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The Structure of the 9(18)-Heteropoly Anion in Potassium 9(18)-Tungstophosphate, $K_6(P_2W_{18}O_{62}).14H_2O$

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The structure of the 9(18)-heteropoly-anion in potassium 9(18)-tungstophosphate has been determined by X-ray analysis,e mploying two-dimensional methods. The crystals are triclinic with $a = 12{\cdot}86$, $b = 14{\cdot}83$, $c = 22{\cdot}34$ Å, $\alpha = 94° 24'$, $\beta = 116° 52'$, $\gamma = 115° 36'$. The space group is $P\bar{1}$, and the unit cell contains two units of empirical formula $3K_2O.P_2O_5.18WO_3.14H_2O$. Complete analyses of the *a*- and *b*-axis Patterson projections show the tungsten framework of the 9(18)-anion to be a layer structure consisting of four rings of atoms, the end two triangular and the central two almost perfectly hexagonal. By comparison of the tungsten framework of the 9(18)-anion with that of the 12-tungstophosphate anion $(PW_{12}O_{40})^{3-}$ it is shown that the complete 9(18)-anion has the formula $(P_2W_{18}O_{62})^{6-}$. The anion is a complex co-ordinated structure, of point group symmetry $3/m$, in which the tungsten and phosphorus atoms are surrounded by octahedra and tetrahedra of oxygen atoms respectively.

1. Introduction

The heteropoly-acids form an extensive series of inorganic compounds (Abegg, 1921; Gmelin, 1933, 1935) of great interest because of the complexity of their anions. They are formed by the union of varying numbers of acid anhydride molecules—most commonly WO_3, MoO_3—with a second acid which must be regarded, in accordance with modern theory, as furnishing the central ion or ions of the whole complex anion. The heteropoly-acids may be represented by the general formula $H_mX_xM_yO_z$ where X is usually P, As, Si or B, and M usually W or Mo. All known compounds obey the rule $6 \leqslant y/x \leqslant 12$ and are classified into series depending on their y/x ratios. The extent and stability of the various series differ considerably, and the 12- and 9-series are of especial interest on account of their ease of preparation and stability in the solid state (Kehrmann, 1894, 1900). Furthermore, these two series are obviously related as, in aqueous solution, the 12-heteropoly-phosphates and -arsenates change into the corresponding 9-compounds on long standing. These transitions are accelerated in the presence of excess phosphoric and arsenic acid, respectively, indicating that, for these two acids at least, the process of heteropoly-anion formation reaches equilibrium when $y/x = 9$.

Comparatively few heteropoly-compounds have been examined by X-ray methods. Keggin and others (Keggin, 1934; Illingworth & Keggin, 1935; Santos, 1935; Kraus, 1935, 1936; Bradley & Illingworth, 1936) have shown that the 12-compounds contain anions of the form $(XM_{12}O_{40})^{8-n}$, where n is the valency of the atom X, i.e. P, As, Si or B. Recently, Evans (1948) has studied potassium telluromolybdate $K_6(TeMo_6O_{24})$, a member of the rather different 6-series, and confirmed the anion proposed by Anderson (1937) for compounds of this series. No X-ray investigation of a 9-heteropoly compound has been reported. A determination of the constitution of the complex anion of a member of the 9-series should be of value, therefore, in clarifying the relationship between the 12- and 9-series mentioned earlier.

The compound chosen for investigation was potassium 9(18)-tungstophosphate.† The derivation, from Patterson projections, of the tungsten-atom framework of the 9(18)-tungstophosphate anion is described first and the structure of the complete anion is then deduced from its relationship to the 12-tungstophosphate anion $(PW_{12}O_{40})^{3-}$.

2. Experimental

(i) *Preparation of potassium* 9(18)-*tungstophosphate*

The compound was prepared by Kehrmann's method (Kehrmann, 1894) and crystallized from aqueous solution. It forms large (up to 1 cm.), transparent, lemon-yellow prisms which, on prolonged exposure to air, effloresce and become opaque. Accurate analysis (Rosenheim & Jaenicke, 1917) has shown that the crystals have the empirical formula $3K_2O.P_2O_5.18WO_3.14H_2O$.

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† The terminology (18)- arises from the use by many chemists of the oxide-type, doubled formulae—thus, here $pK_2O.P_2O_5.18WO_3.qH_2O$.

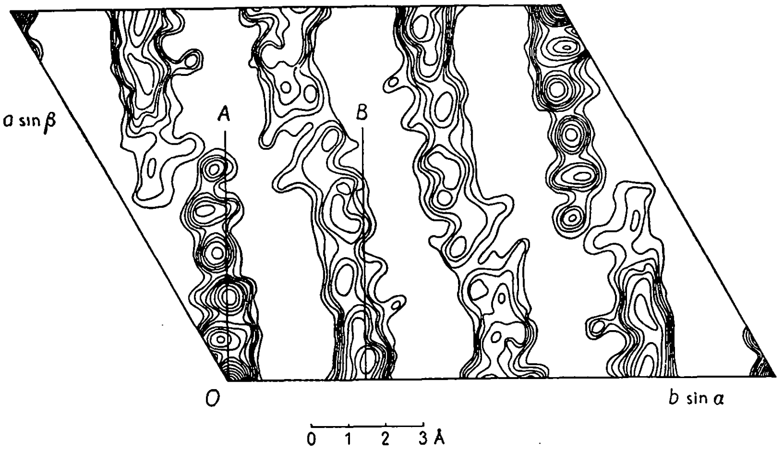

Fig. 1. Orthogonal Patterson projection along *c* axis.

(ii) *Unit cell and space group*

Both Kehrmann (1894) and Groth (1906–19, vol. 2, p. 877) considered the symmetry to be triclinic, although accurate morphological examination is not possible since the crystal faces are usually distorted. The present investigation has confirmed the triclinic symmetry, and the unit cell chosen had the following dimensions:

$a=12\cdot86$, $b=14\cdot83$, $c=22\cdot34$ Å, all $\pm1\%$;
$\alpha=94^\circ 24'$, $\beta=116^\circ 52'$, $\gamma=115^\circ 36'$, all $\pm20'$.

The observed density, $5\cdot07\pm0\cdot03$ g.cm.$^{-3}$, indicated that there were two units (calculated 2·02 units) of formula $3K_2O.P_2O_5.18WO_3.14H_2O$ in the unit cell. A sensitive test for piezoelectricity (kindly performed by Dr W. A. Wooster of this Laboratory) proved negative, suggesting the space group $P\overline{1}$; this was confirmed by the subsequent analysis.

(iii) *Intensity measurements*

Cu $K\alpha$ radiation ($\lambda = 1\cdot542$ Å) was used throughout the investigation. In order to minimize absorption ($\mu = 835$ cm.$^{-1}$), for which no correction was made, crystals of cross-section slightly less than 0·1 mm. and of as regular a shape as possible were used. Zero-level Weissenberg photographs about the three principal axes were taken using a multiple-film technique, and the intensities were estimated visually with calibrated intensity scales. Corrections for Lorentz and polarization factors were made in the usual way, giving a set of coefficients, G^2, proportional to F^2.

