 × 1.94 (1) | 2 × 1.81 (1) |
| O(8) | 1.98 (2) | | 1.79 (2) |
| O(9) | | 2.01 (2) | |

$Rb_xP_8W_{32}O_{112}$ (140° instead of 153°). Moreover, the PO_4 tetrahedra of the P_2O_7 group are rotated with respect to one another by $\pi/3$, whereas they form an eclipsed configuration in the previously studied series (Giroult *et al.*, 1980, 1981a). So, the P_2O_7 groups in $P_8W_{12}O_{52}$ have almost the same geometry as in α - $Mg_2P_2O_7$ described by Calvo (1967).

Concerning the coordination of the tungsten atoms, comparison of the W—O distances in Table 3 shows that they are more homogeneous in the case of the W(2) atoms than for W(1) and W(3) which have a 3 + 3 coordination. The displacement of each W from the centre of gravity of the O atoms is 0.08 (1) Å for W(2), 0.15 (1) Å for W(1) and 0.19 (1) Å for W(3). These values can be compared with the displacements observed in other structures such as those described by Magnéli (1956), the families $Rb_xP_8W_{8n}O_{24n+16}$ and $P_4W_{4n}O_{12n+8}$ (Giroult *et al.*, 1980, 1981a,b) and the hexagonal bronzes In_xWO_3 (Labbé, Goreaud, Raveau & Monier, 1979). The results confirm the observations made on $P_4W_8O_{32}$: here, the mean oxidation number is 5.33 for W and the WO_6 octahedra should be regular. This is almost the case for W(2)O₆ which is linked with one tetrahedron only. In contrast, W(1) and W(3) are more distorted because they have two and three PO_4 neighbours respectively.

The projection on to (001) shows that this structure is related to that of ReO_3 (Fig. 3): it can indeed be considered as an ReO_3 -type framework in which one octahedron out of four is replaced by a P_2O_7 group. So, $P_8W_{12}O_{52}$ can be described by the coupling of chains

whose mean direction is parallel to the **b** axis and running at levels $z = \frac{1}{4}$ and $\frac{3}{4}$. These chains are formed by units of three WO_6 octahedra and one P_2O_7 group. The units of three WO_6 are tilted with an inclination of $\pm 10.5^\circ$ with respect to the [010] direction. The chains are linked together through their O atoms lying at $z \sim 0$ and $\frac{1}{2}$, and the connection between two chains is realized in two different ways: if the chains at levels $z = \frac{1}{4}$ and $\frac{3}{4}$ are strictly parallel, the P_2O_7 groups delimit distorted hexagonal tunnels running in the [001] direction; if the units of the chains are not parallel, then the coupling forms tunnels with a pentagonal section (Fig. 3). Comparison with the hypothetical term $n = 3$ of the series $P_4W_{4n}O_{12n+8}$ (Giroult *et al.*, 1981b) shows that the only difference between the units of the chains is the existence of P_2O_7 groups in $P_8W_{12}O_{52}$ instead of single PO_4 tetrahedra as in $P_4W_{12}O_{44}$. The consequence is very important for the structure because the orientation of two successive units of three WO_6 in the same chain is quite different in the case of single PO_4 (zig-zag chains) and in the case of P_2O_7 groups (almost linear chains). Another consequence is the formation of pseudo-hexagonal tunnels in the second case.

The structure can also be described as ReO_3 -type blocks of two octahedra thick along [100], three octahedra thick along [010] and extending indefinitely along [001]. These blocks, which are connected through P_2O_7 groups, form infinite S_1 and S_2 slabs (Fig. 3) parallel to (100). The connection between two adjacent S_1 and S_2 slabs, made through the corners of their octahedra and P_2O_7 groups, determines an orientation change of the ReO_3 -type blocks from S_1 to S_2 . On the other hand, in two successive S_1 (or S_2) slabs the orientation of the blocks is identical, but those, compared with ReO_3 -type blocks, are shifted with respect to each other by one half the height of an octahedron.

