

## The Crystal Structure of Ta<sub>2</sub>P

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The crystal structure of Ta<sub>2</sub>P has been determined and refined by X-ray single crystal methods. The unit cell is orthorhombic and the dimensions, determined by powder diffraction techniques, are  $a = 14.419 \text{ \AA}$ ,  $b = 11.552 \text{ \AA}$ , and  $c = 3.399 \text{ \AA}$ . There are 12 formula units in the unit cell. The refinement of the structure is based on the space-group  $Pnmm$ . All the atoms occupy the four-fold position  $4(g)$ .

A re-investigation of the binary systems Nb-P, Ta-P and W-P has recently been started at this Institute.<sup>1</sup> In preliminary experiments it has been observed that several new phases are formed at high temperatures. Among these phases, Ta<sub>2</sub>P has already been characterized crystallographically. The present paper gives an account of a complete single-crystal structure determination of this compound.

### EXPERIMENTAL

*Preparation.* The starting materials were tantalum (Hermann Starck, Berlin, claimed purity  $\sim 99.5\%$ ) and red phosphorus (purity higher than 99%). The powders were thoroughly mixed in suitable proportions and pressed to pellets, which were sealed off in evacuated silica tubes. Specimens were then heat-treated at 750°C for 24 h. The sintered pellets were arc-melted in an atmosphere of purified argon. Some phosphorus was lost during the preparation.

*X-Ray work.* X-Ray powder photographs were taken in a Guinier-Hägg focusing camera with CrK $\alpha_1$  radiation ( $\lambda = 2.28962 \text{ \AA}$ ). Si was used as internal calibration standard ( $a = 5.4305 \text{ \AA}$ ).

A single-crystal fragment was picked from an alloy containing Ta<sub>2</sub>P and a small amount of Ta<sub>3</sub>P. A small satellite was attached to the crystal, but there were no serious difficulties in distinguishing the satellite reflexions from those of the main crystal. The crystal size was roughly  $150 \times 50 \times 40 \mu$ , but the exact form was difficult to measure, and in the calculations no absorption correction could be applied to the data. Photographs were taken in an equi-inclination Weissenberg camera with Zr-filtered MoK $\alpha$  radiation. Intensity data were obtained using the multiple film technique with iron foils interleaved between the films. The  $c$ -axis, approximately parallel to the longest edge of the crystal, was used as the rotation-axis and the layer lines 0-2 were recorded. The intensities were estimated visually by comparison with a calibrated intensity scale. A total of 601 independent  $hk0$  and 607 independent  $hkl$  reflexions were measured.

*Calculation.* All the calculations were performed on a CDC 3600 computer using programmes according to the following list:

Least-squares refinement of unit cell dimensions	J. Tegenfeldt, Uppsala
Lorentz-polarisation factor corrections, Fourier summations, structure factor calculations.	A. Zalkin, Berkeley, modified by R. Liminga and J.-O. Lundgren, Uppsala
Least squares refinement	A. Zalkin, Berkeley, a version of the programme originally written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, University of California, Los Angeles, modified by R. Liminga and J.-O. Lundgren, Uppsala
Interatomic distances	A. Zalkin, Berkeley, modified by R. Liminga and J.-O. Lundgren, Uppsala

The cell dimensions were refined by the least squares method. Lorentz and polarisation factors were applied to intensity data. In the structure factor calculation the atomic scattering factors of tantalum and phosphorus were obtained from *Int. Tab. for X-ray Cryst.*<sup>2</sup> The dispersion correction for tantalum was included in these calculations. The structure was refined by the method of least squares employing a weighting scheme according to Cruickshank *et al.*,<sup>3</sup>  $w = 1/(a + |F_o| + c|F_o|^2)$ , where the weighting constants  $a$  and  $c$  were given the values 57.0 and 0.0055, respectively.

#### DETERMINATION OF THE CRYSTAL STRUCTURE

The Weissenberg and oscillation photographs confirmed that the unit cell was orthorhombic. There was no evidence of lower symmetry. The unit cell dimensions were determined by powder diffraction to be  $a = 14.419 \text{ \AA}$ ,  $b = 11.552 \text{ \AA}$ , and  $c = 3.399 \text{ \AA}$  with the standard deviations 0.0009, 0.0007, and 0.0002  $\text{\AA}$ , respectively. Powder diffraction data are given in Table 1.