3. Structure analysis

The tungsten-atom framework of the complex anion was deduced from the three Patterson projections. An abridged account of the vector analysis is given here as full details are available elsewhere (Dawson, 1950). The discussion which follows is in terms of W–W vectors only, compared with which all other vectors are small in magnitude.

(i) *The c-axis Patterson projection*

The vector peaks of this projection (Fig. 1) were grouped into four approximately parallel rows. Row *A*, extending from the origin as a series of peaks of almost constant separation, indicated that the tungsten atoms were arranged nearly equidistantly across the cell-base in lines perpendicular to the *b* axis. The position of row *B*, arising at $\frac{1}{4}b$ from the origin, showed that the predominant spacing between these lines of atoms was also $\frac{1}{4}b$, i.e. 3·7 Å.

In order to obtain information on actual atomic coordinates the projection down the *b* axis, which was almost orthogonal to the *c* axis ($\alpha = 94^\circ 24'$), was examined.

(ii) *The b-axis Patterson projection*

The spatial distribution of the strongest peaks in this projection (Fig. 2), A_1, A_2, A_3, B_1, B_2, B_3 and C_1, C_2, C_3, indicated an hexagonal arrangement of tungsten atoms in the anion. The hexagon was distorted slightly, alternate sides being 3·3 and 3·7 Å in length, and was assumed initially to have its trigonal axis parallel to the *b* axis.

The shape of the complete framework of the anion was then obtained by using the predominant spacing indicated by row *B* of the *c*-axis projection. Construction of theoretical vector maps for different proposed units and comparison with the Patterson projection showed that the framework was that of Fig. 3. The presence of the pairs of peaks D_1, D_2, E_1, E_2, F_1, F_2, G_1, G_2, K_1, K_2 etc. (Fig. 2), which were produced by vectors between atoms in the triangular and hexagonal rings, indicated that the trigonal axis of the framework was not parallel to the *b* axis but inclined slightly at an angle δ (Fig. 3). From the constant separation, 1 Å, of the pairs of peaks, a value $\delta = 6^\circ$ was obtained by assuming that the length l of the unit corresponded to a distance of 3·7 Å between nearest atoms in adjacent rings. The intramolecular vectors of the resultant arrangement of tungsten atoms are compared with the Patterson projection in Fig. 2.

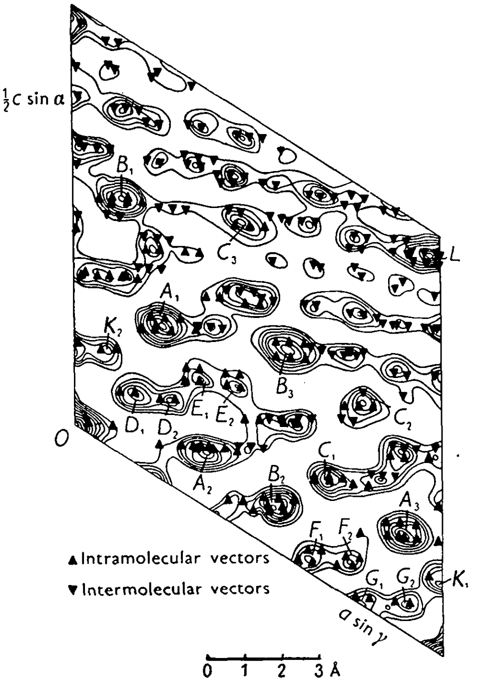

Fig. 2. Orthogonal Patterson projection along b axis showing the agreement with the theoretical vectors of Fig. 4.

The remaining peaks of Fig. 2 were assumed to represent intermolecular vectors and were used to determine atomic coordinates. The height of the strongest peak, L, suggested that it was produced by the 'interhexagonal' vectors 1–4′, 2–3′, 9–12′, 10–11′, 7–6′, 8–5′ etc. (Fig. 4) which were almost identical.

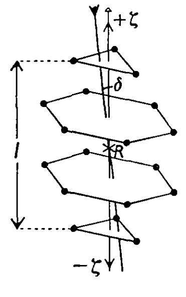

Fig. 3. The tungsten framework of the 9(18)-tungstophosphate anion.

The two units were therefore orientated so that these vectors coincided with L. All intermolecular vectors produced by this arrangement were then calculated and compared with the Patterson projection (Fig. 2). Subsequent Fourier refinement changed no parameter by more than 0·2 Å.

(iii) *The a-axis Patterson projection*

Before analysing this projection it was first necessary to calculate the shape of the unit when viewed along the a axis. Since the trigonal axis of the unit was approximately parallel to the b axis the angular relationship of the b and a axes ($\gamma = 115° 36'$) meant that the latter was inclined to the various rings of atoms, thus giving an oblique view of the unit. The expression used in calculating the shape was, in this case,

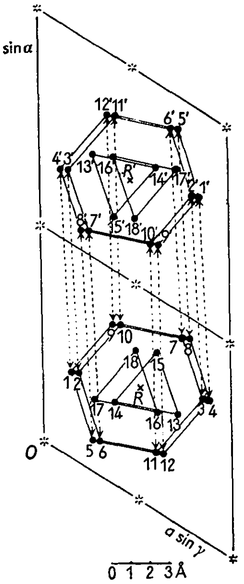

Fig. 4. The tungsten-atom arrangement as seen in projection along the b axis.

$$\begin{aligned} y_i = {} & Y - Z\sin(\alpha-90) - X\sin(\gamma-90) \\ & - \zeta_i/\cos\delta + [X\cos(\gamma-90)\sin\beta^* \\ & - x_i\cos(\gamma-90)\sin\beta^*]\tan\delta \\ & + x_i\sin(\gamma-90) + z_i\sin(\alpha-90)\,, \end{aligned}$$

where α, β^*, γ were direct and reciprocal angles of the unit cell; δ was the angle of tilt (Fig. 3); ζ was the distance of each atom along the trigonal axis, taking the centre of the unit, R, as the origin (Fig. 3); x_i, z_i and X, Z, which could be obtained from the b-axis projection, were the coordinates of the various tungsten atoms and of R respectively. The expression was of the form

$$y_i = Y + a + bx_i + cz_i + d\zeta_i\,, \qquad (1)$$

and a, b, c and d were obtained by numerical evaluation of the constants. For any arbitrary value of Y the relative y_i coordinates of the tungsten atoms could then be calculated, thus giving the shape of the unit as viewed along the a axis.

The hexagonal rings of atoms were assumed to be planar so that all atoms in each ring had the same ζ value. The ζ values used in calculating the shape and dimensions of the unit corresponded to a separation of 3·7 Å between nearest atoms in adjacent rings. The intramolecular vectors of the calculated unit showed excellent agreement with the Patterson projection (Fig. 5), indicating that the ζ values assumed were reasonably correct.

