The Crystal Structure of WOP_2O_7

PEDER KIERKEGAARD

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

WOP_2O_7 has a monoclinic unit cell containing four formula units and with the dimensions

$$a = (15.170 \pm 0.005) \text{ Å}$$
$$b = (5.162 \pm 0.005) \text{ Å}$$
$$c = (6.917 \pm 0.005) \text{ Å}$$
$$\beta = (102.41 \pm 0.05)°$$
$$V = 547.9 \text{ Å}^3$$

A structure is proposed with the symmetry No. 12, $C2/m$. The positions of the wolfram and phosphorus atoms in the unit cell were determined by Fourier methods. The parameters of the oxygen atoms were derived partly from electron density projections and partly from geometrical considerations, interatomic $P-O$ and $O-O$ distances from previously determined structures being used. The crystals are built up of layers parallel to the yz plane and formed of fairly regular WO_6 octahedra coupled together by P_2O_7 groups. The layers are held together by van der Waals' forces and the crystals show pronounced basal cleavage resulting from this layer structure.

In the system WO_3—P_2O_5 the existence of two crystalline compounds with the compositions $2WO_3 . P_2O_5$ and $WO_3 . P_2O_5$ was reported by Schulz [1]. The crystals were insoluble in water, acids and dilute ammonia and difficultly soluble in hot dilute sodium hydroxide. In solutions of $WO_3 . P_2O_5$ only ortho- and diphosphate ion could be proved. Polyphosphate ions were not found. In connection with an X-ray investigation of oxides undertaken at this institute a crystal structure determination of these compounds was started and this paper gives the structure of $WO_3 . P_2O_5$.

PREPARATION OF THE CRYSTALS

A mixture of 4 g WO_3 and 4.8 g P_2O_5, in a platinum crucible, was heated in an auto-clave at 550°C for about a week, when crystals good for X-ray work were obtained. (The method according to Schulz [1].) After being cooled the crystals were washed with hot water and dried in air. Under the microscope they showed to be colourless, elongated plates, which cleft very easily into long, thin plates of various widths.

Analysis. A sample was fused with sodium potassium carbonate in a platinum crucible and the cake dissolved in boiling water. From an ammoniacal solution the *phosphorus*

was precipitated (according to Kolthoff and Sandell[2]) with a magnesium solution. The precipitate was filtered off, washed with water, dissolved in hot 1 M HNO_3 and from this solution the phosphorus was finally precipitated with ammonium molybdate and weighed as $(NH_4)_3PO_4 . 12MoO_3$. The amount of *wolfram* in the filtrate — made neutral — was determined gravimetrically by precipitation with mercury(I)nitrate according to Cumming and Kay[3] and weighed, after ignition, as WO_3. The methods of analysis were tested carefully on samples with known various compositions and this examination showed very low errors.

The *density* of the crystals was determined from the apparent loss of weight in benzene.

	Calculated for $WO_3 \cdot P_2O_5$	Found
% WO_3	62.02	62.0 ± 0.2
% P_2O_5	37.98	38.0 ± 0.2
Density	4.54	4.46 ± 0.01

The density is calculated for 4 formula units per cell.

UNIT CELL AND SPACE GROUP

Two small single crystals of different shape were split from larger ones. For the taking of rotation and Weissenberg photographs (zero, first and second layer) with CuK radiation, one, a needle about 0.2 mm in length and about 0.01 mm in diameter, was rotated around the needle axis [010] and the other, a plate only about 0.04 mm thick, 0.03 mm wide, and 0.2 mm long, was rotated round a diagonal in the plane of the plate [001]. It was concluded that the crystals are monoclinic and that the dimensions of the unit cell are about 15.7_4 Å, 5.0_9 Å, 6.8_4 Å and the monoclinic angle is about 102°.

The reflections were recorded photographically with the multiple film technique and the relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. The F^2 values were then calculated using the polarization and Lorentz' factor given by Lu[4]. No correction was applied for the absorption.

More accurate values for the unit cell dimensions were calculated from a powder photograph, taken with strictly monochromatized Cu$K\alpha_1$ radiation in a focusing camera of Guinier type. KCl was used as an internal standard substance (see Table 1).

$$a = (15.710 \pm 0.005) \text{ Å} \qquad \beta = (102.41 \pm 0.05)°$$
$$b = (5.162 \pm 0.005) \text{ Å} \qquad V = 547.9 \text{ Å}^3$$
$$c = (6.917 \pm 0.005) \text{ Å}$$

The value (4.46) found for the density gives $3.93 \approx 4$ formula units in the unit cell.

The reflections systematically absent are

$$hkl \text{ with } h+k = \text{odd}$$
$$h0l \text{ } » \text{ } h = \text{odd}$$
$$0k0 \text{ } » \text{ } k = \text{odd}$$

This is characteristic of the three space groups No. 5,$C2$, No. 8,Cm and No. 12,$C2/m$. The investigation was started by examining whether the

Table 1. Powder photograph of WOP$_2$O$_7$. CuKa_1-radiation. $\lambda_{\text{Cu}Ka_1} = 1.54050$ Å.

hkl	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	pF^2 calc	I obs	hkl	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	pF^2 calc	I obs
200	101	—	0	—	600	907	—	35	vvw
001	130	129	5	vw	220	992	—	0	—
$20\bar{1}$	182	181	61	st	021	1021	—	3	—
110	248	248	77	vst	$22\bar{1}$	1072	1073	48	vw
201	280	279	88	m	511	1106	1105	48	vvw
$11\bar{1}$	353	353	35	w	312	1117	1117	67	vw
111	403	402	159	vvst	402	1120		37	
400			146		$20\bar{3}$	1123	—	13	—
$40\bar{1}$	435	435	58	w	$51\bar{2}$	1127	1131	77	w
310	449	447	4	vvw	$60\bar{2}$	1132		39	
$31\bar{1}$	506	506	213	st	003	1170	1171	20	w
002	520	520	35	w	221	1171		72	
$20\bar{2}$	522	523	21	vw	601	1185	1187	74	vw
401	632	—	11	—	$40\bar{3}$	1278	1276	37	vvw
311	653	652	79	vw	420	1294	—	42	—
202	719	720	0	vvst	$42\bar{1}$	1326	1327	52	vvw
$11\bar{2}$			361		$11\bar{3}$	1344	—	2	—
$40\bar{2}$	726	—	0	—	$31\bar{3}$	1398	1401	85	vw
112	817	—	4		022	1411		130	
$31\bar{2}$	822	—	0		$22\bar{2}$	1413	1414	100	m
510	853	852	135	vvw	$71\bar{1}$	1415		121	
$51\bar{1}$	860	—	0	—	203	1418		17	
$60\bar{1}$	890	891	14	m	710	1458	—	36	—
020	891		134		113	1492	1493	98	w

Reflections systematically absent in space group $C2/m$ have been omitted.
KCl ($a = 6.2930$ Å) has been used as an internal standard substance.

structure was consistent with the last space-group, that having the highest symmetry.

