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Structures of Two New Polymorphic Forms of Hexavalent Tungsten Oxide Phosphates

Masafumi Hanawa and Hideo Imoto[1]

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Tokyo, 113-0033, Japan
E-mail: imoto@chem.s.u-tokyo.ac.jp

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Two new modifications of tungsten oxide phosphates, $WOP_2O_7(o)$ and $W_2O_3(PO_4)_2(o)$, were prepared, and their structures were determined by single crystal X-ray techniques. $WOP_2O_7(o)$ crystallizes in the orthorhombic system, space group *Pnma* (No. 62) with $a = 16.662(2)$, $b = 5.147(2)$, $c = 6.612(4)$ Å. The structure was refined to an *R* factor of 0.028 ($R_w = 0.022$). The compound has a layered structure, where the layers are not bridged. Diphosphate group has a terminal oxygen atom bonded only with a phosphorus atom. $W_2O_3(PO_4)_2(o)$ also crystallizes in the orthorhombic system, space group *Pnma* (No. 62) with $a = 15.683(1)$, $b = 6.249(1)$, $c = 7.934(1)$ Å. The refinement yielded $R = 0.019$ ($R_w = 0.016$). The structure is composed of dioctahedral W_2O_{11} groups and PO_4 groups to form a three-dimensional network.

INTRODUCTION

Though many tungsten phosphates and oxide phosphates have been reported, only two of them contain tungsten atoms exclusively in the hexavalent state. They are an oxide diphosphate $WOP_2O_7(m)$ (1) and an oxide orthophosphate $W_2O_3(PO_4)_2(m)$ (2, 3). The former is a layered compound, where WO_6 octahedra and P_2O_7 ditetrahedra compose the layers by sharing the corners. The layers are not connected by chemical bonds, and the intercalation chemistry of the compound was investigated by Kinomura *et al.* (4). In the view of the structural chemistry of transition-metal phosphates, this compound is very unique because its diphosphate group has a terminal oxygen atom bonded only with one phosphorus atom. We will call such an oxygen atom a lone terminal atom in this article. So far we know, the compound has been the only example containing the lone terminal oxygen atom among transition-metal phosphates and oxide phosphates. These unique structural features tempted us to explore the chemistry of the hexavalent tungsten phosphates. The experiments of the tungsten–phosphate systems under modified conditions have led us to two new forms of hexavalent tungsten oxide phosphates.

[1]To whom correspondence should be addressed.

EXPERIMENTAL

Preparation of $WOP_2O_7(o)$

Powder of WO_3 (0.50 g) and phosphoric acid (85%; 2.79 g) were mixed in a gold boat (40 mm × 12 mm × 8 mm) in a molar ratio of P/W = 11. The gold boat was placed in a silica tube and heated under an oxygen gas glow. It was first heated at 220°C for 24 h and then at 480°C for 48 h. Colorless long plate crystals of $WOP_2O_7(o)$ were obtained. According to the powder X-ray diffraction, the product contains $WOP_2O_7(o)$ with unidentified species, but no peak of $WOP_2O_7(m)$ was detected. The P/W molar ratio determined by fluorescent X-ray analysis (Seiko SEA-2010) was 1.77. The reaction under a nitrogen or argon gas flow instead of an oxygen gas flow gave $WOP_2O_7(o)$ only in a powder form.

Preparation of $W_2O_3(PO_4)_2(o)$

A mixture of WO_3 (0.23 g) and $(NH_4)_2HPO_4$ (0.66 g) (P/W = 5) in a gold boat was heated at 280°C for 48 h and then at 680°C for 72 h. Colorless plate crystals of $W_2O_3(PO_4)_2(o)$ were obtained with unidentified compounds. The P/W molar ratio determined by fluorescent X-ray analysis (Seiko SEA-2010) was 1.06.

Structure Determination

Table 1 shows crystallographic data for $WOP_2O_7(o)$ and $W_2O_3(PO_4)_2(o)$. Reflection intensities of the crystals were measured on a four-circle automatic diffractometer (Rigaku AFC5R). Graphite-monochromated Mo$K\alpha$ radiation was used. Intensities were recorded using the standard $\omega/2\theta$ scan technique. Absorption (ψ scan method), Lorentz, and polarization corrections were applied to the intensities.