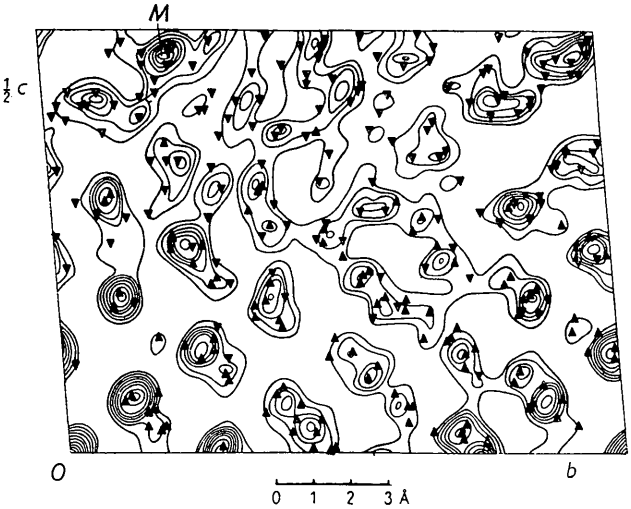

Fig. 5. Patterson projection on (100) showing the agreement with the theoretical vectors of Fig. 6.

The two frameworks in the unit cell were then orientated by means of peak M (Fig. 5) which had the same height and z coordinate as peak L of Fig. 2, suggesting that $M \equiv L$. The intermolecular vectors of the resultant atomic arrangement (Fig. 6) showed excellent agreement with the Patterson projection (Fig. 5) and subsequent Fourier refinement again changed no coordinate by more than 0·2 Å.

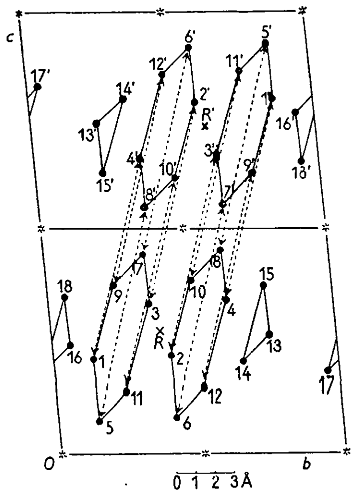

Fig. 6. The tungsten-atom arrangement as seen in projection along the a axis.

(iv) *Electron-density projections*

The coordinates derived from the Patterson projections were refined in the normal manner by Fourier methods. The final parameters enabled the signs of 330 of the 352 $h0l$ and 320 of the 340 $0kl$ reflexions observed to be fixed with certainty. Later structure amplitude calculations made for the complete anion did not change the phases of any of the terms used in the Fourier syntheses.

Strong diffraction ripples in the regions surrounding the tungsten peaks indicated that the termination of the Fourier series at the limit of observation had been too abrupt. It was desirable that the electron-density maps be as accurate as possible in order to assist in the subsequent location of the light oxygen and phosphorus atoms associated with the tungsten atoms in the complex anion. The diffraction ripples were therefore estimated and corrected for by a modified (F_o-F_c) synthesis in which the final tungsten structure amplitudes F_W were used rather than the complete structure amplitudes F_c. This approximation was justified in the later stages of the analysis, where it was found that $F_W \simeq F_c$ for all but 17 of the 650 $h0l$ and $0kl$ reflexions used in calculating the electron-density projections. The final, corrected, maps of the electron density projected along the b and a axes are shown in Figs. 7 and 8 respectively.

The parameters and ζ values of the tungsten atoms in the 9(18)-tungstophosphate anion are listed in Table 1. The numbering of the atoms corresponds to that of Figs. 4 and 6, which are the keys to Figs. 7 and 8. It will be noted, however, that Fig. 6 is for

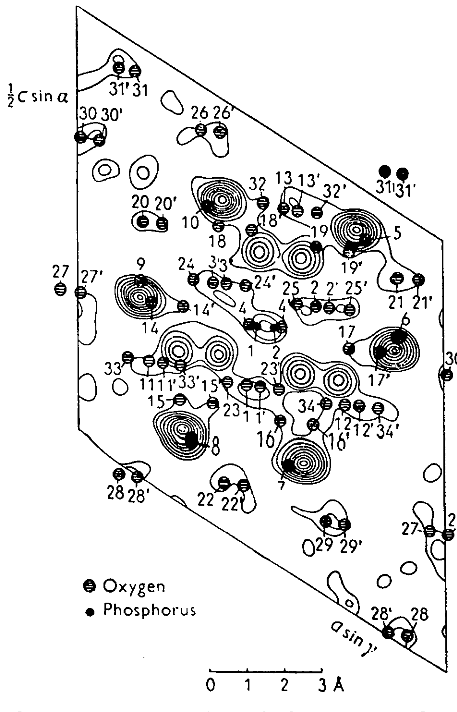

Fig. 7. Orthogonal projection of the electron density along the b axis. Contours at equal intervals on an arbitrary scale.

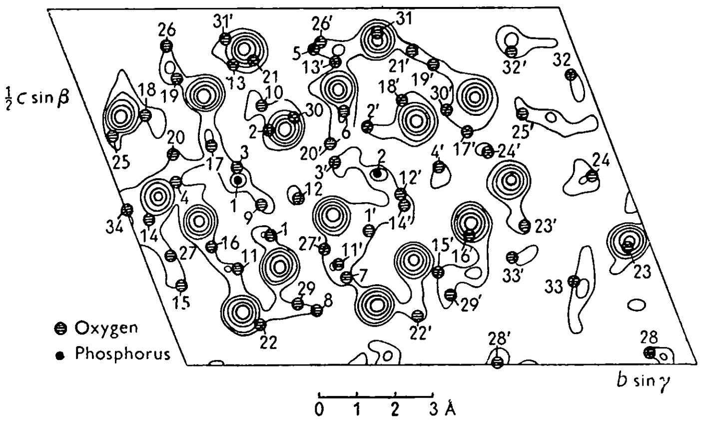

Fig. 8. Orthogonal projection of the electron density along the *a* axis. Contours as in Fig. 7.

projection on to (100), whereas Fig. 8 is for orthogonal projection along the *a* axis.

Table 1. *Tungsten atom parameters*

Atom	*x/a*	*y/b*	*x/c*	ζ (Å)
1	0·149	0·137	0·202	1·87
2	0·190	0·407	0·211	−1·87
3	0·843	0·369	0·330	1·87
4	0·884	0·638	0·340	−1·87
5	0·257	0·152	0·075	1·87
6	0·297	0·422	0·084	−1·87
7	0·741	0·349	0·444	1·87
8	0·782	0·619	0·453	−1·87
9	0·373	0·230	0·373	1·87
10	0·414	0·500	0·383	−1·87
11	0·593	0·261	0·137	1·87
12	0·634	0·531	0·146	−1·87
13	0·713	0·778	0·259	−4·92
14	0·377	0·668	0·196	−4·92
15	0·606	0·763	0·372	−4·92
16	0·606	0·071	0·235	4·92
17	0·269	0·961	0·172	4·92
18	0·496	0·057	0·347	4·92
R	0·512	0·383	0·265	0

The tungsten framework of the 9(18)-tungstophosphate anion has the form shown in Fig. 3, and possesses the point group symmetry 3/*m*. To within the limits of experimental error the hexagonal rings of atoms are planar, as assumed earlier.