In No. 12, $C2/m$ the following point positions are possible

$$(000, \tfrac{1}{2}\tfrac{1}{2}0) +$$

$2(a)$: 000; $2(b)$: $0\tfrac{1}{2}0$; $2(c)$: $00\tfrac{1}{2}$; $2(d)$: $0\tfrac{1}{2}\tfrac{1}{2}$

$4(e)$: $\tfrac{1}{4}\tfrac{1}{4}0$; $\tfrac{1}{4}\tfrac{3}{4}0$; $4(f)$: $\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{2}$; $\tfrac{1}{4}\tfrac{3}{4}\tfrac{1}{2}$

$4(g)$: $\pm(0,y,0)$; $4(h)$: $\pm(0,y,\tfrac{1}{2})$; $4(i)$: $\pm(x,0,z)$

$8(j)$: $\pm(x,y,z)$; $\pm(x,\bar{y},z)$

POSITIONS OF THE WOLFRAM ATOMS

In order to find the four wolfram positions, the Patterson projections $P(uvp)$ and $P(upw)$ were calculated (Figs. 1 and 2).

The four wolfram atoms in the unit cell must occupy two of the twofold, or one of the fourfold, positions. Now $P(upw)$ has no maximum at $u = 0$, $w = \tfrac{1}{2}$ or at $u = \tfrac{1}{2}$, $w = \tfrac{1}{2}$ and $P(uvp)$ has no maximum at $u = 0$, $v = \tfrac{1}{2}$ or at $u = \tfrac{1}{2}$, $v = 0$ so this will exclude the possibility of the wolfram atoms being situated in combinations of the twofold positions or in $4(e)$—(h). Thus the
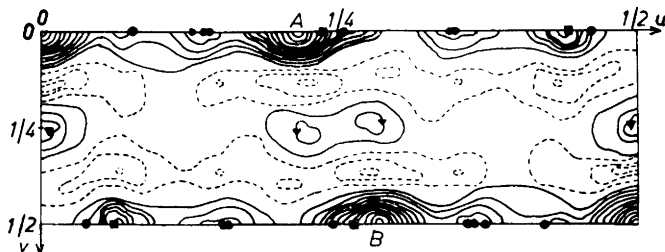
Fig. 1. The Patterson function $P(uvp)$. The $W-P$ (■), $W-O_{1-2}$ (▲) and $W-O_{3-6}$ (●) vectors have been indicated. For the largest maxima (00) and ($\frac{1}{2}\frac{1}{2}$), only every second contour has been marked. Dashed lines indicate negative values.

wolfram atoms must be situated in $4(i)$ and the W—W distances should be

$$\pm(\tfrac{1}{2},\tfrac{1}{2},0); \qquad\qquad \pm(2x,0,2z); \qquad\qquad \pm(\tfrac{1}{2}+2x\ \tfrac{1}{2},2z)$$

The Patterson projections on the uv and uw plane should therefore show (besides the origin maxima) the following maxima

	in the uv plane			in the uw plane	
I.	$(\tfrac{1}{2},\tfrac{1}{2})$	weight 4	IV.	$(\tfrac{1}{2},0)$	weight 4
II.	$\pm(2x,0)$	weight 2	V.	$\pm(2x,2z)$	weight 2
III.	$\pm(\tfrac{1}{2}+2x,\tfrac{1}{2})$	weight 2	VI.	$\pm(\tfrac{1}{2}+2x,2z)$	weight 2

There are two high peaks in $P(uvp)$ at $u = 0.21_2$, $v = 0$ (A in Fig. 1) and at $u = 0.28_8$, $v = \tfrac{1}{2}$ (B in Fig. 1) and one peak at $u = \tfrac{1}{2}$, $v = \tfrac{1}{2}$, whose height is about double that of the other two. (All maxima have been located by the interpolation table given by Booth [5].) These maxima certainly correspond to the W—W vectors I, II, and III so that peak A corresponds to the vector II above (and B to III) and thus we get $x_W = 0.10_6$. (It is sufficient to consider the range $0 \leq x \leq 1/4$, $0 \leq z \leq \tfrac{1}{2}$.)
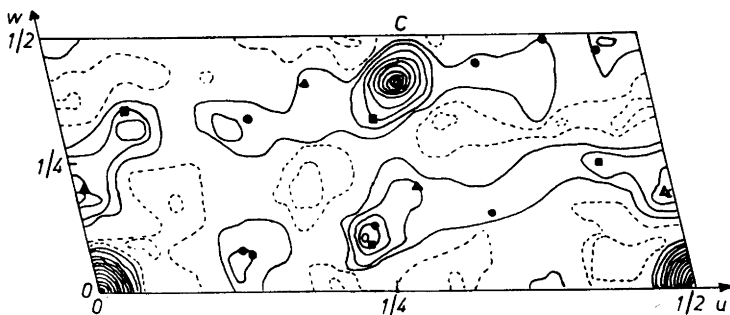

Fig. 2. The Patterson function $P(upw)$. The positions of the vectors have been marked as in Fig. 1. For the largest maxima (00) and ($\tfrac{1}{2}0$), only every second contour has been marked. Dashed lines indicate negative values.
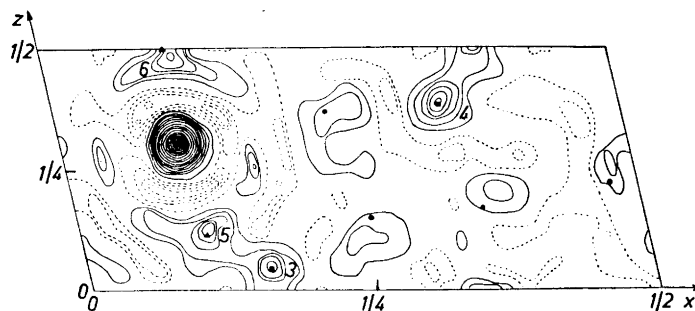
Fig. 3. Electron density projected on the *xz* plane. The positions of the phosphorus atoms (■), oxygen atoms O$_{1-2}$ (▲) and oxygen atoms O$_{3-6}$ (●) have been marked. In the wolfram peak only every second contour has been marked. Dashed lines indicate negative values.

