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BRIEF COMMUNICATION

Crystal Structure of WPO_5, the Second Member of the Monophosphate Tungsten Bronze Series $(WO_3)_{2m}(PO_2)_4$

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Sealed tube reactions of WO_3, P_2O_5, and W metal at 1250°C give crystals of WPO_5. The compound was characterized by single-crystal X-ray diffraction data with $a = 11.174(3)$, $b = 6.550(2)$, $c = 5.228(1)$ Å, $Z = 4$, in the space group $Pna2_1$. The structure was refined to $R(F) = 0.0273$ and $R_w = 0.0268$ for 547 independent reflections with $I > 3.0\ \sigma(I)$. This compound, which contains only W^{5+}, is composed of corner-sharing WO_6 octahedra and PO_4 tetrahedra. Pentagonal tunnels along the c-axis are formed by the edges of three octahedra and two tetrahedra. The framework can also be described as built up from ReO_3-type slabs which are connected through phosphate groups. It corresponds to the second member ($m = 2$) of the monophosphate tungsten bronze series $(WO_3)_{2m}(PO_2)_4$.

Introduction

The structures of several compounds corresponding to the general formula $(WO_3)_{2m}(PO_2)_4$ have been determined from single crystals for $m = 3, 4, 5, 6$, and 8. $W_8P_4O_{32}$ ($m = 4$) (*1*), $W_{12}P_4O_{44}$ ($m = 6$) (*2*), and $W_{16}P_4O_{56}$ ($m = 8$) (*2*) are each built up of ReO_3-type slabs and planes of PO_4 tetrahedra where $m/2$ determines the width of the slabs. $W_{10}P_4O_{38}$ ($m = 5$) (*3*) can be considered an intergrowth of the members $m = 6$ and $m = 4$. Interestingly, $W_6P_4O_{26}$ ($m = 3$) (*4*), which can be described as ReO_3-type blocks connected through P_2O_7 groups, does not seem to be strongly related to the other structures. However, the lower members, especially the second member of the series, were never observed. The structure of the second member, WPO_5, was predicted, but it was considered unstable at high temperature (*5*). In an attempt to prepare a tungsten analog of $Mo_3P_5SiO_{19}$ (*6*) at 1250°C we discovered WPO_5 by chance. The present paper deals with the synthesis and crystal structure of WPO_5 which corresponds to the second member of the monophosphate tungsten bronze series $(WO_3)_{2m}(PO_2)_4$.

Experimental

Synthesis

WO_3 (99.9%), W metal (99.9%), and P_2O_5 (99.9%) were obtained from Cerac. Maroon

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crystals of WPO_5 were discovered as a minor product by heating a mixture of WO_3, W, P_2O_5, and SiO_2 (mole ratio 3 : 3 : 5 : 2) in a fused silica tube at 1250°C for several days. Film work on a selected crystal using a Weissenberg camera gave orthorhombic $a = 11.2$, $b = 6.6$, $c = 5.2$ Å, which corresponded to the second member of the series $(WO_3)_{2m}(PO_2)_4$. Neither the axial oscillation photograph along the c-axis nor the zero-layer Weissenberg ($hk0$) photograph with long exposure time revealed any superstructure spots. Subsequently, a reaction aiming at WPO_5 at 1250°C for three days was conducted. Upon opening the fused silica tube, the product was found to contain many maroon crystals. Based on X-ray powder diffraction polycrystalline WPO_5 was obtained as a major product by heating a mixture containing appropriate amounts of the starting materials at 1100°C for several days.

Single-Crystal X-Ray Structure Determination

Peak profile analysis (ω-scan) on the maroon crystals using a Nicolet R3/V diffractometer indicated that most of them were not single crystals. The $hk0$ reflections often showed multiple peaks due to twinning. Many had to be selected before a satisfactory crystal was obtained. Finally a piece with the dimensions 0.12 × 0.09 × 0.05 mm was chosen. Some of its $hk0$ reflections also showed broad peak profiles but the diffracted rays from the crystal diverged by such a small angle that the intensity data were considered to contain enough information to make an elucidation of the structure possible.