The relation of the structure to the ReO_3 type can be easily understood by considering it along the **b** axis (Fig. 4). The framework is built up from identical puckered sheets S' (Fig. 3) parallel to (010). These sheets which are one octahedron thick are built up from three-octahedra-wide perovskite slabs linked through P_2O_7 groups forming rows of pseudo-hexagonal rings parallel to **c**. Along **b**, S' sheets are stacked together so

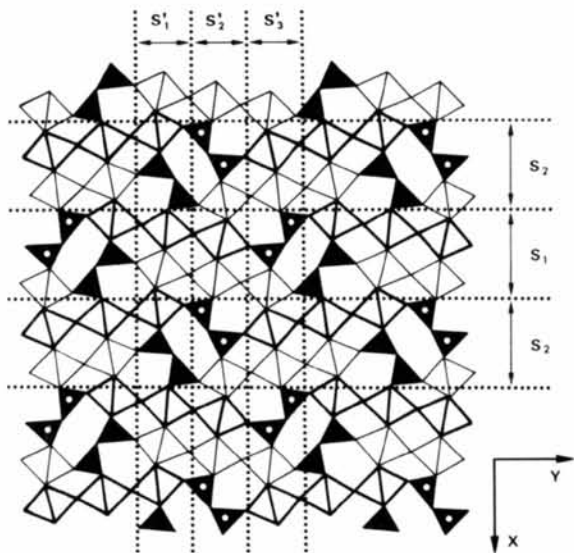


Fig. 3. Schematic projection on (001): the octahedra with dark and light outlines lie at the levels $z = \frac{1}{4}$ and $\frac{1}{2}$ respectively. The tetrahedra with a white circle lie at the level $z = \frac{3}{4}$.

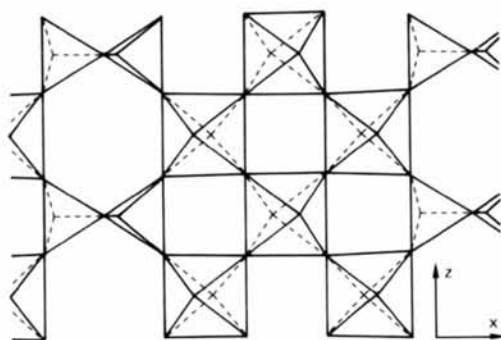


Fig. 4. Projection on (010) showing the ReO_3 -type slabs and the rows of quasi-hexagonal windows.

that they are related either by inversion (e.g. for S'_1 and S'_2) or by an a glide plane (e.g. for S'_2 and S'_3), the period along \mathbf{b} being reached every four slabs (Fig. 3).

This framework delimits two sorts of tunnels running along [001]: distorted pentagonal and distorted hexagonal tunnels. The pentagonal tunnels result from the stacking along c of pentagonal rings, like those of $\text{P}_4\text{W}_8\text{O}_{32}$ (Giroult *et al.*, 1981*b*), but here the rings are made of three WO_6 and one P_2O_7 group instead of two isolated PO_4 as in $\text{P}_4\text{W}_8\text{O}_{32}$. The pentagonal tunnels are narrower than in $\text{Ti}_2\text{W}_4\text{O}_{13}$ (Goreaud, Labbé, Monier & Raveau, 1979) or in the tetragonal bronzes described by Magnéli (1949*a,b*); the minimum distance from the centre of a pentagonal ring to the surrounding O atoms [1.69 (1) Å] is smaller than that observed in $\text{P}_4\text{W}_8\text{O}_{32}$ [1.90 (4) and 1.96 (5) Å]. The distorted hexagonal tunnels result from the stacking along [001] of rings made of two WO_6 and two P_2O_7 groups (Fig.

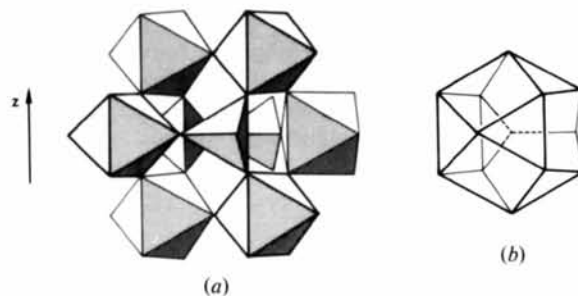


Fig. 5. The ' O_{13} ' cage. (a) The polyhedra delimiting the cage. (b) Figure formed by the 13 O atoms.

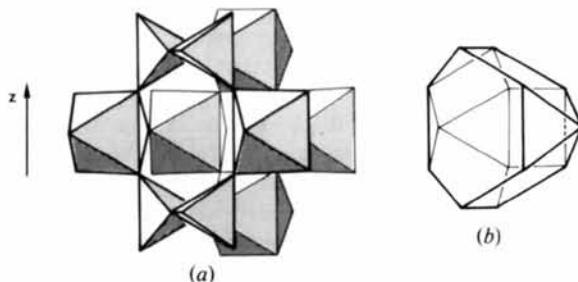


Fig. 6. The ' O_{14} ' cage. (a) The polyhedra delimiting the cage. (b) Figure formed by the 14 O atoms.