The projection $P(upw)$ should therefore have one high peak at $u = \frac{1}{2}$, $w = 0$ (corresponding to the vector IV above) and two peaks with the u coordinates equal to $\pm$ 0.21$_2$ and $\pm$0.712 (corresponding to the vectors V and VI above). Now the projection $P(upw)$ has a pronounced peak at $u = \frac{1}{2}$, $w = 0$ and two peaks (the heights of which are about half that of the first one) at $u = 0.20_8$, $w = 0.60_0$ and at $u = 0.29_2$, $w = 0.40_0$ (C in Fig. 2). Since the height and positions of these peaks correspond to the calculated values we conclude:

$$4 \text{ W in } C2/m \quad 4(i) \text{ with } x = 0.10_5, \quad y = 0, \quad z = 0.30_0.$$

POSITIONS OF THE LIGHT ATOMS

Electron density projections. In the Patterson projections in Figs. 1 and 2 there are, in addition to peaks corresponding to the W—W vectors, several lower maxima which perhaps could be ascribed to the W—P, and maybe also to some W—O, distances. From these small maxima, if real, it would be possible to determine the positions of the phosphorus atoms in the unit
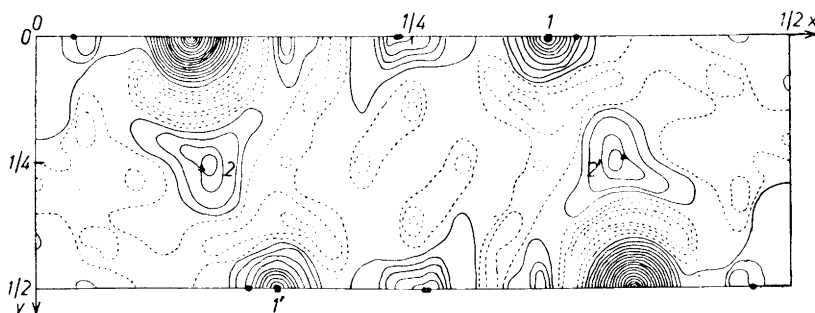

Fig. 4. Electron density projected on the *xy* plane. The positions of the atoms have been indicated as in Fig. 3. In the wolfram peak only every second contour has been marked. Dashed lines indicate negative values.
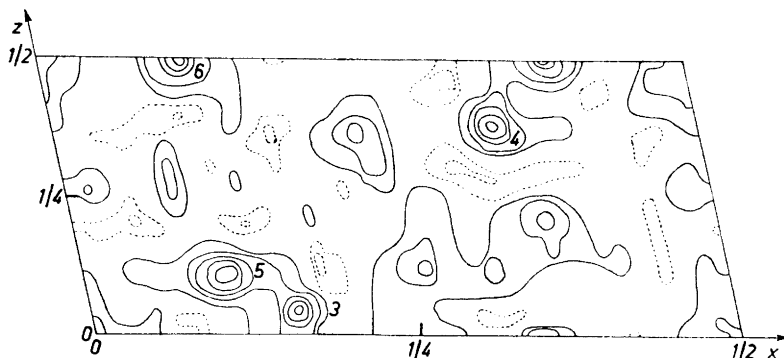
Fig. 5. Electron density projected on the *xz* plane with the wolfram atom subtracted.
Dashed lines indicate negative values.

cell. It would, however, be more favourable to determine their sites from
a map giving electron density, as such a map gives maxima that are sharper
and less in number than those of the corresponding vector map.

For a compound of this type the electron density projections can easily
be calculated since the signs of all the F-values can be determined from the
contributions given by the wolfram atoms because of their dominant scatter-
ing factors. In this way ϱ (xpz) and ϱ (xyp) were calculated and the results
are given in Figs. 3 and 4. We see that the wolfram atoms are clearly indica-
ted at $x = 0.103$, $z = 0.295$ in $\varrho(xpz)$ (Fig. 3) and at $x = 0.103$, $y = 0$ in
ϱ (xyp) (Fig. 4) and from these values we thus obtain the final parameters
of the wolfram atoms: $x = 0.103$, $y = 0$, $z = 0.295$.

Besides the very high wolfram peaks in the calculated electron density
projections there are lower peaks in ϱ (xyp) (Fig. 4) at $x = 0.34$ (0.16), $y = 0$
($\frac{1}{2}$) (1 and 1' in Fig. 4) and at $x = 0.11$ (0.39), $y = 0.25$ (2 and 2' in Fig. 4).
The electron density projected on the xz plane (Fig. 3) also shows lower maxima
(all of about the same heights) with the following sets of parameters

3.	$x = 0.16$	$z = 0.05$
4.	$x = 0.34$	$z = 0.38$
5.	$x = 0.11$	$z = 0.12$
6.	$x = 0.11$	$z = 0.47$

If these lower peaks in the projections are real maxima, and not false
ones formed by errors — diffraction effects or errors in the observed intensi-
ties due to absorption within the crystal [6] — the only atoms, which could
give peaks of this height are the phosphorus atoms or overlapping oxygen
atoms.

In order to find out if the lower maxima from ϱ (xpz) and ϱ (xyp) really
correspond to atom positions in the unit cell, the wolfram atoms were subtract-
ed from these projections and the results are given in Figs. 5 and 6. (The
effect of the temperature factor, calculated by the ordinary procedure was
found to be negligible; probably it roughly cancels out with the absorption
effect.)

From Fig. 5, which shows ϱ (xpz) with the wolfram atoms subtracted, we see that we still have four distinct maxima of about the same height and with the following sets of parameters

3. $x = 0.160$ $z = 0.044$
4. $x = 0.340$ $z = 0.380$
5. $x = 0.111$ $z = 0.113$
6. $x = 0.109$ $z = 0.499$

from which it should be possible to get the positions of the phosphorus atoms. Now, in the unit cell we have eight phosphorus and thirty-two oxygen atoms. In the xz projection never more than two oxygen atoms can overlap (the b-axis is only 5.16 Å). Since the parameters given above are not special, the eight phosphorus atoms must occupy the point positions $8(j)$ or $4(i)$. Moreover, if they are situated in $8(j)$ two phosphorus maxima should overlap in the xz projection and thus we should get only one pronounced maximum in the quadrant of the projection represented in Fig. 5, and the height of this peak should have been at least double that of the other maxima in this quadrant. Now, as mentioned above, we have four distinct maxima, which all have nearly the same height. So we conclude that the phosphorus atoms are situated in two point positions $4(i)$, which will give two peaks in ϱ (xpz). The remaining two maxima should correspond to two sets of oxygen atoms in point positions $8(j)$ each giving a maximum from two superimposed oxygen atoms.

