

## The Crystal Structure of $W_2O_3(PO_4)_2$

### Determination of a Superstructure by Means of Least-Squares Calculations

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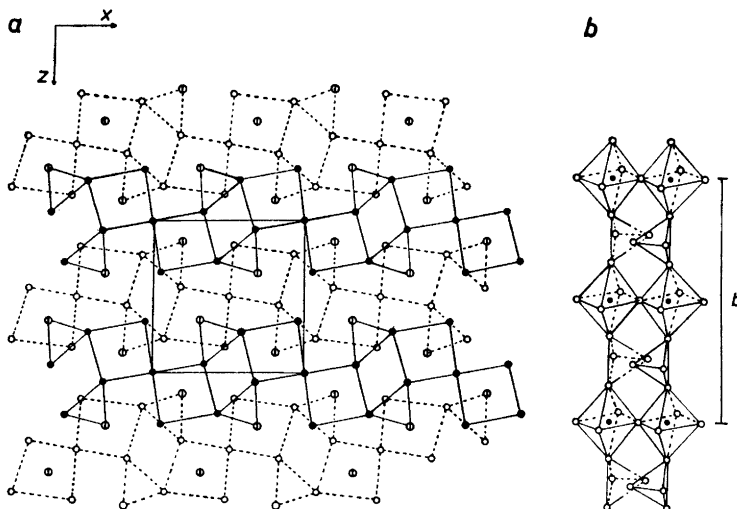
The crystallographic data given for the idealized structure of  $W_2O_3(PO_4)_2$  have been used in the determination of the superstructure by means of least-squares calculations. The character of the superstructure and the procedure of computation are discussed.

Some years ago a paper describing investigations of the structure of  $W_2O_3(PO_4)_2$  was published<sup>1</sup> by one of the present authors. It was found that the crystals are built up of  $PO_4$  groups sharing their corners with four  $WO_6$  octahedra, each of which is coupled with four different  $PO_4$  tetrahedra. Thus, four of the six oxygen atoms in each octahedron are shared with tetrahedra, and, of the remaining two oxygens, one is common with another  $WO_6$  octahedron while the sixth one is unshared. The pairs of octahedra thus obtained are then held together by the  $PO_4$  groups in such a way that a three-dimensional network is formed (Fig. 1).

The arrangement thus arrived at was, however, characterized<sup>1</sup> as an idealized structure that should be slightly distorted in order to account for the occurrence of some weak reflections. Since a program (No. 6023<sup>2</sup>) for least-squares calculation by means of the electronic computer Facit EDB became available, it was possible to perform a further refinement of the idealized structure. The interest in such a refinement was partly to reveal the structural details giving rise to the weak reflections just mentioned, and also to give some elucidation to the more general problem of solving a superstructure by applying least-squares refinement. This article will describe the result thus obtained.

#### THE STRUCTURE DETERMINATION

The X-ray diffraction data used in the refinement study were those collected for the derivation of the idealized structure. This material was recorded photographically using the multiple-film technique. The intensities were



*Fig. 1.* Schematic drawings showing the idealized structure of  $W_2O_5(PO_4)_2$ . *a*) The structure viewed along [010] showing the pairs of  $WO_6$  octahedra and the links between these and the  $PO_4$  tetrahedra. Open and full circles denote oxygen atoms situated in two separate planes  $b/4 = 3.12 \text{ \AA}$  apart. Lined open circles denote oxygen atoms shared between  $WO_6$  octahedra and  $PO_4$  tetrahedra as shown in Fig. 1*b*. The tungsten and phosphorus atoms have not been indicated. *b*) The links in the  $y$ -direction between the pairs of  $WO_6$  octahedra and  $PO_4$  tetrahedra. Open circles denote oxygen atoms and full ones tungsten atoms. The phosphorus atoms in each  $PO_4$  tetrahedron have been omitted. The two remaining unshared oxygens in each  $PO_4$  tetrahedron are linked — as shown in Fig. 1*a* — with two further octahedra which have not been indicated.

estimated visually by comparison with a scale of reflections of known intensities. A correction for anomalous dispersion<sup>3</sup> was applied. This X-ray material was deemed to be adequate to provide information about the detailed architecture of this compound, which was confirmed by the outcome of this work.