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TABLE 1
Crystallographic Data for $WOP_2O_7(o)$ and $W_2O_3(PO_4)_2(o)$

Chemical formula	$WOP_2O_7(o)$	$W_2O_3(PO_4)_2(o)$
Formula weight	373.78	605.62
Crystal system	orthorhombic	orthorhombic
Space group	*Pnma* (No. 62)	*Pnma* (No. 62)
a (Å)	16.662(2)	15.683(1)
b (Å)	5.147(2)	6.249(1)
c (Å)	6.612(4)	7.934(1)
V (Å^3)	567.1(4)	777.6(2)
Z	4	4
ρ calculated (g cm^{-3})	4.378	5.173
Crystal size (mm^3)	$0.14 \times 0.02 \times 0.01$	$0.45 \times 0.04 \times 0.02$
2θ range (deg)	5–60	5–60
T (K)	296	296
Radiation λ(Mo$K\alpha$) (Å)	0.7107	0.7107
Range in *hkl*	$\pm 23,\ \pm 7,\ \pm 9$	$\pm 22,\ +9,\ \pm 11$
Number of reflections measured	6630	4919
R_{int} (on F^2 values)	0.081	0.033
Number of unique reflections with $\lvert F\rvert > 3\sigma(F)$	776	1197
Number of refined parameters	61	86
Transmission factors (min/max)	0.755/0.985	0.514/0.981
μ (mm^{-1})	20.93	30.03
$R(F_0)^a/R_w(F_0)^b$	0.028/0.022	0.019/0.016

[a] $R(F_0) = \sum \lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_0\rvert$.
[b] $R_w(F_0) = \sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2 / \sum w\lvert F_0\rvert^2$, $w = 1/\{\sigma(\lvert F_0\rvert)^2 + p^2\lvert F_0\rvert^2/4\}$, where $p = 0.0018$ for $WOP_2O_7(o)$ and 0.0030 for $W_2O_3(PO_4)_2(o)$.

Examination of equivalent reflections indicated that both of the compounds had the orthrohombic symmetry (*mmm*).

From the systematic absences the space groups of both compounds were deduced to be *Pnma* or $Pna2_1$. The space group *Pnma* gave reasonable structures for both of the compounds. Averaged reflections with $\lvert F\rvert > 3\sigma(F)$ were used for the structure determinations. The positions of W and P atoms were determined by the Patterson method, and all O atoms were located on difference Fourier maps (SHELXS-76, SHELXS-86) (5, 6). Finally, atomic parameters were refined by the full-matrix least-squares method using program ANYBLK (7). Isotropic extinction correction (8) was included in the final refinements of $W_2O_3(PO_4)_2(o)$ ($rT = 3.98 \times 10^{-8}$).

DESCRIPTIONS OF STRUCTURES

Structure of $WOP_2O_7(o)$

While the previously reported form of WOP_2O_7 is monoclinic ($WOP_2O_7(m)$) (1), the new form is orthorhombic ($WOP_2O_7(o)$). The final results of the structure determination of $WOP_2O_7(o)$ are given in Tables 2 and 3. Figure 1 shows the structures of the two polymorphic forms of WOP_2O_7. The structure of $WOP_2O_7(o)$ is composed of the layers of WO_6 octahedra and P_2O_7 ditetrahedra. The layers are stacked along the a axis, and there is no chemical bond between the layers. Among the six terminal oxygen atoms of the P_2O_7 group, five atoms are connected to tungsten atoms, and one is the lone terminal. All of these structural features are also observed in $WOP_2O_7(m)$. The structural difference between the two polymorphic forms is most evident in the position of the lone terminal oxygen atoms. The oxygen atom sticks out of the layer in $WOP_2O_7(o)$ while it is located inside the layer in $WOP_2O_7(m)$.