From Fig. 6, which shows ϱ (xyp) with the wolfram atoms subtracted, we see that the wolfram atoms and most of their diffraction effects have disappeared but there are, however, two pronounced maxima at $x = 0.339$ (0.161), $y = 0$ $(\frac{1}{2})$ (1 and 1′ in Fig. 6) and two small peaks at $x = 0.11_3$, $y = 0.24_0$ and at $x = 0.38_7$, $y = 0.26_0$ (2 and 2′ in Fig. 6). According to the conclusions given above the first two maxima (1 and 1′) correspond to the phosphorus positions and the peaks 2 and 2′ will correspond to the oxygen positions in the point position $8(j)$. Thus we conclude that the maxima 3 and 4 in Fig. 5 will give the parameters of the phosphorus atoms and with these coordinates we find that two phosphorus maxima overlap in the xy-projection. This is in good agreement with observed heights in this projection. Finally the posi-
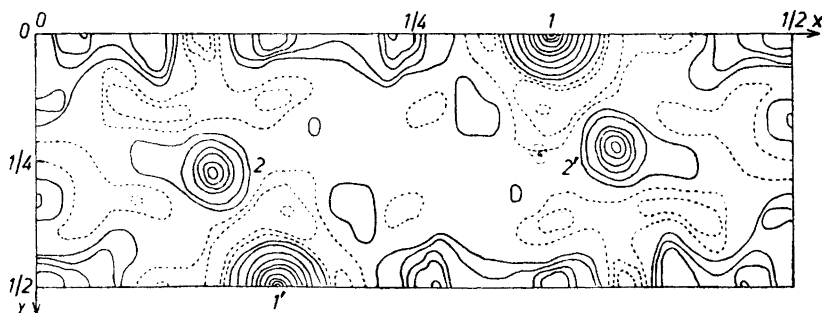

Fig. 6. Electron density projected on the xy plane with the wolfram atoms subtracted. Dashed lines indicate negative values.

tions of the sixteen oxygen atoms in the position $8(j)$ follow immediately from the maxima 5 and 6 in Fig. 5 and 2 and 2' in Fig. 6. The values obtained from ϱ (xpz) should be more correct, since in the calculation of this projection more F-values were used.

Thus, from the electron density projections the following parameters could be obtained:

$$
\begin{array}{llllllll}
4 & \text{W} & \text{in } C2/m & 4(i) & \text{with} & x = 0.103 & y = 0 & z = 0.295 \\
4 & \text{P}_1 & \text{»} & \text{»} & \text{»} & x = 0.34_0 & y = 0 & z = 0.38_0 \\
4 & \text{P}_2 & \text{»} & \text{»} & \text{»} & x = 0.34_0 & y = 0 & z = 0.95_6 \\
8 & \text{O}_1 & \text{»} & 8(j) & \text{»} & x = 0.39_0 & y = 0.24_0 & z = 0.50_1 \\
8 & \text{O}_2 & \text{»} & \text{»} & \text{»} & x = 0.39_0 & y = 0.24_0 & z = 0.88_7
\end{array}
$$

Using these parameters W—P and W—O distances were calculated and the maxima in the Patterson projections (Figs. 1—2) were compared with these W—P and W—O vectors. All of these vectors were found to correspond to maxima (cf. Figs. 1 and 2) in $P(uvp)$ and $P(upw)$ and moreover the heights of the peaks also corresponded to the calculated weights.

The remaining maxima in the Patterson and electron density projections may correspond to W—O vectors or oxygen atom positions but at this stage of the investigation they were not considered, since these peaks are of about the same height as the false maxima [6].

Geometrical considerations. The sixteen oxygen atoms, the positions of which have been found from electron density projections, are situated close to phosphorus atoms with the distances P_1—2 $O_1 = 1.6_0$ Å and P_2—2 $O_2 = 1.6_0$ Å. These distances are in good agreement with P—O distances in previously described structures [7-9] (i.e. P—O = 1.45—1.65 Å). Assuming that the coordination figure around the phosphorus atoms is a tetrahedron, which seems to be very probable, it is then possible to calculate the parameters of the remaining oxygen atoms in the PO_4 tetrahedra. If we assume the bond lengths P—O = 1.5_5 Å and O—O = 2.5_3 Å (these distances are mean values of those published [7-9]) the coordinates of the oxygen atoms O_3—O_5 follow immediately. Thus we obtain

$$
\begin{array}{llllllll}
4 & \text{O}_3 & \text{in } C2/m & 4(i) & \text{with} & x = 0.24_0 & y = 0 & z = 0.36_5 \\
4 & \text{O}_4 & \text{»} & \text{»} & \text{»} & x = 0.35_8 & y = 0 & z = 0.16_8 \\
4 & \text{O}_5 & \text{»} & \text{»} & \text{»} & x = 0.24_2 & y = 0 & z = 0.85_2
\end{array}
$$

Now we have to find the position of the remaining four oxygen atoms in the unit cell. They must occupy two of the twofold, or one of the fourfold, positions. Assuming that the distances between these oxygen atoms and the oxygens already located (i.e. O_1—O_5) are not less than 2.6_0 Å, the twofold $(2(a)$—$(d))$ and the fourfold $(4(e)$—$(h))$ point positions at once can be eliminated and thus we must have four oxygen atoms (O_6) in $4(i)$. In order to determine the coordinates, the section $y = 0$ in the unit cell was drawn and regions forbidden to oxygen atoms were marked out (Fig. 7). From the figure we see that there are only very small areas left free for the centres of these oxygen atoms. The coordinates of the oxygen atoms O_6 would then be

$$
4 \ \text{O}_6 \ \text{in} \ C2/m \ 4(i) \ \text{with} \ x = 0.97_5 \quad y = 0 \quad z = 0.21_7
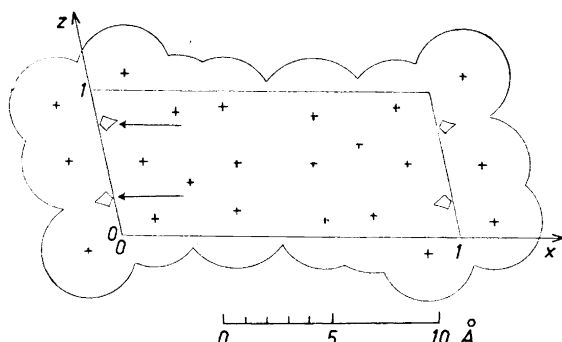$$

Fig. 7. Section at $y = 0$ through the unit cell showing the areas forbidden to the oxygen atoms, O$_6$, in this plane. The circles enclose domains forbidden around the oxygen atoms O$_{1-5}$. The arrows point out the only areas left free for the centres of O$_6$.
$+$ = centre of oxygen.