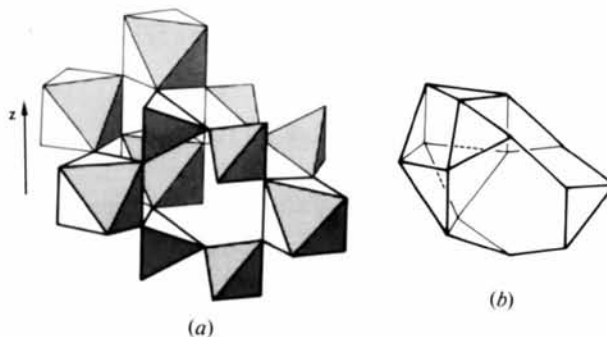


Fig. 7. The ' O_{15} ' cage. (a) The polyhedra delimiting the cage. (b) Figure formed by the 15 O atoms.

3). The minimum distance from the centre of the ring to the O atoms is 1.97 (1) Å and involves the bridging O atom in P_2O_7 .

Another similarity of this structure to the $\text{P}_4\text{W}_8\text{O}_{32}$ structure is the interconnection of the two sorts of tunnels through quasi-hexagonal windows. Once again these windows result from the association of two WO_6 and two P_2O_7 (Fig. 4) but they are symmetrically independent of the previously described rings, and more regular. The pseudo-hexagonal windows of $\text{P}_4\text{W}_8\text{O}_{32}$ are made of three WO_6 and three PO_4 but their sizes, however, are very similar: the minimum distance from the centre of the window to the O atoms in $\text{P}_8\text{W}_{12}\text{O}_{52}$ is 2.43 (1) Å compared with 2.28 (4) or 2.30 (4) Å in $\text{P}_4\text{W}_8\text{O}_{32}$. The number of interconnected tunnels is

different in the two structures: in P₄W₈O₃₂ an infinite number of face-sharing pentagonal tunnels forms a 'plane', while in P₈W₁₂O₅₂ only two pentagonal tunnels are interconnected through a pseudo-hexagonal tunnel, forming units of three face-sharing tunnels. As a result, this structure may also be considered as forming three sorts of face-sharing cages bounded by 13, 14 and 15 O atoms respectively. The 'O₁₃' cages are delimited by six WO₆ octahedra and three PO₄ tetrahedra (Fig. 5), the 'O₁₄' cages are built up from six WO₆ and two P₂O₇ groups (Fig. 6) and the 'O₁₅' cages from five WO₆ and three P₂O₇ groups (Fig. 7). The 'O₁₃' and 'O₁₄' cages share their two pentagonal faces along the pentagonal tunnel axis. For the 'O₁₅' cages, the pseudo-hexagonal faces are common, forming the second sort of tunnel, while the 'O₁₄' and 'O₁₅' cages share a pseudo-hexagonal face which is the pseudo-hexagonal window previously described. It is worth noting that the geometry of these cavities is partly related to the ReO₃ cages. Besides these cavities forming the tunnels, 'O₁₂' cages derived from that of perovskite are observed: they are built up from seven octahedra and one tetrahedron and have already been described in the P₄W₈O₃₂ structure (Giroult *et al.*, 1981*b*). The presence of all these cavities implies that this structure must be considered as an opened framework. The minimum distances from the centre of the cavities to the O atoms are as follows: 2.34 (1) Å for 'O₁₃', 2.66 (1) Å for 'O₁₄',

and 2.45 (1) Å for 'O₁₅'. In 'O₁₂' all the distances are close to 2.7 Å except the distance to the bridging O atom of P₂O₇, which is very short [2.11 (2) Å]. The insertion of ions such as Li⁺ and Na⁺ will be considered.

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Les Complexes à Transfert de Charge Octasoufre–Sulfurimine. Etude Structurale du Composé Octasoufre–Cyclotétraazathiane (3 : 1)

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Abstract

Octasulphur–sulphurimine charge-transfer complexes were prepared and studied by chemical analysis and infrared spectroscopy. 3S₈–S₄(NH)₄ is monoclinic, P2₁/n, with *a* = 8.440 (3), *b* = 13.034 (4), *c* =

8.203 (3) Å, β = 112.49 (2)°, *Z* = 1. It is constituted of two independent eight-membered-ring molecules in a crown conformation in which S and N atoms are distributed at random over all the sites. Refinement of the structure gives an index *R* = 0.039 for 1557 independent reflexions. The arrangement found is