TABLE 2
Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters $WOP_2O_7(o)$

Atom	x/a	y/b	z/c	U_{eq} (Å^2)^a
W	0.12848(2)	0.75	0.12251(6)	0.00625(14)
P1	0.07835(13)	0.25	0.4059(3)	0.0063(10)
P2	0.16843(13)	0.25	0.7911(4)	0.0059(10)
O1	0.0965(3)	0.25	0.6400(10)	0.012(3)
O2	0.1282(3)	0.4856(8)	0.3244(6)	0.013(2)
O3	0.2448(4)	0.25	0.6788(10)	0.012(3)
O4	0.1577(3)	0.0116(9)	0.9222(7)	0.015(2)
O5	− 0.0071(3)	0.25	0.3635(12)	0.014(3)
O6	0.0298(4)	0.75	0.0754(10)	0.015(3)

[a] U_{eq} is defined as one-third of the trace of the $\mathbf{U}_{ij}$ orthogonalized tensor.

TABLE 3
Interatomic Distances (Å) and Angles (deg) in $WOP_2O_7(o)^a$

W	O2	O2^i	O3^{ii}	O4	O4^i	O6
O2	**1.907(4)**	2.722(8)	2.694(7)	3.827(6)	2.705(6)	2.693(7)
O2^i	91.1(3)	**1.907(4)**	2.694(7)	2.705(6)	3.827(6)	2.693(7)
O3^{ii}	83.2(2)	83.2(2)	**2.144(6)**	2.708(7)	2.708(7)	3.818(9)
O4	165.7(2)	89.1(2)	82.7(2)	**1.951(4)**	2.693(9)	2.717(7)
O4^i	89.1(2)	165.7(2)	82.7(2)	87.3(3)	**1.951(4)**	2.717(7)
O6	97.3(2)	97.3(2)	179.3(3)	96.8(2)	96.8(2)	**1.674(7)**
P1	**O1**	**O2**	**O2^i**	**O5**		
O1	**1.577(7)**	2.470(7)	2.470(7)	2.515(9)		
O2	103.7(2)	**1.565(4)**	2.425(8)	2.572(7)		
O2^i	103.7(2)	101.6(4)	**1.565(4)**	2.572(7)		
O5	112.2(4)	117.0(2)	117.0(2)	**1.451(6)**		
P2	**O1**	**O3**	**O4**	**O4^i**		
O1	**1.559(7)**	2.484(8)	2.454(7)	2.454(7)		
O3	109.9(4)	**1.473(6)**	2.491(7)	2.491(7)		
O4	106.0(2)	113.0(2)	**1.513(5)**	2.454(9)		
O4^i	106.0(2)	113.0(2)	108.4(4)	**1.513(5)**		

[a] Symmetry codes: (i) $x,\ -y+\frac{1}{2},\ z$; (ii) $-x+\frac{1}{2},\ -y,\ z+\frac{1}{2}$.

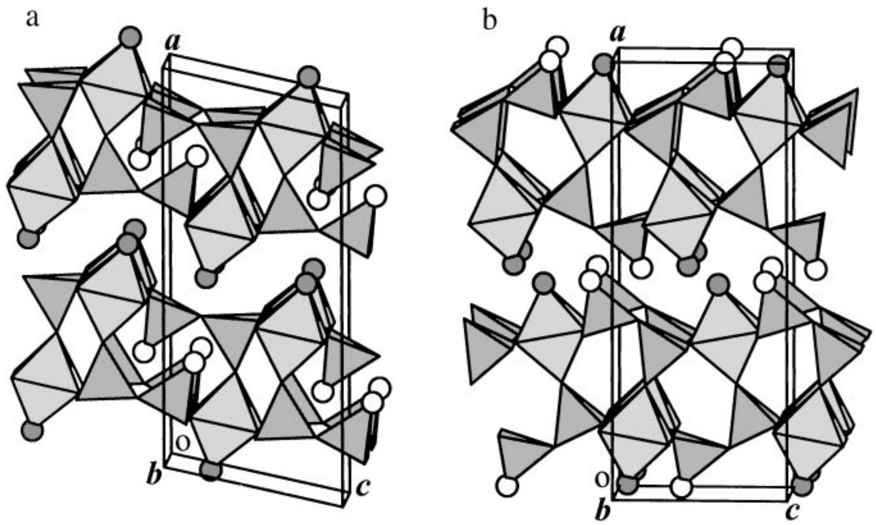

FIG. 1. Polyhedral view of two polymorphic forms of WOP_2O_7. The open circles represent lone terminal oxygen atoms and the shaded circles are the oxygen atoms bonded only with a tungsten atom. (a) The structure of $WOP_2O_7(m)$, which was reported by Kierkegaard (1). (b) The structure of $WOP_2O_7(o)$, which is reported in this work.