Using these oxygen coordinates the remaining W—O distances were calculated and these vectors have been indicated in Figs. 1 and 2. The positions of the oxygen atoms O$_3$—O$_6$ have also been marked in the electron density projections (Figs. 3—4). From the figures we see that these vectors or oxygen positions are situated in positive areas and, in fact, in most cases they coincide fairly well with small peaks in the Patterson and electron density projections. This seems to indicate the coordinate values to be plausible. Moreover with the coordinates found above we obtain contacts W—6O with a coordination figure, within the errors, a regular octahedron, which has been found in previously determined crystal structures of wolfram compounds [11-13]. For the coordination figure around the phosphorus we have presumed a tetrahedron with two P—O distances equal to 1.5$_5$ Å and one O—O distance equal to 2.5$_3$ Å. This will give P$_2$O$_7$-groups (*i.e.* two PO$_4$ tetrahedra sharing an oxygen) with a P—O—P angle at the central oxygen of 142°, which can be compared with 134° found in Na$_4$P$_2$O$_7$.10H$_2$O [9] and 180° found in the curious series of SiP$_2$O$_7$ and related compounds [14]. Thus, the assumptions made above to get the coordinates, give an arrangement of the atoms, which seems to be very probable.

FINAL STRUCTURE PROPOSITION

The following structure is thus proposed for WO$_3$.P$_2$O$_5$. Space group: No. 12, $C2/m$. 4 formula units per unit cell

			x	y	z
4 W	in	4(i)	0.103 ± 0.003	0	0.295 ± 0.003
4 P$_1$	»	4(i)	0.340 ± 0.006	0	0.380 ± 0.006
4 P$_2$	»	4(i)	0.340 ± 0.006	0	0.956 ± 0.006
8 O$_1$	»	8(j)	0.390 ± 0.006	0.24 ± 0.01	0.501 ± 0.006
8 O$_2$	»	8(j)	0.390 ± 0.006	0.24 ± 0.01	0.887 ± 0.006
4 O$_3$	»	4(i)	0.24	0	0.36
4 O$_4$	»	4(i)	0.36	0	0.17
4 O$_5$	»	4(i)	0.24	0	0.85
4 O$_6$	»	4(i)	0.98	0	0.22

$$(000; \tfrac{1}{2}\tfrac{1}{2}0) \pm$$

4 (i): ($x0z$)
8 (j): (xyz); ($x\bar{y}z$)

Table 2. Comparison between calculated and observed structure factors from Weissenberg photographs of WOP_2O_7. CuK radiation.

h k l	F calc	F obs	h k l	F calc	F obs	h k l	F calc	F obs	h k l	F calc	F obs
4 0 8	3	—	16 0 $\bar{5}$	21	—	4 0 $\bar{2}$	−1	—	3 1 7	−69	62
2 0 8	−69	61	18 0 $\bar{5}$	−74	57	6 0 $\bar{2}$	88	110	1 1 7	56	58
0 0 8	−27	30	14 0 4	−67	52	8 0 $\bar{2}$	26	41	1 1 $\bar{7}$	62	91
2 0 $\bar{8}$	37	38	12 0 4	−74	66	10 0 $\bar{2}$	−104	122	3 1 $\bar{7}$	−7	—
4 0 $\bar{8}$	61	53	10 0 4	34	42	12 0 $\bar{2}$	−40	41	5 1 $\bar{7}$	−64	64
6 0 $\bar{8}$	−8	—	8 0 4	64	71	14 0 $\bar{2}$	51	55	7 1 $\bar{7}$	−53	66
8 0 $\bar{8}$	−47	41	6 0 4	37	54	16 0 $\bar{2}$	55	41	9 1 $\bar{7}$	36	45
10 0 $\bar{8}$	−35	35				18 0 $\bar{2}$	−2	—	11 1 $\bar{7}$	93	83
12 0 $\bar{8}$	55	35	4 0 4	−71	71	20 0 $\bar{2}$	−33	36	13 1 $\bar{7}$	−16	—
8 0 7	32	17	2 0 4	−81	84	18 0 1	38	40	11 1 6	67	37
6 0 7	−42	42	0 0 4	24	33	16 0 1	81	79	9 1 6	−27	45
4 0 7	−54	39	2 0 $\bar{4}$	160	167	14 0 1	8	—	7 1 6	−72	71
2 0 7	−18	—	4 0 $\bar{4}$	−2	—	12 0 1	−95	93	5 1 6	−18	—
0 0 7	55	64	6 0 $\bar{4}$	−95	119	10 0 1	−53	58	3 1 6	82	85
2 0 $\bar{7}$	57	86	8 0 $\bar{4}$	−52	63	8 0 1	105	96	1 1 6	49	61
4 0 $\bar{7}$	−56	68	10 0 $\bar{4}$	76	80	6 0 1	122	110	1 1 $\bar{6}$	−39	51
6 0 $\bar{7}$	−80	86	12 0 $\bar{4}$	61	73	4 0 1	−46	45	3 1 $\bar{6}$	−96	124
8 0 $\bar{7}$	27	28	14 0 $\bar{4}$	12	—	2 0 1	−133	117	5 1 $\bar{6}$	5	—
10 0 $\bar{7}$	58	62	16 0 $\bar{4}$	−82	70	0 0 1	−31	34	7 1 $\bar{6}$	64	73
12 0 $\bar{7}$	21	17	18 0 $\bar{4}$	−40	38	2 0 $\bar{1}$	110	102	9 1 $\bar{6}$	48	52
14 0 $\bar{7}$	−25	—	16 0 3	−77	74	4 0 $\bar{1}$	108	100	11 1 $\bar{6}$	−60	50
10 0 6	26	32	14 0 3	−26	26	6 0 $\bar{1}$	−53	61	13 1 $\bar{6}$	−65	55
8 0 6	−52	54	12 0 3	72	60	8 0 $\bar{1}$	−142	139	15 1 $\bar{6}$	−3	—
6 0 6	−76	76	10 0 3	43	48	10 0 $\bar{1}$	−19	—	13 1 5	23	26
4 0 6	39	34	8 0 3	−44	41	12 0 $\bar{1}$	100	102	11 1 5	−74	69
2 0 6	89	97	6 0 3	−69	68	14 0 $\bar{1}$	47	48	9 1 5	−40	41
0 0 6	23	—	4 0 3	−27	23	16 0 $\bar{1}$	−64	61	7 1 5	33	—
2 0 $\bar{6}$	−98	86	2 0 3	59	71	18 0 $\bar{1}$	−71	71	5 1 5	64	68
4 0 $\bar{6}$	−68	73	0 0 3	63	80	20 0 $\bar{1}$	11	11	3 1 5	46	52
6 0 $\bar{6}$	48	56	2 0 $\bar{3}$	−50	63	18 0 0	66	67	1 1 5	−63	82
8 0 $\bar{6}$	92	81	4 0 $\bar{3}$	−86	90	16 0 0	−67	45	1 1 $\bar{5}$	−91	112
10 0 $\bar{6}$	−13	—	6 0 $\bar{3}$	11	—	14 0 0	−104	86	3 1 $\bar{5}$	62	82
12 0 $\bar{6}$	−96	82	8 0 $\bar{3}$	62	75	12 0 0	29	29	5 1 $\bar{5}$	115	111
14 0 $\bar{6}$	−36	27	10 0 $\bar{3}$	48	50	10 0 0	79	87	7 1 $\bar{5}$	−28	41
16 0 $\bar{6}$	59	61	12 0 $\bar{3}$	−16	—	8 0 0	96	113	9 1 $\bar{5}$	−83	82
12 0 5	12	—	14 0 $\bar{3}$	−65	73	6 0 0	−84	80	11 1 $\bar{5}$	−28	—
10 0 5	−92	66	16 0 $\bar{3}$	−13	—	4 0 0	−171	159	13 1 $\bar{5}$	33	—
8 0 5	−58	56	18 0 $\bar{3}$	80	73	2 0 0	8	—	15 1 $\bar{5}$	58	61
6 0 5	105	86	18 0 2	−29	21	3 1 8	−42	26	17 1 $\bar{5}$	5	—
4 0 5	105	90	16 0 2	12	—	1 1 8	−66	53	15 1 4	−3	—
2 0 5	−67	77	14 0 2	63	41	1 1 $\bar{8}$	−12	—	13 1 4	−78	50
0 0 5	−93	94	12 0 2	37	42	3 1 $\bar{8}$	81	78	11 1 4	−42	24
2 0 $\bar{5}$	0	—	10 0 2	−45	54	5 1 $\bar{8}$	42	49	9 1 4	58	68
4 0 $\bar{5}$	82	75	8 0 2	−96	106	7 1 $\bar{8}$	−46	37	7 1 4	96	90
6 0 $\bar{5}$	79	79	6 0 2	52	54	9 1 $\bar{8}$	−62	45	5 1 4	−58	66
8 0 $\bar{5}$	−41	57	4 0 2	86	99	11 1 $\bar{8}$	18	—	3 1 4	−94	90
10 0 $\bar{5}$	−130	115	2 0 2	−10	38				1 1 4	2	—
12 0 $\bar{5}$	5	—	0 0 2	−84	72	7 1 7	30	36	1 1 $\bar{4}$	91	69
14 0 $\bar{5}$	112	104	2 0 $\bar{2}$	−65	68	5 1 7	−79	80	3 1 $\bar{4}$	58	70