The unit-cell dimensions were recalculated by means of a least-squares program (No. 6018<sup>2</sup>) using data already published<sup>1</sup> from a powder photograph taken with strictly monochromatized  $CuK\alpha_1$  radiation. The dimensions and standard deviations were found to be:

$$\begin{aligned} a &= 7.822 \pm 0.004 \text{ \AA} \\ b &= 12.50 \pm 0.01 \text{ \AA} \\ c &= 7.754 \pm 0.007 \text{ \AA} \\ \beta &= 91.05 \pm 0.05^\circ \end{aligned}$$

The idealized atomic arrangement reported in Ref.<sup>1</sup> does not explain the occurrence of the weak reflections with odd  $k$ . The appearance of these reflections could very likely be accounted for by assuming a distortion of the structure, in such a way that some or all of the atoms are displaced from the positions of the idealized structure. Such distortions could for instance imply that some of the atoms are moved slightly out of the planes  $y = \pm 1/4$ ,

Table 1. The starting coordinates for the least-squares refinement of  $W_2O_3(PO_4)_2$ .

Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$
2 $W_1$	0.310	0.000	0.653	2 $O_4$	0.93	0.00	0.22
2 $W_1'$	0.690	0.000	0.347	2 $O_4'$	0.07	0.00	0.78
2 $W_2$	0.195	0.250	0.137	2 $O_5$	0.50	0.00	0.50
2 $W_3$	0.805	0.250	0.863	2 $O_6$	0.00	0.25	0.00
				2 $O_7$	0.05	0.25	0.34
2 $P_1$	0.12	0.00	0.25	2 $O_8$	0.95	0.25	0.66
2 $P_1'$	0.88	0.00	0.75	2 $O_9$	0.42	0.25	0.27
2 $P_2$	0.61	0.25	0.24	2 $O_{10}$	0.58	0.25	0.73
2 $P_3$	0.39	0.25	0.76	2 $O_{11}$	0.67	0.25	0.06
				2 $O_{12}$	0.33	0.25	0.94
2 $O_1$	0.20	0.10	0.14	2 $O_{13}$	0.47	0.00	0.83
2 $O_1'$	0.80	0.90	0.86	2 $O_{13}'$	0.53	0.00	0.17
2 $O_2$	0.20	0.90	0.14	2 $O_{14}$	0.31	0.15	0.65
2 $O_2'$	0.80	0.10	0.86	2 $O_{14}'$	0.69	0.85	0.35
2 $O_3$	0.17	0.00	0.44	2 $O_{15}$	0.31	0.85	0.65
2 $O_3'$	0.83	0.00	0.56	2 $O_{15}'$	0.69	0.15	0.35

which are mirror planes in the preliminary structure described with the symmetry  $P2_1/m$ . Therefore, the refinement work was started assuming that the parameters obtained for the atoms are nearly correct but that the symmetry is the lower space group  $P2_1$ . This implies that all the atoms are in point positions  $2(a)$ :  $x, y, z$ ;  $\bar{x}, \frac{1}{2} + y, \bar{z}$ . Accordingly, all the atoms in a position  $4(f)$  of  $P2_1/m$  were placed in two positions  $2(a)$  of  $P2_1$ , giving the starting coordinates for the least-squares refinement (listed in Table 1).

The calculations were started with a refinement of the  $x$  and  $z$  parameters of the wolfram atoms using only  $F$  values with  $k$  even and with all other coordinates ( $y$  for the wolfram atoms and  $x, y$ , and  $z$  for the light atoms, phosphorus and oxygen) at fixed values. This led, after a few cycles of refinement, to minor changes of the coordinates of the heavy atoms. Next phase of computing was concerned with the  $x$  and  $z$  parameters of two ( $P_1$  and  $P_3$ ) of the four phosphorus atoms and the  $x, y$ , and  $z$  coordinates of the two oxygen atoms  $O_1$  and  $O_{14}$ . When after some cycles coordinate shifts were fairly small, the  $x$  and  $z$  parameters of six more oxygen atoms ( $O_3, O_4, O_7, O_9, O_{11}$ , and  $O_{13}$ ) were released, all other coordinate parameters being kept at fixed values. By proceeding in this stepwise manner, contributions to the calculated  $F$  values were obtained after several cycles even for indices with  $k$  odd, and from this stage of the refinement work it was thus possible to include the observed  $F$  values with  $k$  odd in the subsequent cycles.

Finally, the coordinates of all the atoms were released and the refinement carried to a stage corresponding to a value of 13.4 % of the reliability index  $R$ .

However, it was found that the parameters of two ( $P_1$ ) of the eight phosphorus atoms could not be refined in this way. The shifts and the standard deviations were always big and the temperature factor rose to high values, indicating a tendency to remove these atoms. The interatomic distances calculated at this stage also showed that the coordinates of these phosphorus atoms were very likely to be incorrect, some P—O distances being too short.