No systematic extinctions of  $hkl$  reflexions could be detected. This indicates a primitive cell.  $h0l$  reflexions were observed only for  $h + l = 2n$ , and  $0kl$  reflexions were observed only for  $k + l = 2n$ . Thus the most probable space-groups are  $Pnmm$  and  $Pnn2$ . The unit cell volume suggests a cell content of twelve formula units. The fact that the  $c$ -axis is very short, and the ratio  $F_o(hk0)/F_o(hk2)$  is constant within the errors of visual intensity estimation, indicates that the symmetry is  $Pnmm$  with all atoms in  $4(g)$  positions.

The Patterson sections  $P(xy0)$  and  $P(xy\frac{1}{2})$  were evaluated. From the analysis of these sections, a reasonable arrangement of the tantalum atoms was found. An electron density map  $\rho(xy0)$  was calculated with the approximate parameters for the metal atoms. In addition to the maxima of the tantalum atoms, phosphorus maxima appeared at positions expected from space considerations. This indicated strongly that the correct structure had been found, and the atomic positions were therefore directly refined by the least squares technique using a full matrix programme. The following parameters were varied: the atomic positional parameters, individual isotropic temperature factors, and two scale factors. The material was weighted according to the formula of Cruickshank and the last weighting analysis is given in Table 2. The refinement was stopped when the shifts for all the parameters were less than one-tenth of their standard deviations. 37 strong low-angle reflexions were omitted from the last cycles of refinement as they were strongly affected by extinction. The

Table 1. Powder diffraction data for Ta<sub>2</sub>P. CrK $\alpha_1$  radiation,  $\lambda = 2.28962$  Å.

<i>h k l</i>	$\sin^2\theta_{\text{obs}} \cdot 10^4$	$\sin^2\theta_{\text{calc}} \cdot 10^4$	<i>I</i> <sub>obs</sub>	$p  F_{\text{calc}} ^2 \cdot 10^{-4}$
1 1 0	—	161.2	—	0.0
2 0 0	252.3	252.2	w	1.2
2 1 0	349.5	350.4	w	2.7
0 2 0	392.4	392.8	w+	6.1
1 2 0	—	455.9	—	0.1
2 2 0	—	645.0	—	0.3
3 1 0	—	665.5	—	0.9
1 3 0	—	946.9	—	0.0
3 2 0	957.3	960.2	w-	2.5
4 0 0	—	1008.6	—	2.0
4 1 0	1107.3	1106.8	m	33.0
2 3 0	—	1136.0	—	1.7
1 0 1	—	1197.4	—	1.5
0 1 1	1233.3	1232.5	w-	4.8
1 1 1	1296.2	1295.5	w+	27.6
4 2 0	1401.5	1401.5	w+	20.2
3 3 0	—	1451.2	—	3.5
2 1 1	1484.3	1484.7	w+	24.0
0 4 0	1571.8	1571.4	w+	33.8
1 2 1	1588.5	1590.2	w	21.1
1 4 0	1634.2	1634.4	m-	45.8
5 1 0	1674.4	1674.2	w	14.3
3 0 1	1702.0	1701.7	w	24.9
2 2 1	1779.2	1779.3	m+	121.9
3 1 1	—	1799.9	—	10.7
2 4 0	824.	1823.5	w	29.2
4 3 0	1891.7	1892.5	w-	8.9
5 2 0	1967.8	1968.8	w+	31.8
0 3 1	2018.0	2018.2	st-	210.7
1 3 1	2080.5	2081.2	m	64.0
3 2 1	—	2094.6	—	16.9
3 4 0	2140.0	2138.7	w+	60.3
4 1 1	2241.0	2241.1	st	271.4
6 0 0 } 2 3 1 }	2268.6	2269.4 2270.3	m	{ 84.6 32.8
6 1 0	—	2367.5	—	0.7
5 3 0	2459.8	2459.9	m+	193.3
1 5 0	2518.6	2518.3	m	124.2
4 2 1 <sup>a</sup>	2536.4	2535.8	st+	450.9
4 4 0 } 3 3 1 }	2585.4	2580.0 2585.5	st	{ 26.1 326.9
6 2 0	2663.3	2662.2	w+	69.1
2 5 0 } 5 0 1 }	2708.5	2707.4 2710.3	m+	{ 93.8 167.2
1 4 1	2768.5	2768.7	w+	43.5
5 1 1	—	2808.5	—	3.8
2 4 1	2957.1	2957.8	m	134.6
3 5 0	3023.9	3022.6	w-	25.6
4 3 1	—	3026.9	—	1.6
5 2 1 <sup>a</sup>	3103.0	3103.2	m+	15.7
5 4 0 } 6 3 0 }	3149.3	3147.3 3153.3	w+	{ 39.7 29.2
7 1 0	3187.0	3187.1	m-	78.4
3 4 1	—	3273.1	—	8.7
4 5 0	3463.7	3463.9	m-	80.4
7 2 0	—	3481.7	—	0.0