In $WOP_2O_7(o)$, six oxygen atoms coordinating to a tungsten atom form a slightly distorted octahedron, where the edge O–O distances fall in a narrow range (2.693(4)–2.722(8) Å). However, the tungsten atom is located at the position 0.24 Å apart from the center of the octahedron toward the terminal oxygen atom O6, and the W–O distances exhibit a large variation (1.674(7)–2.144(6) Å). The oxygen atom with the longest W–O bond has a shorter P–O bond distance (1.473(6) Å) than other oxygen atoms bridging phosphorus and tungsten atoms (1.513(5), 1.565(4) Å). However, the distance is longer than that of the lone terminal oxygen atom (1.451(6) Å).

Since the P–O distances were fixed in the structure refinement of $WOP_2O_7(m)$, the structure of $WOP_2O_7(o)$ gives the first example of the P–O distance for the lone terminal oxygen atom in the transition metal phosphates. As described above the distance (1.451(6) Å) is shorter than the P–O distances of other oxygen atoms (1.473(6)–1.577(7) Å) in $WOP_2O_7(o)$. The distance is comparable to those of the lone terminal oxygen atoms in the varieties of phosphorus pentaoxides (1.431(3)–1.452(3) Å) (9–11).

Infrared spectrum of $WOP_2O_7(o)$ shows a small band centered at 1350 cm^{-1}, which is much higher than normal frequencies for the P–O stretching vibration in the metal diphosphates (1080–1120 cm^{-1}) (12). Our measurement of the IR spectrum of one of the P_2O_5 modifications with a three-dimensional network structure (9) showed a large absorption at 1344 cm^{-1} assignable to the P–O stretching vibration of the terminal oxygen atoms (13). Therefore, we have concluded that the absorption observed at 1350 cm^{-1} is due to the P–O stretching vibration of the lone terminal oxygen atom.

Pauling's electrostatic valence rule (14) explains why lone terminal oxygen atoms are observed only in the highly oxidized phosphates. By the rule, we can calculate the average valence bond strength of the P–O (PM) bonds around

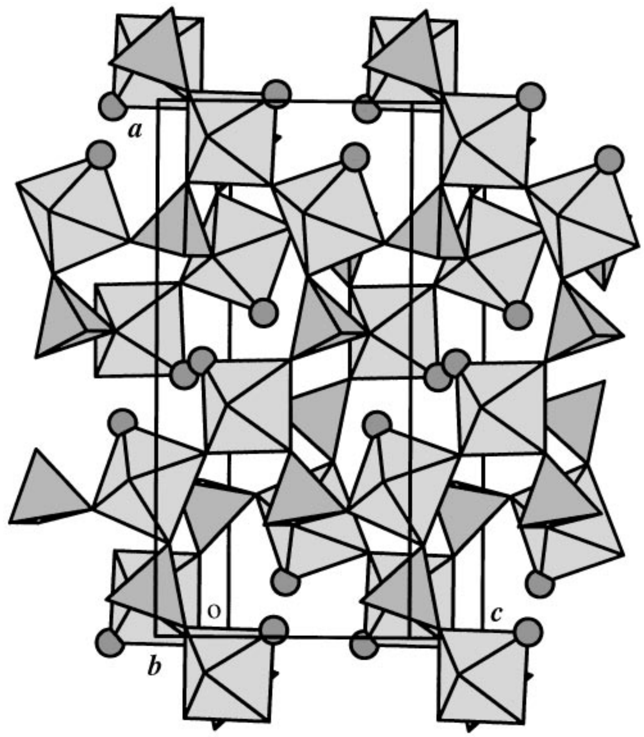

FIG. 2. Polyhedral view of $W_2O_3(PO_4)_2(o)$. Shaded circles represent terminal oxygen atoms connected to a tungsten atom.