(v) *The constitution of the* 9(18)*-tungstophosphate anion*

The constitution of the 9(18)-tungstophosphate anion was derived from a comparison with the 12-tungstophosphate anion. Keggin (1934) and Bradley & Illingworth (1936) showed that in $(PW_{12}O_{40})^{3-}$ the tungsten atoms and the phosphorus atom are, respectively, octahedrally and tetrahedrally coordinated with oxygen atoms, as would be expected from the radii of the three atoms, $r(W^{6+}) = 0{\cdot}62$ Å, $r(P^{5+}) = 0{\cdot}34$ Å, $r(O^{2-}) = 1{\cdot}35$ Å (Pauling, 1927). In view of the relationship between the 9(18)- and 12-anions mentioned in § 1 it appeared that the 9(18)-tungstophosphate anion would also consist of WO_6 octahedra and PO_4 tetrahedra. The relationship between the two anions suggested a similarity in more than polyhedral types, however, and to test this the dimen-

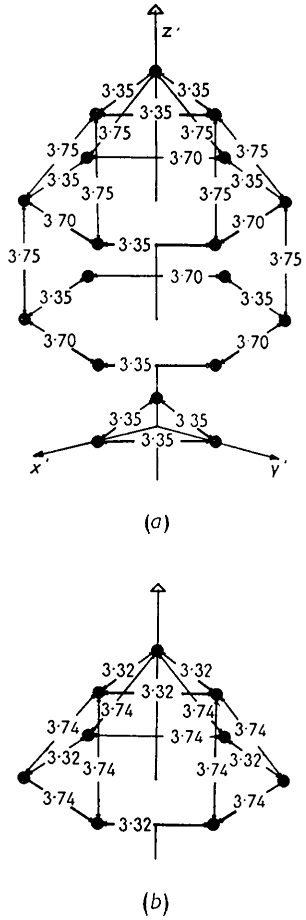

Fig. 9. (*a*) Dimensions of the tungsten framework of the 9(18)-tungstophosphate anion. (*b*) Dimensions of part of the tungsten framework of the 12-tungstophosphate anion $(PW_{12}O_{40})^{3-}$.

Table 2. *Parameters of oxygen and phosphorus atoms in the anion* $(P_2W_{18}O_{62})^{6-}$

Type	Atom	x/a	y/b	z/c	ζ (Å)	Atom	x/a	y/b	z/c	ζ (Å)
O_1	1	0·460	0·265	0·180	1·35	1′	0·500	0·460	0·190	−1·35
	2	0·655	0·340	0·325	1·35	2′	0·690	0·535	0·335	−1·35
	3	0·375	0·250	0·275	1·35	3′	0·410	0·445	0·285	−1·35
	4	0·475	0·125	0·255	3·60	4′	0·565	0·645	0·275	−3·60
O_2	5	0·785	0·490	0·445	0					
	6	0·870	0·500	0·355	0					
	7	0·570	0·385	0·125	0					
	8	0·310	0·300	0·075	0					
	9	0·170	0·275	0·225	0					
	10	0·355	0·345	0·360	0					
	11	0·195	0·175	0·135	1·40	11′	0·230	0·380	0·140	−1·40
	12	0·730	0·350	0·235	1·40	12′	0·765	0·555	0·240	−1·40
	13	0·565	0·320	0·415	1·40	13′	0·600	0·525	0·425	−1·40
	14	0·200	0·040	0·205	3·55	14′	0·280	0·550	0·225	−3·55
	15	0·280	0·055	0·115	3·55	15′	0·370	0·565	0·130	−3·55
	16	0·560	0·145	0·165	3·55	16′	0·645	0·655	0·185	−3·55
	17	0·745	0·215	0·305	3·55	17′	0·830	0·730	0·325	−3·55
	18	0·390	0·115	0·350	3·55	18′	0·475	0·625	0·370	−3·55
	19	0·655	0·200	0·400	3·55	19′	0·745	0·710	0·420	−3·55
O_3	20	0·180	0·135	0·295	2·20	20′	0·235	0·450	0·310	−2·20
	21	0·880	0·365	0·425	2·20	21′	0·940	0·680	0·440	−2·20
	22	0·400	0·175	0·055	2·20	22′	0·455	0·490	0·070	−2·20
	23	0·410	0·955	0·165	5·70	23′	0·550	0·770	0·200	−5·70
	24	0·320	0·940	0·265	5·70	24′	0·455	0·755	0·300	−5·70
	25	0·610	0·030	0·320	5·70	25′	0·745	0·850	0·350	−5·70
O_4	26	0·340	0·205	0·445	2·10	26′	0·390	0·510	0·455	−2·10
	27	−0·050	0·055	0·150	2·10	27′	0·005	0·360	0·165	−2·10
	28	0·105	0·085	−0·015	2·10	28′	0·155	0·385	−0·005	−2·10
	29	0·675	0·265	0·085	2·10	29′	0·720	0·570	0·100	−2·10
	30	1·010	0·400	0·345	2·10	30′	1·060	0·705	0·355	−2·10
	31	0·840	0·370	0·535	2·10	31′	0·885	0·675	0·545	−2·10
	32	0·510	0·970	0·405	6·25	32′	0·655	0·870	0·440	−6·25
	33	0·130	0·825	0·120	6·25	33′	0·280	0·720	0·155	−6·25
	34	0·680	0·005	0·220	6·25	34′	0·830	0·900	0·255	−6·25
P_1		0·490	0·245	0·260	2·00	P_2	0·540	0·520	0·270	−2·00

sions of the tungsten frameworks of the two anions were compared. It was found that the arrangement of nine of the twelve such atoms in $(PW_{12}O_{40})^{3-}$ was practically identical with that of either half of the 9(18)-unit (Fig. 9). This similarity of heavy-atom frameworks suggested a corresponding similarity in the oxygen arrangements surrounding them, and a 9(18)-anion which consisted of two of the appropriate 12-anion residues linked together was therefore postulated.

The formula of the proposed anion was $(P_2W_{18}O_{62})^{6-}$. The charge agreed with that suggested by the salt being investigated, $3K_2O.P_2O_5.18WO_3.14H_2O$, which could now be formulated as $K_6(P_2W_{18}O_{62}).14H_2O$. This indicated that all water present was merely water of hydration. Indirect confirmation of this last point (and, therefore, of the oxygen content of the 9(18)-tungstophosphate anion) could be obtained if it were assumed that all 9(18)-heteropoly anions possessed the same structural form. This assumption was also based on § 1, where it was shown that all 12-heteropoly anions have the same structural form $[XM_{12}O_{40}]$ and that the relationship between the 12- and 9(18)-anions applies to the heteropoly-arsenates as well as to the heteropoly-phosphates. On this basis the anhydrous salt thallous 9(18)-arsenomolybdate, $3Tl_2O.As_2O_5.18MoO_3$ or $Tl_6As_2Mo_{18}O_{62}$ (Pufahl, 1888), suggested that the formula $(P_2W_{18}O_{62})^{6-}$ proposed for the 9(18)-tungstophosphate anion was correct.