<i>h k l</i>	$\sin^2\theta_{\text{obs}} \cdot 10^4$	$\sin^2\theta_{\text{calc}} \cdot 10$	<i>I</i> <sub>obs</sub>	$p  F_{\text{calc}} ^2 \cdot 10^{-4}$
6 1 1	—	3501.9	—	1.4
0 6 0	—	3535.5	—	3.1
0 5 1	—	3589.6	—	0.4
5 3 1	—	3594.2	—	0.3
1 6 0	—	3598.6	—	14.2
1 5 1	3653.0	3652.6	m—	79.1
4 4 1	—	3714.3	—	0.0
2 6 0	—	3787.7	—	17.3
6 2 1	—	3796.6	—	0.4
6 4 0	—	3840.7	—	13.8
2 5 1	—	3841.8	—	0.3
7 3 0	—	3972.7	—	4.6
5 5 0	—	4031.2	—	5.9
8 0 0	—	4034.4	—	0.0
3 6 0	—	4102.9	—	2.6
8 1 0	4132.4	4132.7	w	63.5
3 5 1	—	4157.0	—	0.1
7 0 1	—	4223.2	—	2.8
5 4 1	—	4281.7	—	1.3
6 3 1	—	4287.6	—	6.1
7 1 1	—	4321.4	—	0.2
8 2 0	4427.0	4427.3	w—	26.2
0 0 2	4538.7	4537.2	st—	372.4

<sup>a</sup> overlapped by a line belonging to Ta<sub>3</sub>P.

discrepancies between observed and calculated structure factors for these reflexions were, however, included in the *R*-value which was 0.114 after the last cycle. The temperature factors are lower than expected and some of them are even negative. It is probable that this is an absorption effect. Final structure data for Ta<sub>2</sub>P are given in Table 3. Interatomic distances are listed in Table 4. The standard deviations for the metal—metal distances are 0.002 Å or smaller, for metal—non-metal distances 0.009 Å or smaller, and for non metal—non-metal distances 0.013 Å or smaller.

Table 2. Weight analysis for the last cycle of refinement.

$\Delta =  F_o - F_c $ .					
<i>F</i> <sub>o</sub> interval	$\overline{w\Delta^2}$	No. of reflexions	Sin $\theta$ interval	$\overline{w\Delta^2}$	No. of reflexions
0.0—65.9	1.4269	117	0.0000—0.4642	0.9568	312
65.9—74.8	1.2370	117	0.4642—0.5848	0.8688	160
74.8—98.5	0.7601	117	0.5848—0.6694	1.1505	130
98.5—116.7	0.7001	117	0.6694—0.7368	0.9711	97
116.7—133.9	0.8404	117	0.7368—0.7937	0.9268	98
133.9—152.6	0.9685	117	0.7937—0.8434	0.8587	90
152.6—177.9	1.1632	117	0.8434—0.8879	0.8243	78
177.9—211.5	1.0996	117	0.8879—0.9283	0.6708	81
211.5—260.0	1.1133	117	0.9283—0.9655	0.7186	71
260.0—480.1	0.6909	118	0.9655—1.0000	2.0536	54

Table 3. Space group *Pnmm* ( $D_{2h}^{12}$ ),  $z = 12$ ;  $a = 14.419 \text{ \AA}$ ,  $b = 11.552 \text{ \AA}$ ,  $c = 3.399 \text{ \AA}$ ;  $U = 566.2 \text{ \AA}^3$ .