By applying three-dimensional Fourier synthesis, it should, however, be possible to find the correct position of the phosphorus atoms  $P_1$ . Therefore  $\rho(x0z)$  with the heavy wolfram atoms subtracted was computed using the programs<sup>2</sup> Nos. 6015 and 6014. Besides peaks corresponding to atomic positions as found from the least-squares calculations, a rather high maximum at  $x = 0.36$ ,  $z = 0.08$  was observed. From the height and the position (tetrahedrally surrounded by four oxygens) of that peak, it was interpreted as being caused by phosphorus atoms  $P_1$ .

Coordinates of the  $P_1$  atom thus obtained, together with the parameters for the rest of the atoms obtained from the least-squares calculations described above, formed the basis for the subsequent stage of the structural analysis.

The least-squares treatment was thus continued until after a considerable number of cycles the shifts of the parameters had decreased to minor fractions of the standard deviations. Cruickshank's weighting function

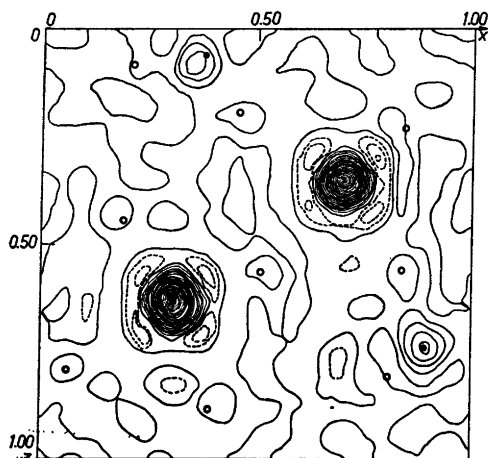
$$w = (A + |F_{\text{obs}}| + C|F_{\text{obs}}|^2)^{-1}$$

was used in the refinement with the following final values for the parameters:  $A = +1$ ,  $C = +0.010$ . A weight analysis obtained in the last cycle is given in Table 2. The value of  $R$ , reached after these calculations was 11.9 %. A list of the observed and calculated  $F$ -values is included in a document<sup>4</sup> which may be obtained on request from the secretary of this Institute.

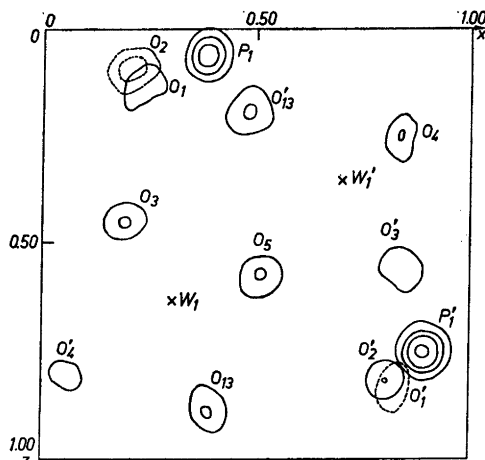
In order to check further the coordinates thus obtained, some three-dimensional electron density calculations were carried out. As most of the atoms were found to be situated close to the planes  $y = 0$  (or  $\frac{1}{2}$ ) and  $y = \frac{1}{4}$  (or  $\frac{3}{4}$ ), the electron density functions  $\rho(x0z)$  and  $\rho(x\frac{1}{4}z)$  were computed. The results are shown in Figs. 2a and 3a. As can be seen, the wolfram and phosphorus atoms stand out clearly while the oxygen atoms appear less marked, which may be due to termination of series effects and also to displacements of the atoms from the planes,  $y = 0$  and  $\frac{1}{4}$ . In order to reduce the influence of the

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of  $W_2O_3(PO_4)_2$ .  $w$  = weighting factor,  $\Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$

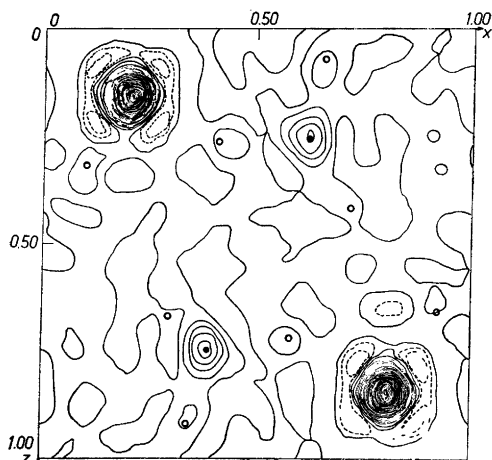
Interval sin $\Theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval $F_{\text{obs}}$	Number of independent reflections	$\overline{w\Delta^2}$
0.00—0.46	158	0.85	0—30	111	0.47
0.46—0.58	119	0.62	30—60	228	0.78
0.58—0.67	104	0.70	60—90	137	1.11
0.67—0.74	100	0.79	90—120	79	1.25
0.74—0.79	82	1.06	120—150	100	0.96
0.79—0.84	99	1.03	150—180	87	1.16
0.84—0.89	78	1.28	180—210	68	1.42
0.89—0.93	105	0.92	210—240	71	1.34
0.93—0.97	100	1.32	240—270	51	1.28
0.97—1.00	35	2.97	270—300	48	0.93