TABLE 4
Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters $W_2O_3(PO_4)_2(o)$

Atom	x/a	y/b	z/c	U_{eq} ($Å^2$)[a]
W1	0.19748(2)	0.25	0.39638(3)	0.00560(13)
W2	0.06031(2)	0.25	0.76215(3)	0.00575(13)
P1	0.25372(11)	− 0.25	0.4892(2)	0.0066(8)
P2	0.08451(11)	− 0.25	0.9062(2)	0.0078(8)
O1	0.1587(3)	0.25	0.6217(6)	0.012(2)
O2	0.1034(3)	0.25	0.2962(6)	0.015(3)
O3	− 0.0134(3)	0.25	0.6060(6)	0.017(3)
O4	0.2085(2)	− 0.0564(6)	0.4093(4)	0.011(2)
O5	0.3271(3)	0.25	0.4801(6)	0.010(2)
O6	0.2633(3)	0.25	0.1796(6)	0.011(2)
O7	0.0676(2)	− 0.0554(6)	0.7910(4)	0.011(2)
O8	0.1526(3)	0.25	0.9579(6)	0.011(2)
O9	− 0.0180(3)	0.25	0.9545(6)	0.012(3)

[a] U_{eq} is defined as one-third of the trace of the $\mathbf{U}_{ij}$ orthogonalized tensor.

TABLE 5
Interatomic Distances (Å) and Angles (deg) in $W_2O_2(PO_4)_2(o)$[a]

W	O1	O2	O4	O4^{i}	O5	O6
O1	**1.888(4)**	2.724(7)	2.667(4)	2.667(4)	2.870(7)	3.872(6)
O2	99.5(2)	**1.676(5)**	2.681(5)	2.681(5)	3.800(7)	2.673(7)
O4	88.76(9)	95.97(10)	**1.925(4)**	3.829(7)	2.728(5)	2.780(5)
O4^{i}	88.76(9)	95.97(10)	168.1(2)	**1.925(4)**	2.728(5)	2.780(5)
O5	90.7(2)	169.8(2)	84.17(10)	84.17(10)	**2.139(5)**	2.585(6)
O6	167.8(2)	92.7(2)	89.98(9)	89.98(9)	77.1(2)	**2.006(4)**

W2	O1	O3	O7	O7^{i}	O8	O9
O1	**1.903(5)**	2.701(7)	2.737(5)	2.737(5)	2.669(6)	3.828(7)
O3	97.2(2)	**1.694(5)**	2.722(5)	2.722(5)	3.817(7)	2.765(7)
O7	91.24(10)	97.32(10)	**1.926(4)**	3.817(7)	2.679(5)	2.670(5)
O7^{i}	91.24(10)	97.32(10)	164.7(2)	**1.926(4)**	2.679(5)	2.670(5)
O8	82.9(2)	180.0(2)	82.68(10)	82.68(10)	**2.123(5)**	2.676(7)
O9	164.7(2)	98.2(2)	86.82(10)	86.82(10)	81.8(2)	**1.959(5)**

P1	O4	O4^{i}	O6^{ii}	O8^{ii}
O4	**1.539(4)**	2.420(7)	2.502(5)	2.522(6)
O4^{i}	103.6(3)	**1.539(4)**	2.502(5)	2.522(6)
O6^{ii}	109.0(2)	109.0(2)	**1.535(5)**	2.472(7)
O8^{ii}	112.7(2)	112.7(2)	109.6(3)	**1.490(5)**

P2	O5^{ii}	O7	O7^{i}	O9^{iii}
O5^{ii}	**1.505(5)**	2.541(5)	2.541(5)	2.483(7)
O7	112.9(2)	**1.544(3)**	2.432(7)	2.482(5)
O7^{i}	112.9(2)	103.9(3)	**1.544(3)**	2.482(5)
O9^{iii}	110.4(3)	108.2(2)	108.2(2)	**1.520(5)**

[a] Symmetry codes: (i) $x,\ -y+\frac{1}{2},\ z$; (ii) $-x+\frac{1}{2},\ -y,\ z+\frac{1}{2}$; (iii) $-x,\ y+\frac{1}{2},\ -z$.