Atom	Position	Positional parameters and standard deviations				Temperature factors and standard deviations	
		$x$	$\sigma(x)$	$y$	$\sigma(y)$	$B$	$\sigma(B)$
Ta <sub>I</sub>	4( <i>g</i> )	0.07775	0.00008	0.12237	0.00010	0.015	0.011
Ta <sub>II</sub>	4( <i>g</i> )	0.29501	0.00008	0.19686	0.00009	-0.016	0.011
Ta <sub>III</sub>	4( <i>g</i> )	0.10897	0.00008	0.52997	0.00010	-0.017	0.011
Ta <sub>IV</sub>	4( <i>g</i> )	0.24502	0.00008	0.92143	0.00010	0.062	0.012
Ta <sub>V</sub>	4( <i>g</i> )	0.47722	0.00009	0.84758	0.00011	0.091	0.012
Ta <sub>VI</sub>	4( <i>g</i> )	0.42028	0.00008	0.41362	0.00010	-0.013	0.011
P <sub>1</sub>	4( <i>g</i> )	0.15113	0.0006	0.31533	0.0007	-0.031	0.074
P <sub>2</sub>	4( <i>g</i> )	0.29297	0.0006	0.57784	0.0008	0.066	0.085
P <sub>3</sub>	4( <i>g</i> )	0.08400	0.0006	0.75622	0.0008	0.101	0.087

Table 4. Interatomic distances in Ta<sub>2</sub>P. Distances shorter than 4.0 Å are listed. The figure in brackets denotes the number of equivalent distances.

	Ta <sub>I</sub>	Ta <sub>II</sub>	Ta <sub>III</sub>	Ta <sub>IV</sub>	Ta <sub>V</sub>	Ta <sub>VI</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>
Ta <sub>I</sub>	3.39 <sub>9</sub> (2) 3.60 <sub>9</sub>	3.24 <sub>9</sub>		3.34 <sub>7</sub>	3.20 <sub>7</sub> (2)	2.86 <sub>7</sub> (2) 2.95 <sub>0</sub> (2)	2.47	2.57(2)	2.72
Ta <sub>II</sub>	3.24 <sub>9</sub>	3.39 <sub>9</sub> (2)	2.91 <sub>9</sub> (2)	3.15 <sub>5</sub> (2) 3.26 <sub>2</sub>	3.32 <sub>4</sub>	3.08 <sub>7</sub>	2.48	2.53(2)	2.53(2)
Ta <sub>III</sub>		2.91 <sub>9</sub> (2)	3.21 <sub>8</sub> 3.39 <sub>9</sub> (2)	2.98 <sub>2</sub> (2)	2.91 <sub>5</sub> (2) 2.97 <sub>9</sub> (2)		2.55	2.71	2.64
Ta <sub>IV</sub>	3.34 <sub>7</sub>	3.15 <sub>5</sub> (2) 3.26 <sub>2</sub>	2.98 <sub>2</sub> (2)	3.39 <sub>9</sub> (2)	3.45 <sub>5</sub>	2.92 <sub>9</sub> (2)	2.58(2)	2.54(2)	3.00
Ta <sub>V</sub>	3.20 <sub>7</sub> (2)	3.32 <sub>4</sub>	2.91 <sub>5</sub> (2) 2.97 <sub>9</sub> (2)	3.45 <sub>5</sub>	3.39 <sub>9</sub> (2) 3.58 <sub>2</sub>	3.36 <sub>0</sub>	2.54(2)		2.59(2)
Ta <sub>VI</sub>	2.86 <sub>7</sub> (2) 2.95 <sub>0</sub> (2)	3.08 <sub>7</sub>		2.92 <sub>9</sub> (2)	3.36 <sub>0</sub>	3.04 <sub>4</sub> 3.39 <sub>9</sub> (2)		2.65	2.49(2)
P <sub>1</sub>	2.47	2.48	2.55	2.58(2)	2.54(2)		3.39 <sub>9</sub> (2)	3.33(2) 3.66	3.49
P <sub>2</sub>	2.57(2)	2.53(2)	2.71	2.54(2)		2.64	3.33(2) 3.66	3.39 <sub>9</sub> (2)	3.65
P <sub>3</sub>	2.72	2.53(2)	2.64	3.00	2.59(2)	2.49(2)	3.49	3.65	3.39 <sub>9</sub> (2)