(vi) *Determination of oxygen and phosphorus atom coordinates*

Although corrections had been made for series-termination errors, the electron-density projections were still not accurate enough to permit the direct derivation of the coordinates of these light atoms, particularly the oxygen atoms. In this respect the problem was similar to that of locating hydrogen atoms in organic molecules when using structure-amplitude data obtained by the eye-estimation method, even if corrections for absorption and extinction have been made. In the present case the ratio of the atomic scattering factors of oxygen and tungsten was less favourable than that of hydrogen and carbon. In addition, no correction was made for the very heavy absorption (μ = 835 cm.$^{-1}$) or extinction so that the likelihood of spurious peaks of significant size was increased.

The atomic coordinates were derived from a consideration of the distortions likely in WO_6 octahedra linked by shared edges. The close similarity of the tungsten frameworks shown in Fig. 9 suggested that the distortion of octahedra in $(P_2W_{18}O_{62})^{6-}$ was much the same as that found in $(PW_{12}O_{40})^{3-}$. The PO_4 tetrahedra were assumed to be undistorted, as in the 12-anions. Hexagonal coordinates x', y', z'), relative to the set of axes shown in Fig. 9(*a*), were first calculated for the sixty-two oxygen and two phosphorus atoms. The z' coordinates were thus the ζ values defined earlier. Knowing the coordinates (X, Z) of R, the centre of the anion, and also δ, the angle of inclination, the x and z coordinates of each atom could be obtained. From these, the y coordinates were calculated by equation (1), using the value of Y obtained from the *a*-axis electron-density projection. All proposed atomic positions lay within positive regions of the electron-density projections, and the phosphorus atoms coincided with peaks of appropriate height (Figs. 7 and 8).

The coordinates were then used in structure-amplitude calculations which, for the oxygen atoms, were confined to those planes with $\sin\theta < 0{\cdot}5$. At this limiting value the atomic scattering factor of oxygen was less than 10% of that of tungsten, and a further extension of the considerable labour involved in computing for sixty-two atoms did not appear justified. Inclusion of the oxygen and phosphorus contributions reduced the discrepancy factors, for the relevant reflexions, from 19·6% to 16·6% for the *h0l* set and from 22·4% to 19·5% for the *0kl* set. The essential correctness of the proposed coordinates was therefore confirmed. No refinement of the parameters was possible, however, because of the errors in the electron-density maps discussed above.

The coordinates and ζ values of the oxygen and phosphorus atoms in $(P_2W_{18}O_{62})^{6-}$ are given in Table 2. The oxygen atoms have been divided into four groups whose significance will be discussed later. The numbering of the atoms corresponds to that of Figs. 7 and 8.

(vii) *Location of the other atoms in the unit cell*

No guiding conditions of the type which governed the location of the anionic oxygen atoms could be used in determining the coordinates of the fourteen water molecules, and it was therefore necessary to rely more directly on the evidence of the electron-density projections. As a result, the presence of spurious peaks was now more serious than before, and has so far prevented an unambiguous analysis of the positions of the water molecules around the complex anion. Because of this uncertainty it has not been possible to fix the potassium atoms either, since two water molecules which are unresolved in projection affect both the electron-density maps and the calculated structure amplitudes to practically the same extent as one potassium atom. Further work on this part of the structure analysis will be reported later.

A small number of *h0l* and *0kl* terms were not used in the electron-density calculations because of doubt as to whether the phases given by the F_{anion} calculations were correct. The terms, which were all small in magnitude, are marked with an asterisk in Table 4.

The overall discrepancy factors were 17·2% for the *h0l* reflexions and 18·4% for the *0kl* reflexions. Certain individual discrepancies were quite considerable, and may be due to absorption errors or to omission of the

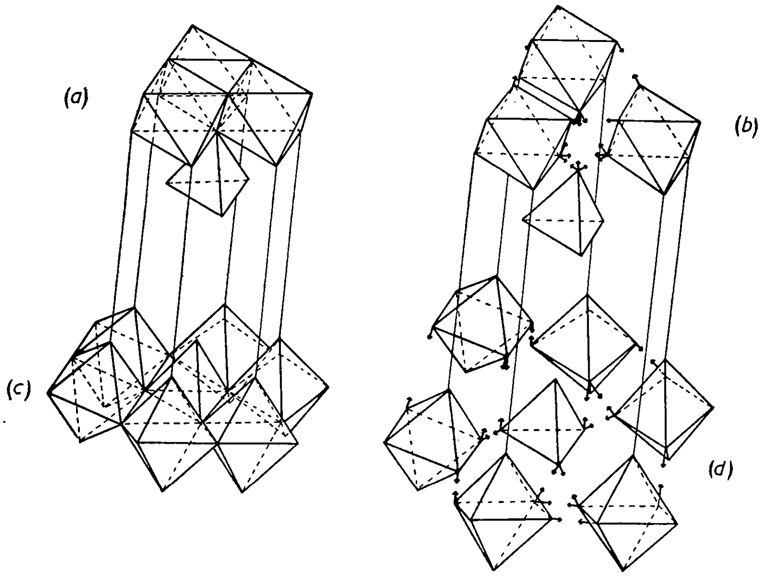

Fig. 10. The constitution of the 'half-unit' of the 9(18)-tungstophosphate anion.

contributions of the potassium atoms and the water molecules.

4. Description of structure

The 9(18)-tungstophosphate anion, $(P_2W_{18}O_{62})^{6-}$, is a complex coordinated structure of point-group symmetry $3/m$. The complete anion consists, therefore, of two identical 'half-units' related by the plane of symmetry perpendicular to the trigonal axis. The 'half-units' are linked together by six oxygen atoms situated in the plane of symmetry, so that these atoms are shared equally by the two halves.

The constitution of the anion is best seen from an analysis of the 'half-unit', including the six atoms situated in the plane of symmetry. This portion of the anion consists of a central PO_4 tetrahedron surrounded by nine WO_6 octahedra linked together by sharing both corners and edges (Fig. 10). Fig. 10(*a*) shows the manner in which three WO_6 octahedra share oxygen atoms so as to form a compact group in which each octahedron is linked to its neighbour on either side by a shared edge. The corner common to the three octahedra is then shared with the PO_4 tetrahedron. Fig. 10(*b*) shows this arrangement exploded outwards for simplicity. The arrows indicate the shared corners. The other six WO_6 octahedra are arranged around the trigonal axis in three groups of two (Fig. 10(*c*)). The two octahedra in each group share two oxygen atoms as a common edge, and, in addition, one of these atoms is also shared with the PO_4 tetrahedron. The three groups are then linked together by each octahedron sharing a corner with its neighbour in the adjacent group. Fig. 10(*d*) shows this arrangement exploded outwards for simplicity, the arrows again indicating the shared corners. The ring of six octahedra is then linked to the compact group of three octahedra by further sharing of corners (Fig. 10(*a*) and (*c*) or (*b*) and (*d*)), and the resultant arrangement has the form shown in Fig. 11. The corners marked as black dots are the oxygen atoms situated in the plane of symmetry and are shared between the two 'half-units' of the anion.