The unit cell parameters, $a = 11.174(3)$, $b = 6.550(2)$, $c = 5.228(1)$ Å, were determined by a least-square fit of 22 peak maxima with 2θ ranging from 14 to 30°, excluding $hk0$ reflections. If the $hk0$ reflections with broad peak profiles were included, the automatic indexing program would lead to a monoclinic cell ($a = 6.5$, $b = 5.2$, $c = 11.2$ Å) with the β angle slightly off 90°. The extent of deviation from 90° was dependent upon the number of the $hk0$ reflections with broad peak profiles. The orthorhombic cell corresponds to the subcell of the monoclinic supercell for β-$NbPO_5$ ($a_m \simeq (2/\sqrt{3})a_o$, $b_m = c_o$, $c_m = 2b_o$, $\beta \simeq 120°$) (5). In order to verify the orthorhombic unit cell for WPO_5, an intensity data set based on the monoclinic supercell was collected with slow scan speed. However, a systematic absence of hkl reflections with $l = 2n + 1$ was observed, suggesting that the WPO_5 crystal does not exhibit the monoclinic supercell. Since the intensity data showed mmm Laue symmetry with $R_{int} = 0.032$, the crystal structure of WPO_5 was determined in the orhorhombic unit cell.

The intensities were collected up to $2\theta = 60°$ with ω-2θ scan. The scan width was 1.2° + $K\alpha_1$, α_2 separation. A periodic check of three reference reflections did not reveal any significant variation in intensity. A total of 547 unique reflections with $I > 3\sigma(I)$ were corrected for absorption and Lorentz and polarization effects. Corrections for absorption effects were based on ψ scans of five suitable reflections with χ values close to 90° (T_{max}, T_{min} = 0.999, 0.623). Based on the systematic absences ($0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$) and statistical test ($\langle|E^2 - 1|\rangle = 0.834$ for $0kl$, 0.601 for $hk0$, 0.883 for $h0l$, and 0.836 for the remaining reflections), the noncentrosymmetric space group $Pna2_1$ (No. 33) was considered. Classical methods for structure determination were used: direct method and successive Fourier syntheses. Only the W atom was refined with anisotropic temperature factors since most of the light atoms gave nonpositive definite values. It should also be noted that the thermal parameters for O2, O3, and O4 are considerably larger than those for O1 and O5. These phenomena could be attributed to incomplete absorption correction, poor crystal quality, or

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS[a] FOR WPO_5

Atom	x	y	z	U_{eq} (Å^2) × 10^2
W	0.43894(3)	0.16885(6)	0	0.37(1)
P	0.1552(2)	−0.0295(4)	0.007(4)	0.64(5)
O1	0.2128(7)	−0.479(1)	0.479(3)	0.8(2)
O2	0.0853(9)	0.166(1)	0.976(3)	1.6(2)
O3	0.131(1)	−0.120(2)	0.734(3)	1.6(3)
O4	0.123(1)	−0.176(2)	0.207(3)	2.3(3)
O5	−0.005(1)	−0.524(2)	0.275(3)	0.9(2)

[a] U_{eq} is defined as one-third of the orthogonalized U_{ij} tensor. Only the W atom was refined with anisotropic temperature factors.

TABLE II

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR WPO_5

O1–W	1.957(8)					
O2–W	1.963(10)	172.2(6)				
O3–W	2.004(14)	92.2(5)	89.1(5)			
O4–W	1.964(16)	84.7(6)	87.6(6)	88.9(6)		
O5a–W	1.872(14)	88.3(6)	90.2(6)	178.6(6)	89.8(6)	
O5b–W	1.837(14)	94.9(6)	92.8(6)	90.7(6)	179.5(6)	90.5(1)
		O1	O2	O3	O4	O5a
O2–P	1.511(10)					
O3–P	1.572(22)	98(1)				
O1–P	1.518(8)	107.9(6)	99(1)			
O4–P	1.462(21)	120(1)	111.0(8)	117(1)		
		O2	O3	O1		

even the presence of a supercell. Electron diffraction investigation would be informative with regard to the presence of a supercell.