$h\,k\,l$	F calc	F obs	$h\,k\,l$	F calc	F obs	$h\,k\,l$	F calc	F obs	$h\,k\,l$	F calc	F obs
5 1 $\bar{4}$	−18	—	13 1 1	−56	55	2 4 0	10	—	3 3 $\bar{1}$	114	114
7 1 $\bar{4}$	−89	78	11 1 1	−67	74	4 4 0	−105	114	5 3 $\bar{1}$	2	—
9 1 $\bar{4}$	−17	—	9 1 1	20	—	6 4 0	−54	53	7 3 $\bar{1}$	−93	97
11 1 $\bar{4}$	105	102	7 1 1	104	82	8 4 0	62	57	9 3 $\bar{1}$	−58	46
13 1 $\bar{4}$	49	43	5 1 1	69	59	10 4 0	63	41	11 3 $\bar{1}$	37	37
15 1 $\bar{4}$	−63	55	3 1 1	−89	95	12 4 0	23	22	13 3 $\bar{1}$	69	80
17 1 $\bar{4}$	−67	58	1 1 1	−126	121				15 3 $\bar{1}$	3	—
19 1 $\bar{4}$	19	—	1 1 $\bar{1}$	59	68	14 4 0	−87	80	17 3 $\bar{1}$	−75	89
			3 1 $\bar{1}$	146	114						
15 1 3	−55	50	5 1 $\bar{1}$	−3	—	1 5 0	51	56	14 4 1	5	—
13 1 3	−1	—	7 1 $\bar{1}$	−110	90	3 5 0	4	—	12 4 1	−79	63
11 1 3	76	74	9 1 $\bar{1}$	−66	66	5 5 0	−76	84	10 4 1	−42	30
9 1 3	45	63	11 1 $\bar{1}$	39	51	7 5 0	−37	31	8 4 1	78	56
7 1 3	−89	88	13 1 $\bar{1}$	73	93	9 5 0	89	55	6 4 1	86	69
5 1 3	−101	91	15 1 $\bar{1}$	4	—	11 5 0	45	37			
3 1 3	45	52	17 1 $\bar{1}$	−79	85				4 4 1	−31	33
1 1 3	99	130	19 1 $\bar{1}$	−42	37	0 6 0	98	86	2 4 1	−88	102
1 1 $\bar{3}$	15	18				2 6 0	4	—	0 4 $\bar{1}$	−22	28
3 1 $\bar{3}$	−92	83	19 1 0	41	41	4 6 0	−55	46	2 4 $\bar{1}$	73	93
5 1 $\bar{3}$	−83	86	17 1 0	10	—	6 6 0	−29	16	4 4 $\bar{1}$	72	95
7 1 $\bar{3}$	50	66	15 1 0	−73	59				6 4 $\bar{1}$	−37	44
9 1 $\bar{3}$	120	93	13 1 0	−67	55	18 2 1	39	39	8 4 $\bar{1}$	−103	112
11 1 $\bar{3}$	−2	—	11 1 0	59	60	16 2 1	68	72	10 4 $\bar{1}$	−14	—
13 1 $\bar{3}$	−91	90	9 1 0	130	120	14 2 1	−1	—	12 4 $\bar{1}$	82	75
15 1 $\bar{3}$	−24	—	7 1 0	−60	51	12 2 1	−80	82	14 4 $\bar{1}$	40	32
17 1 $\bar{3}$	55	55	5 1 0	−116	118	10 2 1	−35	33			
19 1 $\bar{3}$	54	45	3 1 0	20	29	8 2 1	87	60	11 5 1	−53	49
			1 1 0	88	113	6 2 1	84	72	9 5 1	16	—
17 1 2	−50	78				4 2 1	−39	48	7 5 1	73	63
15 1 2	68	55	0 2 0	164	185	2 2 1	−85	85	5 5 1	40	31
13 1 2	89	78	2 2 0	−6	—	0 2 1	−17	25	3 5 1	−59	71
11 1 2	−41	58	4 2 0	−65	65	2 2 $\bar{1}$	69	82	1 5 1	−74	93
9 1 2	−69	64	6 2 0	−35	43	4 2 $\bar{1}$	73	89	1 5 $\bar{1}$	34	37
7 1 2	−43	49	8 2 0	38	37	6 2 $\bar{1}$	−32	34	3 5 $\bar{1}$	87	109
5 1 2	78	71	10 2 0	33	40	8 2 $\bar{1}$	−107	94	5 5 $\bar{1}$	3	—
3 1 2	82	78	12 2 0	46	53	10 2 $\bar{1}$	−22	16	7 5 $\bar{1}$	−73	69
1 1 2	−19	19	14 2 0	−62	73	12 2 $\bar{1}$	79	81	9 5 $\bar{1}$	−48	25
1 1 $\bar{2}$	−190	170	16 2 0	−67	63	14 2 $\bar{1}$	43	47	11 5 $\bar{1}$	31	35
3 1 $\bar{2}$	1	—	18 2 0	32	50	16 2 $\bar{1}$	−49	49	13 5 $\bar{1}$	59	65
5 1 $\bar{2}$	88	78	1 3 0	76	91	18 2 $\bar{1}$	−64	74			
7 1 $\bar{2}$	62	61	3 3 0	3	—				6 6 1	60	37
9 1 $\bar{2}$	−63	73	5 3 0	−103	129	15 3 1	39	43	4 6 1	−24	16
11 1 $\bar{2}$	−67	71	7 3 0	−46	46	13 3 1	−52	47	2 6 1	−61	61
13 1 $\bar{2}$	−32	51	9 3 0	119	121	11 3 1	−64	68	0 6 1	−14	13
15 1 $\bar{2}$	93	106	11 3 0	55	43	9 3 1	17	—	2 6 $\bar{1}$	50	49
17 1 $\bar{2}$	56	53	13 3 0	−65	65	7 3 1	91	77	4 6 $\bar{1}$	51	49
19 1 $\bar{2}$	−58	55	15 3 0	−70	55	5 3 1	55	57	6 6 $\bar{1}$	−24	14
			17 3 0	12	16	3 3 1	−74	93	8 6 $\bar{1}$	−74	49
17 1 1	78	68				1 3 1	−98	106			
15 1 1	40	49	0 4 0	170	212	1 3 $\bar{1}$	45	55			