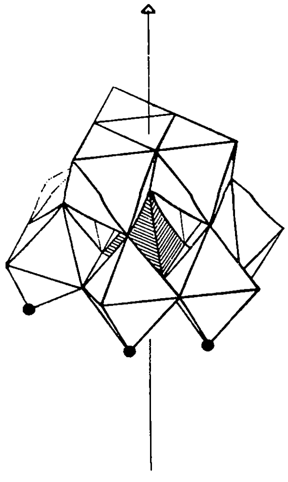

Fig. 11. The complete 'half-unit'.

The complete 9(18)-tungstophosphate anion is shown in Fig. 12. It has the formula $(P_2W_{18}O_{62})^{6-}$ and its charge is that of the two central $(PO_4)^{3-}$ groups.

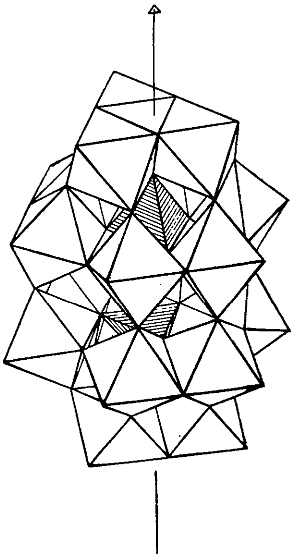

Fig. 12. The 9(18)-tungstophosphate anion $(P_2W_{18}O_{62})^{6-}$.

The oxygen atoms in $(P_2W_{18}O_{62})^{6-}$ have been divided into four types, O_1, O_2, O_3, O_4, according to the manner in which they are shared. The O_1 atoms define the PO_4 tetrahedra; the O_2 atoms are shared between two octahedra as a common corner: the O_3 atoms are shared between two octahedra as part of a common edge O_1–O_3; the O_4 atoms are completely unshared. The WO_6 octahedra are distorted, and the tungsten atoms are close to, but not quite at, their centres. The interatomic distances used in deriving the coordinates listed in Table 2 are given in Table 3.

Table 3. *Interatomic distances in* $(P_2W_{18}O_{62})^{6-}$

O_1–O_1 = 2·80 Å	
O_1–O_2 = 2·70	W–O_1 = 2·35 Å
O_1–O_3 = 2·65	W–O_2 = 1·85
O_2–O_2 = 2·65	W–O_3 = 2·00
O_2–O_3 = 2·60	W–O_4 = 1·85
O_2–O_4 = 3·10	
O_3–O_4 = 2·80	

The definition of the O_1 atoms has implied that the PO_4 tetrahedra are undistorted. The coordinates of the phosphorus atoms are those of the centres of the tetrahedra, and the agreement of the proposed atomic positions with the electron-density projections is shown in Figs. 7 and 8. It is possible, however, that the tetrahedra may be slightly distorted. This could result from the fact that while three corners share two octahedra each (Fig. 10(*c*) or (*d*)), the fourth corner shares three octahedra (Fig. 10(*a*) or (*b*)). A subdivision of the O_1-type atoms may therefore be