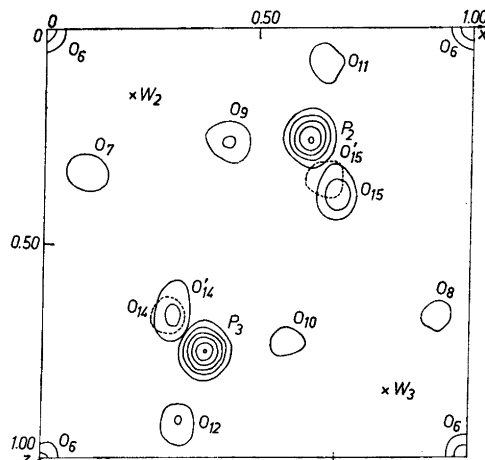
*Fig. 2a.* The electron density function  $\rho(x0z)$  for  $W_2O_3(PO_4)_2$ . The final positions of the phosphorus (●) and oxygen (○) atoms have been marked. In the wolfram peak every second contour has been marked. Dashed lines indicate negative values.



*Fig. 2b.* The results of the calculations of the three-dimensional electron density function for  $W_2O_3(PO_4)_2$ , calculated (for atoms with  $-0.12 < y < 0.12$ ) with the wolfram atoms subtracted. The heights of the observed peaks have been projected on the plane  $y=0$ . Dashed lines indicate the oxygen atoms,  $O_1'$  and  $O_2'$ , situated below the plane.



*Fig. 3a.* The electron density function  $\rho(x \frac{1}{4} z)$  for  $W_2O_3(PO_4)_2$ . The final positions of the atoms have been indicated as in Fig. 2a. In the wolfram peak every second contour has been marked. Dashed lines indicate negative values.



*Fig. 3b.* The results of the calculations of the three-dimensional electron density function for  $W_2O_3(PO_4)_2$ , calculated (for atoms with  $0.15 < y < 0.35$ ) with the wolfram atoms subtracted. The heights of the observed peaks have been projected on the plane  $y = \frac{1}{4}$ . Dashed lines indicate the oxygen atoms  $O_{14}'$  and  $O_{15}'$ , situated below the plane  $y = \frac{1}{4}$ .

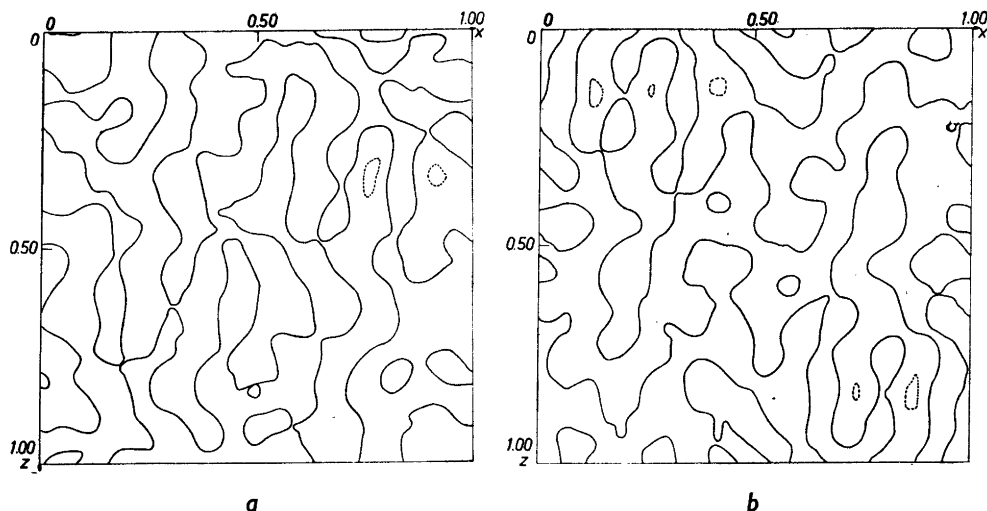


Fig. 4. The difference Fourier synthesis for  $W_2O_3(PO_4)_2$ . Dashed lines indicate negative values. *a*) The function  $D(x0z)$ , *b*) The function  $D(x\frac{1}{2}z)$ .

diffraction effects, the wolfram atoms were subtracted and the subsequent electron density calculations were carried out around each of the light atoms. The composite projections are shown in Figs. 2b and 3b.