a phosphorus atom, where O(PM) is an oxygen atom bridging a phosphorus atom and a metal atom. The value is equal to or larger than 1.25 in the phosphates without a lone terminal oxygen atom (1.25 in orthophosphates, 1.333 in diphosphates, and 1.5 in metaphosphates) while it is 1.0 around a phosphorus atoms with a lone terminal oxygen atom. Then, average valence bond strength of the M–O(PM) bond is equal to or smaller than 0.75 in the former and 1.0 in the latter. Higher M–O(PM) valence bond strength in the latter requires the metal atom to have higher oxidation states. Observed bond distances in $WOP_2O_7(o)$ are consistent with this discussion. The O2 atom, which is bonded to the phosphorus atom with a lone terminal oxygen atom, has shorter W–O distance (1.907(4) Å) than other O(PM) atoms (1.951(4) and 2.144(6) Å).

Structure of $W_2O_3(PO_4)_2(o)$

The new form of $W_2O_3(PO_4)_2$ is orthorhombic ($W_2O_3(PO_4)_2(o)$) though the form reported by Kierkegaard

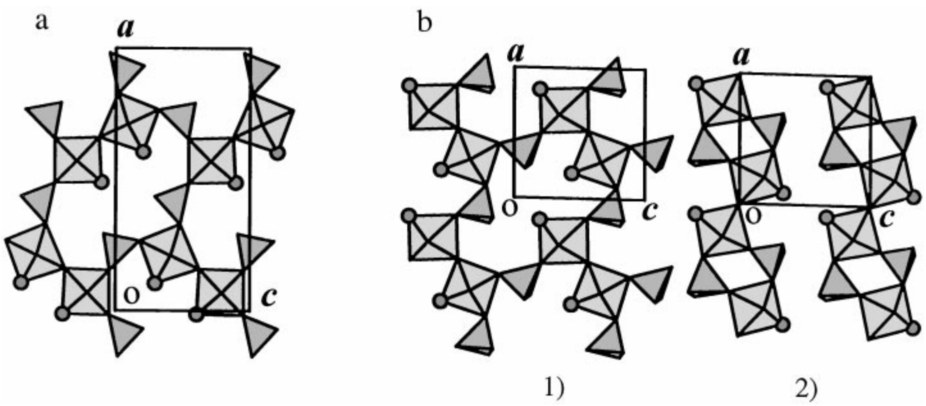

FIG. 3. Illustrations of two forms of $W_2O_3(PO_4)_2$ emphasizing the positions of terminal oxygen atoms connected to tungsten atoms. (a) Projection of $W_2O_3(PO_4)_2(o)$ along the *b* axis ($y \approx 1/4$). (b) Projection of $W_2O_3(PO_4)_2(m)$ (Kierkegaard *et al.* (2, 3)) along the *b* axis ($b-1$, $y \approx 1/8$; $b-2$, $y \approx 3/8$).

et al. is monoclinic ($W_2O_3(PO_4)_2(m)$) (2, 3). Figure 2 shows the structure of $W_2O_3(PO_4)_2(o)$. The atomic positions and thermal parameters are given in Table 4, and interatomic distances are given in Table 5. The structure of this compound is built up from corner-sharing PO_4 tetrahedra and WO_6 octahedra, where two WO_6 octahedra are linked together through a bridging oxygen atom to form a W_2O_{11} dioctahedral unit. Each tungsten atom has a terminal oxygen atom. As observed in $WOP_2O_7(o)$, the position of the tungsten atom is shifted from the center of gravity of six surrounding oxygen atoms toward the terminal oxygen atom (W1, 0.22 Å; W2, 0.21 Å). The shifts cause large deviations of W–O distances (W1–O, 1.676(5)–2.139(5) Å; W2–O, 1.694(5)–2.123(5) Å). The other modification $W_2O_3(PO_4)_2(m)$ also has a similar W_2O_{11} dioctahedral unit. Figure 3 shows the projections of two modifications on the plane containing the pair of tungsten atoms and the bridging oxygen. In $W_2O_3(PO_4)_2(o)$, two terminal W–O bonds are arranged almost in the same direction (Fig. 3a). However, the two W–O bonds project in different directions in $W_2O_3(PO_4)_2(m)$ (Fig. 3b).

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