Table 4. *Comparison of observed and calculated structure amplitudes*

* Values omitted from the Fourier synthesis

(i) ($h0l$) zone

h	l	F_c	F_o
0	0	2112	
1		-494	380
2		-337	284
3		3	< 45
4		-175	187
5		168	189
6		-135	74
7		110	143
8		303	267
9		-360	323
10		133	94
11		3	< 75
12		-43	< 65
13		-17	< 50
$\overline{13}$	1	-19	< 50
$\overline{12}$		26	< 69
$\overline{11}$		54	< 75
$\overline{10}$		-117	117
$\overline{9}$		- 9	< 76
$\overline{8}$		-106	123
$\overline{7}$		213	176
$\overline{6}$		43	*92
$\overline{5}$		-49	< 50
$\overline{4}$		7	< 50
$\overline{3}$		8	*89
$\overline{2}$		-53	< 40
$\overline{1}$		28	< 30
0		-139	111
1		32	< 30
2		-179	152
3		272	262
4		62	119
5		-72	101
6		- 7	< 54
7		48	< 65
8		-43	111
9		-75	< 78
10		55	92
11		125	145
12		-91	105
$\overline{13}$	2	-23	< 57
$\overline{12}$		66	< 65
$\overline{11}$		-49	< 76
$\overline{10}$		-112	90
$\overline{9}$		286	257
$\overline{8}$		42	*80
$\overline{7}$		-83	60
$\overline{6}$		-341	360
$\overline{5}$		15	< 47
$\overline{4}$		234	225
$\overline{3}$		-246	221
$\overline{2}$		257	211
$\overline{1}$		538	452
0		-404	362
1		-242	211
2		-370	364
3		370	465
4		137	158
5		-98	72
6		71	< 60
7		-39	< 68
8		-124	90
9		120	100
10		-32	< 75
11		-95	< 70
12		48	< 55
$\overline{13}$	3	-18	< 50
$\overline{12}$		65	105
$\overline{11}$		-59	< 65
$\overline{10}$		33	< 70
$\overline{9}$		-43	*70
$\overline{8}$		149	129
$\overline{7}$		9	< 60
$\overline{6}$		-76	< 55
$\overline{5}$		-97	< 50
$\overline{4}$		99	< 50
$\overline{3}$		-163	152
$\overline{2}$		42	*120
$\overline{1}$		0	< 30
0		-79	*97
1		-10	< 41
2		401	335
3		-106	109
4		-199	237
5		-224	209
6		223	186
7		33	< 70
8		- 75	< 70
9		69	106
10		95	< 70
11		-137	177
$\overline{13}$	4	82	113
$\overline{12}$		-96	< 70
$\overline{11}$		63	< 70
$\overline{10}$		11	< 70
$\overline{9}$		62	69
$\overline{8}$		-296	257
$\overline{7}$		-70	127
$\overline{6}$		145	112
$\overline{5}$		209	192
$\overline{4}$		297	261
$\overline{3}$		-302	288
$\overline{2}$		-396	390
$\overline{1}$		204	223
0		-320	370
1		245	205
2		78	*69
3		51	*71
4		77	*62
5		-295	336
6		18	< 65
7		77	< 75
8		-56	< 77
9		85	93
10		-92	90
11		52	< 62
$\overline{13}$	5	64	67
$\overline{12}$		-30	< 75
$\overline{11}$		3	< 75
$\overline{10}$		81	< 75
$\overline{9}$		-119	119
$\overline{8}$		104	121
$\overline{7}$		-18	< 54
$\overline{6}$		53	< 50
$\overline{5}$		12	< 46
$\overline{4}$		-247	245
$\overline{3}$		224	214
$\overline{2}$		161	138
$\overline{1}$		-149	159
0		199	213
1		-64	< 50
2		-25	< 53
3	5	-215	201
4		-137	125
5		420	388
6		7	< 70
7		-97	< 75
8		55	< 75
9		-90	105
10		-23	< 70
$\overline{14}$	6	45	< 50
$\overline{13}$		-116	98
$\overline{12}$		74	< 75
$\overline{11}$		-22	< 75
$\overline{10}$		-157	161
$\overline{9}$		64	68
$\overline{8}$		221	185
$\overline{7}$		-135	113
$\overline{6}$		301	269
$\overline{5}$		37	< 46
$\overline{4}$		-381	372
$\overline{3}$		-209	236
$\overline{2}$		114	89
$\overline{1}$		466	486
0		57	< 45
1		-286	254
2		244	201
3		-140	212
4		-48	< 50
5		33	*89
6		25	< 70
7		-19	< 75
8		78	< 75
9		-53	< 70
10		26	< 65
$\overline{14}$	7	24	*57
$\overline{13}$		-34	< 65
$\overline{12}$		4	< 75
$\overline{11}$		119	118
$\overline{10}$		-245	200
$\overline{9}$		136	115
$\overline{8}$		49	< 60
$\overline{7}$		-73	< 51
$\overline{6}$		-146	133
$\overline{5}$		54	*86
$\overline{4}$		168	164
$\overline{3}$		146	112
$\overline{2}$		-152	129
$\overline{1}$		- 4	< 47
0		-258	246
1		51	< 53
2		119	124
3		90	83
4		65	< 57
5		-14	< 65
6		-102	141
7		6	< 75
8		-166	100
$\overline{14}$	8	-54	< 58
$\overline{13}$		72	< 70
$\overline{12}$		-65	113
$\overline{11}$		-122	102
$\overline{10}$		373	357
$\overline{9}$		-78	67
$\overline{8}$		-36	< 60
$\overline{7}$		-149	161
$\overline{6}$		-105	94
$\overline{5}$	8	210	261
$\overline{4}$		-274	261
$\overline{3}$		177	147
$\overline{2}$		396	356
$\overline{1}$		-301	293
0		-51	*134
1		-218	226
2		148	211
3		142	134
4		-173	159
5		73	69
6		-23	< 69
7		76	< 75
8		2	< 70
$\overline{14}$	9	-33	< 60
$\overline{13}$		44	< 70
$\overline{12}$		82	106
$\overline{11}$		-234	198
$\overline{10}$		113	70
$\overline{9}$		85	66
$\overline{8}$		-174	147
$\overline{7}$		88	126
$\overline{6}$		145	152
$\overline{5}$		-26	*50
$\overline{4}$		10	< 47
$\overline{3}$		-294	269
$\overline{2}$		4	< 50
$\overline{1}$		-171	155
0		169	200
1		540	505
2		-224	243
3		-245	223
4		-42	< 66
5		-23	*70
6		140	90
7		-164	90
8		169	167
$\overline{14}$	10	- 6	< 60
$\overline{13}$		21	< 70
$\overline{12}$		- 2	< 75
$\overline{11}$		92	< 75
$\overline{10}$		-21	< 70
$\overline{9}$		-71	< 65
$\overline{8}$		-395	368
$\overline{7}$		307	272
$\overline{6}$		183	209
$\overline{5}$		43	< 51
$\overline{4}$		-145	150
$\overline{3}$		-113	131
$\overline{2}$		182	173
$\overline{1}$		-213	303
0		-256	244
1		386	495
2		136	132
3		43	< 63
4		-81	128
5		71	73
6		42	< 70
7		-106	148
$\overline{13}$	11	-82	< 75
$\overline{12}$		-55	< 75
$\overline{11}$		94	80
$\overline{10}$		-18	< 70
$\overline{9}$		-18	< 65
$\overline{8}$		199	183

Table 4 (*cont.*)