From final electron density difference syntheses,  $D(x0z)$  and  $D(x\frac{1}{2}z)$ , shown in Fig. 4, further evidence was obtained of the correctness of the structure.

The structure thus derived from the least-squares refinement is given in Table 3. Mean values of the isotropic "temperature factors" ( $B$  in  $\text{\AA}^2$ ) were found to be 0.20 for the wolfram atoms and 0.40 for the light atoms (phosphorus and oxygen). As the data were not corrected for absorption, the "temperature factors" have no real physical meaning.

The interatomic distances within the  $PO_4$  and  $WO_6$ -groups are given in Table 4. They all have reasonable values as is the case also with the other distances between neighbouring atoms. A complete list is given in the document <sup>4</sup> mentioned above.

#### DISCUSSION

The complete structure refinement of  $W_2O_3(PO_4)_2$  has not changed the validity of the description of the structural architecture given in the introduction of this article. The wolfram, oxygen, and six of the eight phosphorus atoms all remain essentially at their positions in the idealized structure.

In the determination described earlier <sup>1</sup> the symmetry had been assumed to be  $P2_1/m$ , and from this assumption and subsequent structure analysis four phosphorus atoms ( $P_1$ ) were found to be situated in the point position 4(*f*):

Table 3. The crystal structure of  $W_2O_3(PO_4)_2$ . Space group:  $P2_1$ . Cell content:  $4 W_2O_3(PO_4)_2$ . 8 W, 8 P and 44 O in  $30 \times 2(a)$ :  $(x, y, z)$ ;  $(\bar{x}, \frac{1}{2} + y, \bar{z})$ .

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B) \text{ \AA}^2$
1 $W_1$	$0.3082 \pm 0.0003$	$0.9976 \pm 0.0005$	$0.6351 \pm 0.0003$	} $0.20 \pm 0.05$
2 $W_1'$	$0.7024 \pm 0.0003$	$0.9929 \pm 0.0005$	$0.3585 \pm 0.0003$	
3 $W_2$	$0.1913 \pm 0.0005$	$0.2501 \pm 0.0003$	$0.1533 \pm 0.0004$	
4 $W_3$	$0.8074 \pm 0.0004$	$0.2557 \pm 0.0003$	$0.8462 \pm 0.0004$	
5 $P_1$	$0.3226 \pm 0.0018$	$0.0046 \pm 0.0028$	$0.0737 \pm 0.0018$	} $0.40$
6 $P_1'$	$0.8943 \pm 0.0016$	$0.9916 \pm 0.0022$	$0.7508 \pm 0.0016$	
7 $P_2$	$0.6178 \pm 0.0026$	$0.2582 \pm 0.0018$	$0.2607 \pm 0.0025$	
8 $P_3$	$0.3820 \pm 0.0020$	$0.2606 \pm 0.0014$	$0.7514 \pm 0.0019$	
9 $O_1$	$0.224 \pm 0.003$	$0.099 \pm 0.003$	$0.084 \pm 0.004$	
10 $O_1'$	$0.796 \pm 0.005$	$0.889 \pm 0.004$	$0.811 \pm 0.005$	
11 $O_2$	$0.258 \pm 0.006$	$0.904 \pm 0.005$	$0.129 \pm 0.006$	
12 $O_2'$	$0.839 \pm 0.008$	$0.079 \pm 0.006$	$0.842 \pm 0.008$	
13 $O_3$	$0.193 \pm 0.004$	$0.009 \pm 0.005$	$0.442 \pm 0.004$	
14 $O_3'$	$0.852 \pm 0.004$	$0.995 \pm 0.007$	$0.561 \pm 0.005$	
15 $O_4$	$0.834 \pm 0.006$	$0.017 \pm 0.006$	$0.197 \pm 0.006$	} $0.40$
16 $O_4'$	$0.086 \pm 0.004$	$0.976 \pm 0.004$	$0.788 \pm 0.004$	
17 $O_5$	$0.517 \pm 0.004$	$0.988 \pm 0.004$	$0.570 \pm 0.004$	
18 $O_6$	$0.991 \pm 0.004$	$0.229 \pm 0.003$	$0.991 \pm 0.004$	
19 $O_7$	$0.088 \pm 0.006$	$0.243 \pm 0.004$	$0.331 \pm 0.005$	
20 $O_8$	$0.911 \pm 0.007$	$0.300 \pm 0.005$	$0.665 \pm 0.007$	
21 $O_9$	$0.421 \pm 0.005$	$0.263 \pm 0.003$	$0.257 \pm 0.005$	
22 $O_{10}$	$0.584 \pm 0.009$	$0.267 \pm 0.006$	$0.722 \pm 0.009$	
23 $O_{11}$	$0.652 \pm 0.007$	$0.239 \pm 0.004$	$0.082 \pm 0.006$	
24 $O_{12}$	$0.326 \pm 0.004$	$0.287 \pm 0.003$	$0.922 \pm 0.004$	
25 $O_{13}$	$0.410 \pm 0.004$	$0.010 \pm 0.005$	$0.888 \pm 0.004$	
26 $O_{13}'$	$0.497 \pm 0.004$	$0.007 \pm 0.005$	$0.208 \pm 0.004$	} $0.40$
27 $O_{14}$	$0.279 \pm 0.007$	$0.162 \pm 0.006$	$0.664 \pm 0.007$	
28 $O_{14}'$	$0.687 \pm 0.003$	$0.842 \pm 0.003$	$0.389 \pm 0.003$	
29 $O_{15}$	$0.301 \pm 0.007$	$0.841 \pm 0.006$	$0.669 \pm 0.007$	
30 $O_{15}'$	$0.640 \pm 0.006$	$0.155 \pm 0.005$	$0.343 \pm 0.006$	