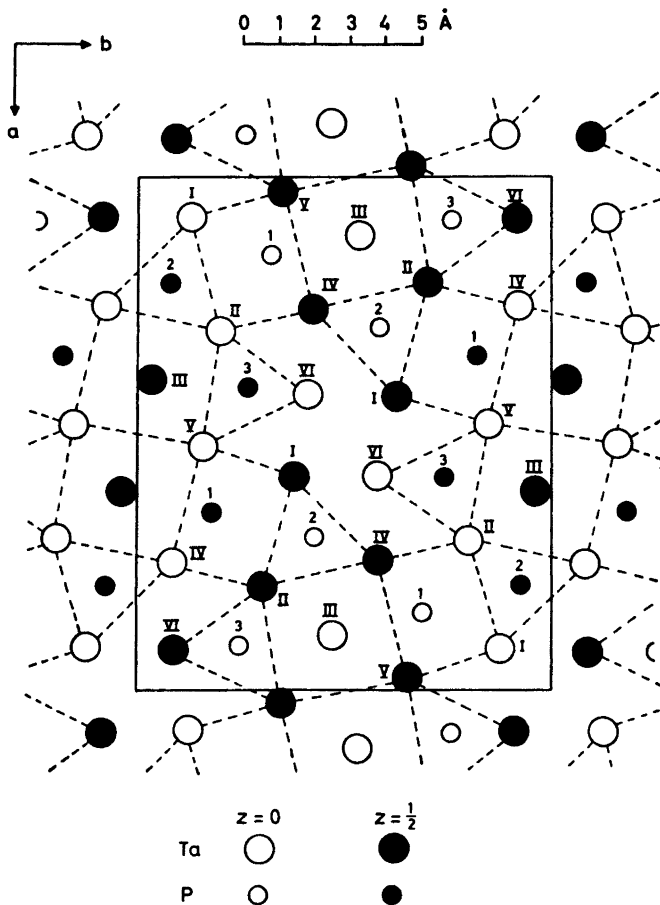


Fig. 1. The structure of  $Ta_2P$  projected on (001).

Table 5. The coordination in  $Ta_2P$ . Neighbours within 3.1 Å are listed for the phosphorus atoms and within 3.7 Å for the tantalum atoms.

Central atom	$P_1$	$P_2$	$P_3$	$Ta_I$	$Ta_{II}$	$Ta_{III}$	$Ta_{IV}$	$Ta_V$	$Ta_{VI}$
$M_{Me}$	7	8	8(9)	11	11	11	11	12	11
$N_P$	—	—	—	4	5	3	5	4	3

#### DESCRIPTION OF THE STRUCTURE

A projection of the structure on (001) is shown in Fig. 1. The coordination of the phosphorus atoms is summarized in Table 5. There are no P—P distances shorter than 3.3 Å in the structure and the immediate environment of the phosphorus atoms, accordingly, consists of tantalum atoms only. The

phosphorus atom P<sub>1</sub> has seven tantalum neighbours, six of which are situated at the corners of a triangular prism, while the seventh is situated outside one of the quadrilateral faces of the prism. The environment of the phosphorus atom P<sub>2</sub> also has a triangular prismatic arrangement but as the number of neighbours are eight there are metal atoms outside two of the quadrilateral faces. In describing the coordination of the phosphorus atom P<sub>3</sub>, it is not easy to say whether the number of neighbours is eight or nine. For the eight nearest neighbours the arrangement is the same as that around the atom P<sub>2</sub>, except that there is a ninth tantalum atom outside the third quadrilateral face and situated at a distance somewhat greater than the other similarly situated atoms. The general structural architecture can be described in terms of a packing of triangular metal prisms containing a phosphorus atom. The packing of these prisms is illustrated in Fig. 1. The triangular faces of the prisms surrounding P<sub>1</sub> atoms are perpendicular to (001), while the triangular faces of the remaining prisms are parallel to this plane. The packing of the prisms leaves voids which are filled by tantalum atoms Ta<sub>III</sub>.

The coordination of the tantalum atoms is summarized in Table 5. Each tantalum atom is surrounded by 10–12 tantalum atoms at distances between 2.87 and 3.61 Å and 3–5 phosphorus neighbours at distances between 2.47 and 3.00 Å. Distances to further neighbours exceed 4 Å.

The mean Ta–Ta distance (average of 21 non-equivalent distances) is 3.18 Å, which exceeds the Goldschmidt CN 12 metal diameter of 2.92 Å by 9%. The mean Ta–P distance (average of 16 non-equivalent distances) is 2.60 Å, which is 0.04 Å greater than the sum of the metal radius for tantalum, 1.46 Å, and the tetrahedral covalent radius for phosphorus, 1.10 Å.