The accuracy of the parameters of the oxygen atoms O$_3$—O$_6$ is estimated to be about ± 0.01.

Table 3. Comparison between calculated and observed structure factors of some reflections from Weissenberg photographs of WOP_2O_7. CuK radiation.

h k l	F_W calc	F_P calc	$F_W + F_P$ calc	F_O calc	F_{tot} calc	F obs
3 3 0	−38	+32	−6	+9	+3	—
7 3 0	−17	−20	−37	−9	−46	46
9 3 0	+81	+25	+106	+13	+119	121
7 5 0	−15	−16	−31	−6	−37	31
8 0 $\bar{7}$	+6	+22	+28	−1	+27	28
10 0 $\bar{5}$	−83	−23	−106	−24	−130	115
2 0 $\bar{4}$	+105	+19	+124	+36	+160	167
4 0 $\bar{3}$	−114	−15	−129	+43	−86	90
13 1 $\bar{3}$	−84	−15	−99	+8	−91	90
4 0 $\bar{2}$	+56	−38	+18	−19	−1	—
5 1 $\bar{2}$	+106	+22	+128	−40	+88	78
7 1 $\bar{2}$	+75	−30	+45	+17	+62	61
9 1 0	+93	+29	+122	+8	+130	120
2 2 0	+33	−17	+16	−22	−6	—
4 2 0	−98	−24	−122	+57	−65	65
1 1 2	−44	+17	−27	+8	−19	19
3 1 2	+96	+20	+116	−34	+82	78
5 1 2	+87	−30	+57	+21	+78	71
6 0 3	−102	+20	−82	+13	−69	68
10 0 3	+76	−14	+62	−19	+43	48
8 0 5	−24	−21	−45	−13	−58	56
5 1 5	+87	−24	+63	+1	+64	68
9 1 5	−65	+17	−48	+8	−40	41

Using these parameters the F values were calculated for the reflexions and compared with the observed ones. They are given in Table 2 for $hk0$, $h0l$, $hk1$ and $h1l$. Table 3 gives the details for some reflexions which have more pronounced phosphorus and oxygen contributions to the magnitudes of the structure factors. The reliability index, R, calculated according to Booth (see Ref.[5], p. 101), was found to be 0.14 for $hk0$ and 0.13 for $h0l$ (absent reflexions not included) and 0.34 or 0.24 for the same reflexions calculated *without* the phosphorus and oxygen atoms, and 0.24 or 0.19 calculated without the oxygen atoms, showing that the structure should be essentially correct as regards the heavy atoms and also indicating that the proposed coordinates of the phosphorus and the oxygen atoms will give much better agreement between observed and calculated intensities.

In the structure determination described above we have assumed that the structure is consistent with the space group $C2/m$ having the highest symmetry. This will give that the y coordinates for W, P, O_3—O_6 must be equal to 0 or $\frac{1}{2}$. From the Patterson projection $P(uvp)$ we see that these atoms at least will be situated close to these planes. In fact it does not seem possible to get any essential difference for the atom arrangement even if the less symmetrical space groups are considered but this will increase the errors in the parameters, as most of the coordinates will be obtained from overlapping peaks [10]. Moreover, since the electron density projections show distinct
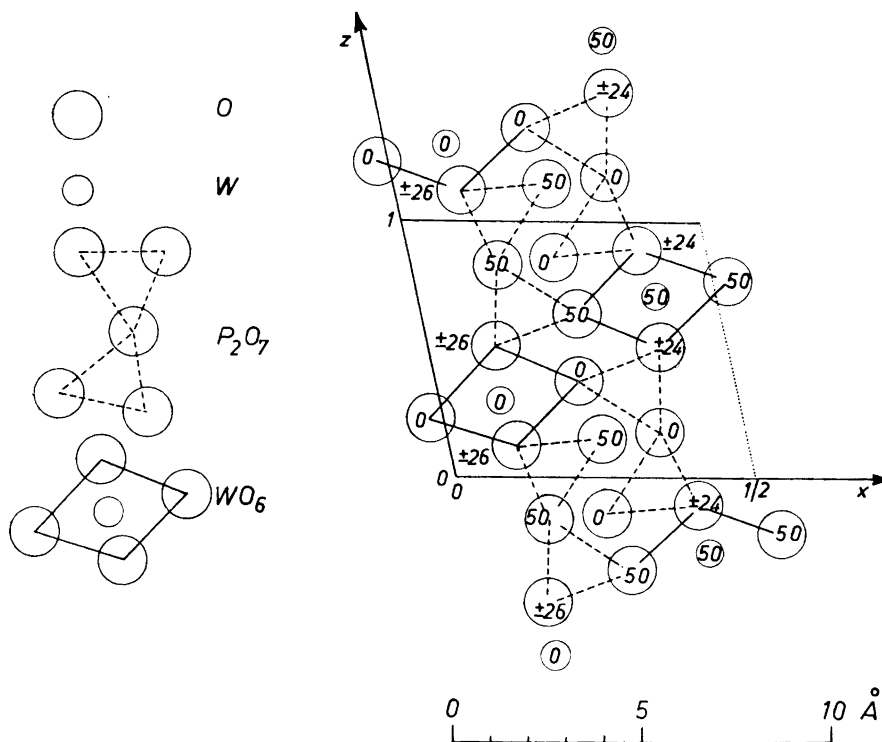
Fig. 8. The layer of WOP_2O_7. Only one layer has been indicated (*i. e.* wolfram and oxygen atoms with x parameters within the limits $-0.02 \le x \le 0.52$). The figures denote the height of the atoms in percentages of b.