$\pm (x, y, z)$ ;  $\pm (x, \frac{1}{2} - y, z)$  with  $y = 0$ . This gives two atoms in each of the planes  $y = 0$  and  $\frac{1}{2}$  which overlap in the (010) projection.

Now with the symmetry  $P2_1$  arrived at from the present study, all atoms have to be situated in positions  $2(a)$ . This means that such overlapping in the (010) projection is not required by symmetry. As described above it was also found that only two ( $P_1'$ ) of the four phosphorus atoms of the  $4(f)$  position of the idealized structure retained their positions, while the two remaining ones ( $P_1$ ) were subject to considerable positional shifts during the refinement process. Thus, the arrangement of the phosphorus atoms in the plane  $y = 0$  is different from the one in  $y = \frac{1}{2}$  (for the sake of simplicity we omit that the

Table 4. Interatomic distances and estimated standard deviations (in Å) within the PO<sub>4</sub> tetrahedra and WO<sub>6</sub> octahedra in W<sub>2</sub>O<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

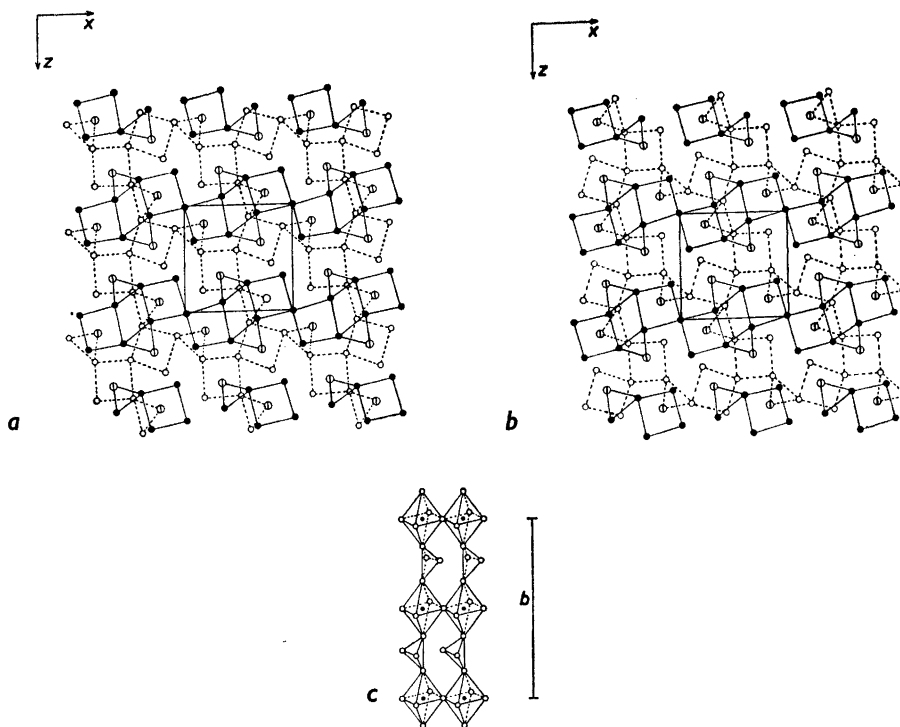
$\left. \begin{array}{l} W_1 - O_3 = 1.74 \pm 0.04 \\ - O_4' = 2.14 \pm 0.04 \\ - O_5 = 1.72 \pm 0.03 \\ - O_{13} = 2.11 \pm 0.04 \\ - O_{14} = 2.08 \pm 0.08 \\ - O_{15} = 1.97 \pm 0.08 \end{array} \right\} \overline{W_1 - O} = 1.96$	$\left. \begin{array}{l} W_1' - O_3' = 1.94 \pm 0.04 \\ - O_4 = 1.66 \pm 0.05 \\ - O_5 = 2.21 \pm 0.03 \\ - O_{13}' = 1.98 \pm 0.04 \\ - O_{14}' = 1.90 \pm 0.04 \\ - O_{15}' = 2.08 \pm 0.07 \end{array} \right\} \overline{W_1' - O} = 1.96$