At convergence $R = 0.0273$, $R_w = 0.0268$, $w = 1.0/(\sigma^2(F) + 0.000132\ F^2)$, $\sigma^2(F)$ based on counting statistics, $S = 2.03$, $(\Delta\rho)_{max} = 2.4$ e/Å^3, $(\Delta\rho)_{min} = -2.7$ e/Å^3. Neutral atom scattering factors and anomalous dispersion terms were taken from "International Tables for X-Ray Crystallography" (*7*). All calculations were performed on a DEC MicroVAX II computer system using the SHELXTL PLUS programs. Atomic and thermal parameters are given in Table I. Selected bond distances and angles are listed in Table II.

Description of the Structure and Discussion

WPO_5 appears to be one of the few well-defined structures containing only W^{5+} in oxygen lattice. Other examples are $AlWO_4$ (*8*) and $CrWO_4$ (*9*). Figure 1 shows the

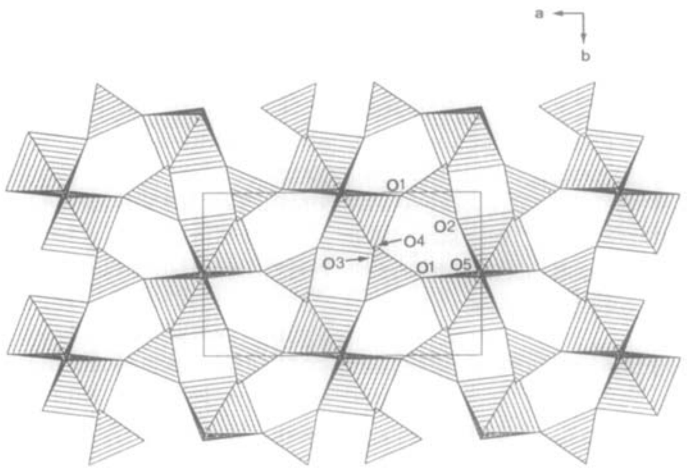

FIG. 1. STRUPLO84 drawing displaying the framework of WPO_5. The *c*-axis is perpendicular to this plane.

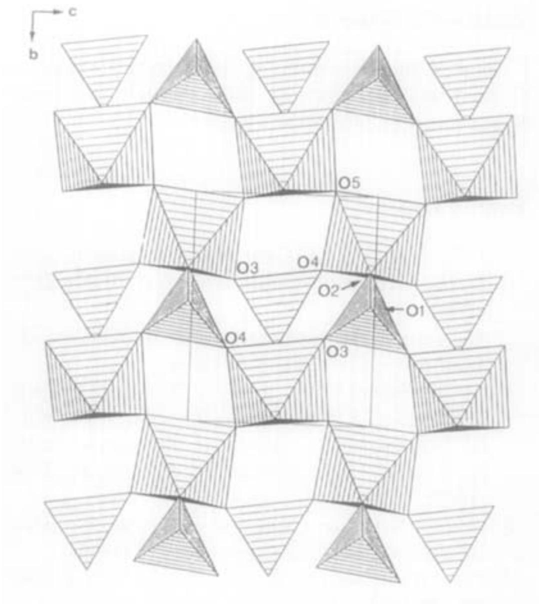

FIG. 2. A section of the structure of WPO_5 along the *a*-axis.

crystal structure of WPO_5 along the *c*-axis. The structure consists of strings of corner-sharing WO_6 octahedra parallel to [001] which are connected to each other through PO_4 tetrahedra. The structure can be regarded as close-packed files of corner-sharing octahedra with all the interstitial sites filled with files of tetrahedra. Pentagonal tunnels are formed by the edges of three octahedra and two tetrahedra. A section of the structure of WPO_5 along the *a*-axis is shown in Fig. 2. ReO_3-type slabs are separated by phosphate groups. Consequently, WPO_5 can be considered the second member ($m = 2$) of the monophosphate tungsten bronze series $(WO_3)_{2m}(PO_2)_4$. A major structural difference between WPO_5 and the other members of the series is that the ReO_3-type slabs in WPO_5 are not directly connected to each other.