#### DISCUSSION OF THE STRUCTURE

In a recent review of binary transition metal phosphides<sup>4</sup> a tetrakaidecahedron was used as an auxiliary means of describing the packing of atoms in structures. In this coordination polyhedron phosphorus atoms (denoted C) have triangularly prismatic environments of metal atoms (denoted A) with three additional metal atoms (denoted B) outside the quadrilateral faces. A tetrakaidecahedron built up in this way of atoms approximating to rigid spheres deviates from a regular tetrakaidecahedron because the phosphorus atom is too large to be accommodated in the central void formed by the close-packed metal atoms. This requires a radius ratio between the phosphorus atom and the metal atom which is less than or equal to 0.53 and this condition is never fulfilled for a transition metal phosphide, where the A atoms are thus pushed apart but the A and B atoms are still in contact for radius ratios less than or equal to 0.79. In this region there are contacts established between A and C atoms but for B and C atoms to be contact, the radius ratio must exceed 0.79. When the B–C contacts are established and the radius ratio increases, the A and B atoms no longer touch. If the packing of atoms strictly followed these geometrical considerations, the interatomic distances for different radius ratios in a tetrakaidecahedron would be as listed in Table 6. But when the tetrakaidecahedra are to be linked to one another difficulties arise.

Table 6.  $r_P$  = tetrahedral covalent radius for phosphorus.  $R_{Me}$  = Goldschmidt metal radius CN 12.  $d_{AA'}$  = distance between two A atoms (see text);  $d_{AB'}$  = distance between an A and a B atom, etc.;  $l$  see Fig. 2a.

Me	$r_P/R_{Me}$	$d_{AA'}$	$d_{AB'}$	$d_{AC'}$	$d_{BC'}$	$l/2R_{Me}$
Ta	0.75	3.35	2.92	2.56	2.68	0.75
Re	0.80	3.23	2.75	2.47	2.47	0.89
Ru	0.83	3.17	2.70	2.42	2.42	0.90
Co	0.87	3.09	2.63	2.36	2.36	0.92

If the polyhedra have one ABA face in common (Fig. 2a), as is the case in the structures discussed below, the  $B_1-B_2$  distance called  $l$  will be too short. There will then not be space enough for two metal atoms. For no distortion,  $l$  ought to be at least  $2R_{Me}$ , where  $R_{Me}$  is the Goldschmidt CN 12 metal radius.

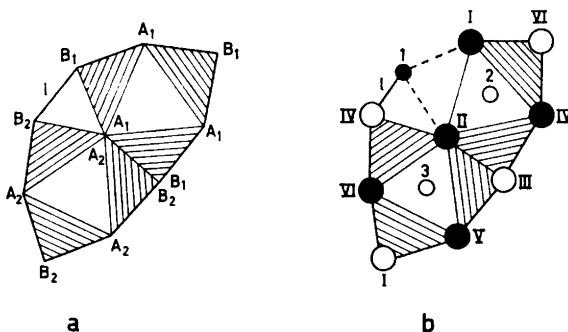


Fig. 2. a) Two connected tetrakaidecahedra  
b) The tetrakaidecahedral mode of coordination in  $Ta_2P$ . For notations see Fig. 1 and Table 3.

The arrangement in some  $Me_2P$  phases will now be discussed from this point of view. Fig. 2b shows how the atoms are adapted to a tetrakaidecahedral mode of coordination in  $Ta_2P$ . It is only the  $P_3$  atom which has a complete tetrakaidecahedral environment. The ninth metal atom is missing in the  $P_2$ -polyhedron. One could say that it has been replaced by two phosphorus atoms  $P_1$  situated in the same plane as the A atoms, but as the  $P_1-P_2$  distances are 3.3 Å they cannot be regarded as coordinated to  $P_2$ . They are instead enclosed in triangular prisms of tantalum atoms with an edge in the triangular face coinciding with an AB-edge in the  $P_3$ -polyhedron. The  $P_3$ -tetrakaidecahedron is distorted so that  $Ta_{IV}$  (Fig. 2b) is more remote than the other two B atoms and there is a contraction between  $Ta_{II}$  and  $Ta_{VI}$ .

In the structure of  $Re_2P^5$  two complete tetrakaidecahedra share one B atom. Thus the  $l$  distance is zero and the  $B_1$  and  $B_2$  positions coincide. The coordination number is still nine for both phosphorus atoms. There is however a considerable distortion of the tetrakaidecahedra as revealed by the large spread in the individual Re—Re and Re—P distances. This distortion is also evident from the values in Table 7.