$\left. \begin{array}{l} W_2 - O_1 = 1.98 \pm 0.04 \\ - O_1' = 1.76 \pm 0.06 \\ - O_6 = 2.01 \pm 0.04 \\ - O_7 = 1.61 \pm 0.05 \\ - O_9 = 1.96 \pm 0.04 \\ - O_{12} = 2.15 \pm 0.04 \end{array} \right\} \overline{W_2 - O} = 1.91$	$\left. \begin{array}{l} W_3 - O_2 = 1.93 \pm 0.07 \\ - O_2' = 2.24 \pm 0.08 \\ - O_6 = 1.84 \pm 0.04 \\ - O_8 = 1.73 \pm 0.06 \\ - O_{10} = 1.99 \pm 0.08 \\ - O_{11} = 2.23 \pm 0.05 \end{array} \right\} \overline{W_3 - O} = 1.99$
$\left. \begin{array}{l} P_1 - O_1 = 1.55 \pm 0.05 \\ - O_3 = 1.52 \pm 0.07 \\ - O_{13} = 1.52 \pm 0.04 \\ - O_{13}' = 1.52 \pm 0.04 \end{array} \right\} \overline{P_1 - O} = 1.53$	$\left. \begin{array}{l} P_1' - O_1' = 1.57 \pm 0.06 \\ - O_2' = 1.37 \pm 0.08 \\ - O_3' = 1.50 \pm 0.04 \\ - O_4' = 1.53 \pm 0.04 \end{array} \right\} \overline{P_1' - O} = 1.49$
$\left. \begin{array}{l} P_2 - O_9 = 1.54 \pm 0.05 \\ - O_{11} = 1.44 \pm 0.06 \\ - O_{15} = 1.33 \pm 0.07 \\ - O_{15}' = 1.45 \pm 0.07 \end{array} \right\} \overline{P_2 - O} = 1.44$	$\left. \begin{array}{l} P_3 - O_{10} = 1.60 \pm 0.08 \\ - O_{12} = 1.44 \pm 0.04 \\ - O_{14} = 1.61 \pm 0.07 \\ - O_{14}' = 1.58 \pm 0.04 \end{array} \right\} \overline{P_3 - O} = 1.56$