maxima and the electron density projected on two different planes (xy and xz) show mutual agreement, it seems very probable that the atoms belong to the space group $C2/m$.

DESCRIPTION OF THE STRUCTURE

The structure of $WO_3.P_2O_5$ may be described as built up of WO_6-octahedra and P_2O_7-groups. Every wolfram atom is in contact with five P_2O_7-groups and every P_2O_7-group with five wolfram atoms. Every wolfram atom is also in contact with one oxygen atom (O_6), which is bonded only to this wolfram atom, so that the crystals are built up of WOP_2O_7-layers parallel to the yz plane (Fig. 8). The layers are thus electrically neutral, so that in the crystals there are only feeble attractive forces between neighbouring layers, which will explain the pronounced basal cleavage along the yz plane. The building principle might be expressed by the formula WOP_2O_7 and the compound should then be written according to this rather than $WO_3.P_2O_5$.

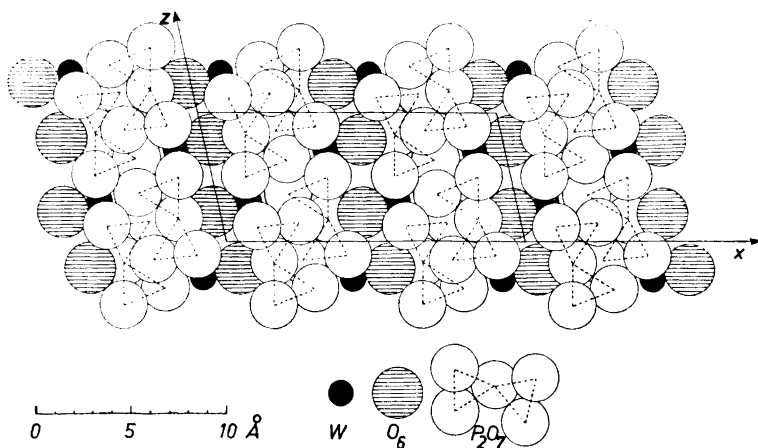The xz projection of the structure is shown in Fig. 9.

Fig. 9. Projection on the *xz* plane of the structure of WOP$_2$O$_7$.

The distances between neighbouring atoms in WOP$_2$O$_7$ will be (in Å)

W—2 O$_1$;	O$_1$—W	$= 1.9_6$
W—2 O$_2$;	O$_2$—W	$= 1.8_9$
W—O$_3$;	O$_3$—W	$= 2.1_0$
W—O$_6$;	O$_6$—W	$= 1.9_7$
P$_1$—2 O$_1$;	O$_1$—P	$= 1.6_0$
P$_1$—O$_3$;	O$_3$—P$_1$	$= 1.5_5$ *
P$_1$—O$_4$;	O$_4$—2 P$_{1,2}$	$= 1.5_5$ *
P$_2$—O$_2$;	O$_2$—P$_2$	$= 1.5_9$
P$_2$—O$_4$;	O$_4$—2 P$_{1,2}$	$= 1.5_5$ *
P$_2$—O$_5$;	O$_5$—P$_2$	$= 1.5_5$ *
O$_1$—3 O$_1$		$= 2.4_8$; 2.6_8; 3.4_6
O$_1$—O$_2$;	O$_2$—O$_1$	$= 2.6_7$
O$_1$—2 O$_3$;	O$_3$—2 O$_1$	$= 2 \times 2.6_5$; $2 \times 2.7_6$
O$_1$—O$_4$;	O$_4$—2 O$_1$	$= 2.5_7$
O$_1$—O$_5$;	O$_5$—2 O$_1$	$= 3.1_4$
O$_1$—2 O$_6$;	O$_6$—4 O$_1$	$= 2 \times 2.8_8$; $2 \times 2.9_3$
O$_2$—3 O$_2$		$= 2.4_8$; 2.6_8; 3.4_7
O$_2$—O$_3$;	O$_3$—2 O$_2$	$= 2.7_3$
O$_2$—O$_4$;	O$_4$—2 O$_2$	$= 2.4_5$
O$_2$—2 O$_5$;	O$_5$—2 O$_2$	$= 2 \times 2.6_0$; $2 \times 3.3_2$
O$_2$—2 O$_6$;	O$_6$—4 O$_2$	$= 2 \times 2.7_3$; $2 \times 2.7_4$
O$_3$—O$_3$		$= 3.1_6$
O$_3$—O$_4$;	O$_4$—O$_3$	$= 2.5_3$ *
O$_3$—3 O$_5$;	O$_5$—3 O$_3$	$= 3.0_3$; 3.3_6 (3.5_6)
O$_4$—2 O$_5$;	O$_5$—2 O$_4$	$= 2.5_3$ *; 3.0_1
O$_4$—O$_6$;	O$_6$—O$_4$	$= 3.1_4$
O$_5$—O$_6$;	O$_6$—O$_5$	$= 3.3_4$
O$_6$—O$_6$		$= 3.2_6$

* These distances were taken from previously determined structures and used directly in the determination of the oxygen positions.

The O—O distances are all within the normal range — the shortest O—O distances 2.4$_5$ Å are within the P$_2$O$_7$ group — showing that the lattice is also supported by O—O contacts. However, they may be in error by a few tenths of an Ångström unit.

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