The absence of mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ leads to a tilting of the WO_6 octahedra in the ReO_3-type slab. The tilting of the WO_6 octahedra in each slab occurs in the same direction. In contrast to this, the tilting of the NbO_6 octahedra in a ReO_3-type slab in β-$NbPO_5$ is in opposite direction from those in adjacent slabs, which results in the doubling of the *b* parameter (6.55 Å × 2) (*5*). The WO_6 octahedra are distorted as shown by the O–O distances ranging from 2.634(3) to 2.85(2) Å. The shortest edge of an octahedron (O5–O5) is formed by the oxygen atoms common to two octahedra. According to Leclaire *et al.* (*5*), the tilting and distortion of the octahedra are due to the adjustment stresses in the too-narrow ReO_3-type slabs which are induced by the difference in size between NbO_6 octahedron and PO_4 tetrahedron. The PO_4 tetrahedra also appear distorted (d(O–O) = 2.32(2)–2.58(2) Å). However, it should be noted that the e.s.d.'s of the oxygen coordinates are large.

In WPO_5 each WO_6 octahedron shares its six corners with two WO_6 octahedra and four PO_4 tetrahedra. The two WO_6 octahedra are in *cis*-position. Each PO_4 tetrahedron shares its four corners with four different WO_6 octahedra. As discussed by Domengès *et al.* (*10*), WO_6 octahedra that share corners with PO_4 tetrahedra will of necessity be distorted. Each W atom exhibits two short and four long W–O bonds. The shorter W–O bonds involve the oxygen atom (O5) bridging two WO_6 octahedra, which can be readily explained by Pauling's second rule (electrostatic valence rule). The distortion $\Delta = \langle |R - \langle R \rangle| \rangle = 0.052$ of the WO_6 octahedron in WPO_5 is in agreement with the plot of Δ vs the oxidation state of W in the paper by Domengès *et al.* (*10*).

An assessment of the oxidation state of the W atom in WPO_5 using the bond-length bond-strength formula $s = (R/1.898)^{-5.75}$ by Domengès *et al.* (*10*) yields an unsatisfactory value of 5.50 for W. The parameter R_0 in the formula $s = R/R_0)^{-n}$ is then changed to 1.866 in order to make the oxidation state equal to 5.0 while keeping the value of $n = 5.75$. The valence sum at each oxygen atom can be calculated by using the revised formula for W–O bonds and $(R/1.607)^{-4.29}$ for P–O bonds. The calculated valence sums are: O1, 2.04; O2, 2.05; O3, 1.76; O4, 2.24; O5, 2.08. The above results indicate that some of the oxygen atomic positions are not known with sufficient accuracy.

Presently, WPO_5 is the smallest m member in the monophosphate tungsten bronze series $(WO_3)_{2m}(PO_2)_4$ of which the single-crystal structure has been determined. The existence of WPO_5 was considered unfavorable because a strong distortion in the WO_6 octahedra in the very narrow slabs was expected. It should be noted that the W atom in WPO_5, which is in a lower oxidation state compared with that of the other members of the series, is less prone to distortion. In fact, the distribution of the six W–O bond distances in WPO_5 is quite narrow. The lowest member of the series, which corresponds to the composition of WP_2O_7, has not been reported, although a series of pyrophosphates containing tetravalent cations including Mo^{4+} with ionic radii ranging from Si^{4+} to Th^{4+} adopt the well-known ZrP_2O_7-type structures (*11*).

Acknowledgments

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