O-O:  $\sigma \approx \pm 0.12$ 

$\begin{array}{l} O_3 - O_4' = 2.86 \\ - O_5 = 3.15 \\ - O_{14} = 2.65 \\ - O_{15} = 2.85 \\ O_4' - O_{13} = 2.67 \\ - O_{14} = 2.95 \\ - O_{15} = 2.56 \\ O_5 - O_{13} = 2.64 \\ - O_{14} = 2.97 \\ - O_{15} = 2.62 \\ O_{13} - O_{14} = 2.76 \\ - O_{15} = 2.82 \end{array}$	$\begin{array}{l} O_3' - O_4 = 2.84 \\ - O_5 = 2.63 \\ - O_{14}' = 2.65 \\ - O_{15}' = 3.08 \\ O_4 - O_{13}' = 2.64 \\ - O_{14}' = 2.89 \\ - O_{15}' = 2.57 \\ O_5 - O_{13}' = 2.81 \\ - O_{14}' = 2.66 \\ - O_{15}' = 2.90 \\ O_{13}' - O_{14}' = 2.88 \\ - O_{15}' = 2.40 \end{array}$	$\begin{array}{l} O_1 - O_6 = 2.53 \\ - O_7 = 2.85 \\ - O_9 = 2.88 \\ - O_{12} = 2.79 \\ O_1' - O_6 = 3.00 \\ - O_7 = 2.32 \\ - O_9 = 2.37 \\ - O_{12} = 2.62 \\ O_8 - O_7 = 2.73 \\ - O_{12} = 2.78 \\ O_7 - O_9 = 2.69 \\ O_9 - O_{12} = 2.71 \end{array}$	$\begin{array}{l} O_2 - O_6 = 3.07 \\ - O_3 = 2.46 \\ - O_{10} = 2.40 \\ - O_{11} = 2.74 \\ O_2' - O_6 = 2.51 \\ - O_3 = 3.15 \\ - O_{10} = 3.22 \\ - O_{11} = 3.12 \\ O_6 - O_8 = 2.74 \\ - O_{11} = 2.76 \\ O_8 - O_{10} = 2.64 \\ O_{10} - O_{11} = 2.86 \end{array}$
$\begin{array}{l} O_1 - O_2 = 2.48 \\ - O_{13} = 2.40 \\ - O_{15} = 2.60 \\ O_2 - O_{13} = 2.59 \\ - O_{15} = 2.34 \\ O_{13} - O_{13}' = 2.56 \end{array}$	$\begin{array}{l} O_1' - O_2' = 2.40 \\ - O_3' = 2.39 \\ - O_4' = 2.52 \\ O_2' - O_3' = 2.41 \\ - O_4' = 2.36 \\ O_3' - O_4' = 2.52 \end{array}$	$\begin{array}{l} O_9 - O_{11} = 2.30 \\ - O_{15} = 2.45 \\ - O_{15}' = 2.27 \\ O_{11} - O_{15} = 2.35 \\ - O_{15}' = 2.28 \\ O_{15} - O_{15}' = 2.38 \end{array}$	$\begin{array}{l} O_{10} - O_{12} = 2.58 \\ - O_{14} = 2.74 \\ - O_{14}' = 2.45 \\ O_{12} - O_{14} = 2.56 \\ - O_{14}' = 2.51 \\ O_{14} - O_{14}' = 2.30 \end{array}$

atoms not are situated exactly in the planes), while the arrangements in the planes  $y = \pm \frac{1}{4}$  are nearly the same. The schematic drawings in Fig. 5 show the structure of W<sub>2</sub>O<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. The chemical implications of the structural ion formation thus derived will be treated elsewhere.





*Fig. 5.* Schematic drawings showing the structure of  $W_2O_3(PO_4)_2$  viewed along  $[010]$  showing the pairs of  $WO_6$  octahedra and the links between these and the  $PO_4$  tetrahedra. Open and full circles denote oxygen atoms situated in or very close to two separate planes  $b/4 = 3.12 \text{ \AA}$  apart. *a)* The planes  $y = 0$  and  $\frac{1}{4}$  and *b)* the planes  $y = \frac{1}{2}$  and  $\frac{3}{4}$ . Lined open circles denote oxygen atoms shared between  $WO_6$  octahedra and  $PO_4$  tetrahedra as shown in Fig. 5c. The wolfram and phosphorus atoms have not been indicated. *c)* The links in the  $y$ -direction between the pairs of  $WO_6$  octahedra and  $PO_4$  tetrahedra. Open circles denote oxygen atoms and full ones wolfram atoms. The phosphorus atoms in each  $PO_4$  tetrahedron have been omitted. The two remaining unshared oxygens in each  $PO_4$  tetrahedron are linked as shown in Figs. 5*a* and *b* — with two further octahedra which have not been indicated.

The successful performance of the present structural refinement has demonstrated the possibility of determining a superstructure, starting from a knowledge of an idealized structure, by applying least-squares computing techniques. The procedure implies successive release of the atomic parameters of groups of atoms chosen in a rational way. Further aspects on this question will be presented elsewhere.

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## REFERENCES

1. Kierkegaard, P. *Acta Chem. Scand.* **14** (1960) 657.
2. *World List of Crystallographic Computer Programs*, 1st Ed., Sept. 1962. (International Union of Crystallography).
3. Dauben, C. H. and Templeton, D. H. *Acta Cryst.* **8** (1955) 841.
4. Kierkegaard, P. *Univ. Stockholm, Inorg. Chem. DIS No.* **9** (1964).

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