h	*l*	F_c	F_o
$\bar{7}$	11	−55	95
$\bar{6}$		12	< 50
$\bar{5}$		−402	400
$\bar{4}$		42	*71
$\bar{3}$		273	249
$\bar{2}$		−72	107
$\bar{1}$		205	212
0		217	226
1		−344	370
2		−178	148
3		−106	148
4		304	309
5		62	< 75
6		−116	145
7		39	< 70
$\bar{14}$	12	107	92
$\bar{13}$		89	91
$\bar{12}$		−64	< 75
$\bar{11}$		109	90
$\bar{10}$		−141	101
$\bar{9}$		26	< 70
$\bar{8}$		66	< 65
$\bar{7}$		181	249
$\bar{6}$		228	252
$\bar{5}$		−700	642
$\bar{4}$		212	169
$\bar{3}$		258	228
$\bar{2}$		−214	196
$\bar{1}$		65	110
0		−26	*54
1		100	93
2		79	< 65
3		−159	140
4		217	207
5		−178	197
6		− 72	129
7		157	123
$\bar{14}$	13	−173	141
$\bar{13}$		118	139
$\bar{12}$		− 3	< 75
$\bar{11}$		− 5	< 70
$\bar{10}$		86	70
$\bar{9}$		−46	69
$\bar{8}$		−43	< 65
$\bar{7}$		−152	191
$\bar{6}$		−228	238
$\bar{5}$		512	479
$\bar{4}$		72	*53
$\bar{3}$		133	130
$\bar{2}$		−313	329
$\bar{1}$		−146	183
0		108	136
1		62	< 65
2		26	< 70
3		237	277
4		−72	< 75
5		− 2	< 75
6		−187	233
7		118	153
$\bar{14}$	14	−84	66
$\bar{13}$		−91	129
$\bar{12}$		148	106
$\bar{11}$		16	< 75
$\bar{10}$		55	< 75
$\bar{9}$		−105	121
$\bar{8}$		134	146
$\bar{7}$		−43	< 60
$\bar{6}$		−239	210
$\bar{5}$	14	90	78
$\bar{4}$		89	102
$\bar{3}$		−11	< 54
$\bar{2}$		24	< 56
$\bar{1}$		−50	*73
0		129	110
1		−63	< 70
2		3	< 75
3		− 2	*75
4		−132	75
5		18	< 70
6		216	190
$\bar{14}$	15	96	148
$\bar{13}$		15	< 70
$\bar{12}$		−46	< 75
$\bar{11}$		−11	< 75
$\bar{10}$		−72	104
$\bar{9}$		−39	< 70
$\bar{8}$		19	< 65
$\bar{7}$		172	168
$\bar{6}$		50	105
$\bar{5}$		36	93
$\bar{4}$		−71	91
$\bar{3}$		−457	455
$\bar{2}$		74	113
$\bar{1}$		230	246
0		158	210
1		−41	< 70
2		−137	127
3		95	70
4		−63	106
5		−124	67
6		161	166
$\bar{14}$	16	−31	< 63
$\bar{13}$		169	144
$\bar{12}$		−71	< 75
$\bar{11}$		46	< 75
$\bar{10}$		−49	< 75
$\bar{9}$		−196	218
$\bar{8}$		144	153
$\bar{7}$		82	< 65
$\bar{6}$		−167	141
$\bar{5}$		127	88
$\bar{4}$		−118	88
$\bar{3}$		265	238
$\bar{2}$		−101	112
$\bar{1}$		−153	144
0		80	164
1		−80	155
2		−17	< 75
3		63	75
4		−21	< 75
5		176	176
6		−184	148
$\bar{14}$	17	66	< 65
$\bar{13}$		−175	163
$\bar{12}$		53	< 75
$\bar{11}$		−79	< 75
$\bar{10}$		56	75
$\bar{9}$		279	200
$\bar{8}$		−66	< 70
$\bar{7}$		−153	90
$\bar{6}$		− 5	< 65
$\bar{5}$		−207	180
$\bar{4}$		166	174
$\bar{3}$		−82	147
$\bar{2}$		274	274
$\bar{1}$		155	165
0	17	−308	319
1		−89	< 75
2		57	< 75
3		2	< 75
4		99	132
5		−49	*89
$\bar{13}$	18	−111	< 70
$\bar{12}$		174	151
$\bar{11}$		−90	< 75
$\bar{10}$		−174	168
$\bar{9}$		191	157
$\bar{8}$		38	< 75
$\bar{7}$		16	*99
$\bar{6}$		−163	182
$\bar{5}$		88	85
$\bar{4}$		251	203
$\bar{3}$		−296	247
$\bar{2}$		−92	90
$\bar{1}$		76	< 75
0		−28	< 75
1		146	140
2		26	< 75
3		−32	< 75
4		−27	< 70
$\bar{13}$	19	47	< 70
$\bar{12}$		27	< 75
$\bar{11}$		146	160
$\bar{10}$		−36	< 75
$\bar{9}$		−97	130
$\bar{8}$		−167	134
$\bar{7}$		−125	159
$\bar{6}$		211	245
$\bar{5}$		230	188
$\bar{4}$		−83	< 75
$\bar{3}$		−11	< 75
$\bar{2}$		−135	138
$\bar{1}$		79	119
0		−139	166
1		6	< 75
2		135	218
3		57	< 75
4		−104	128
$\bar{13}$	20	89	< 70
$\bar{12}$		−23	< 75
$\bar{11}$		−83	< 75
$\bar{10}$		−20	< 75
$\bar{9}$		168	150
$\bar{8}$		54	75
$\bar{7}$		−226	209
$\bar{6}$		183	163
$\bar{5}$		−121	103
$\bar{4}$		−74	< 75
$\bar{3}$		−37	< 75
$\bar{2}$		111	100
$\bar{1}$		116	149
0		16	< 75
1		−44	< 75
2		−54	98
3		−142	90
4		109	90
$\bar{13}$	21	237	207
$\bar{12}$		−194	181
$\bar{11}$		−119	95
$\bar{10}$		78	< 75
$\bar{9}$		−141	75
$\bar{8}$		168	140
$\bar{7}$		57	< 75
$\bar{6}$	21	144	148
$\bar{5}$		60	< 77
$\bar{4}$		−604	593
$\bar{3}$		250	260
$\bar{2}$		210	189
$\bar{1}$		−170	137
0		69	< 70
1		−58	< 70
2		174	150
$\bar{12}$	22	−34	< 70
$\bar{11}$		−39	< 75
$\bar{10}$		107	90
$\bar{9}$		54	76
$\bar{8}$		−125	93
$\bar{7}$		−68	119
$\bar{6}$		−65	< 75
$\bar{5}$		132	130
$\bar{4}$		60	< 75
$\bar{3}$		114	96
$\bar{2}$		−30	< 75
$\bar{1}$		−133	168
0		−62	65
1		31	< 65
2		−11	< 60
$\bar{13}$	23	−310	270
$\bar{12}$		72	70
$\bar{11}$		46	< 70
$\bar{10}$		197	239
$\bar{9}$		− 6	< 75
$\bar{8}$		−222	212
$\bar{7}$		238	214
$\bar{6}$		−128	113
$\bar{5}$		−330	270
$\bar{4}$		330	302
$\bar{3}$		12	< 70
$\bar{2}$		100	156
$\bar{1}$		−189	268
0		−24	< 65
1		198	171
$\bar{13}$	24	119	153
$\bar{12}$		−100	102
$\bar{11}$		−24	< 70
$\bar{10}$		72	< 70
$\bar{9}$		−110	100
$\bar{8}$		−78	75
$\bar{7}$		146	150
$\bar{6}$		95	75
$\bar{5}$		84	< 75
$\bar{4}$		−106	140
$\bar{3}$		−97	< 70
$\bar{2}$		−144	155
$\bar{1}$		52	65
0		175	176
$\bar{12}$	25	155	164
$\bar{11}$		113	99
$\bar{10}$		−233	214
$\bar{9}$		−54	< 70
$\bar{8}$		−15	< 73
$\bar{7}$		96	145
$\bar{6}$		40	< 75
$\bar{5}$		−95	103
$\bar{4}$		131	151
$\bar{3}$		9	< 70
$\bar{2}$		−102	101
$\bar{12}$	26	−76	76
$\bar{11}$		− 5	< 65

Table 4 (*cont.*)

h	*l*	F_c	F_o
$\overline{10}$	26	68	67
$\overline{9}$		37	< 70
$\overline{8}$		161	141
$\overline{7}$		−94	80
$\overline{6}$		−68	< 65
$\overline{5}$		−102	78
$\overline{4}$	26	−24	< 65
$\overline{3}$		14	< 65
$\overline{2}$		124	136
$\overline{11}$	27	81	89
$\overline{10}$		−133	175
$\overline{9}$	27	− 5	< 55
$\overline{8}$		215	246
$\overline{7}$		− 9	< 60
$\overline{6}$		−78	70
$\overline{5}$		−64	177
$\overline{4}$		122	102
$\overline{10}$	28	30	77
$\overline{9}$		−11	< 50
$\overline{8}$		−263	236
$\overline{7}$		−34	< 55
$\overline{6}$		112	90

(ii) (0*kl*) zone

k	*l*	F_c	F_o
1	0	−261	190
2		−10	*36
3		78	127
4		−103	155
5		82	97
6		−78	87
7		−319	304
8		270	335
9		−83	107
10		−276	256
11		−174	256
12		30	< 77
13		52	92
14		175	74
15		−30	< 65
$\overline{15}$	1	128	92
$\overline{14}$		−131	117
$\overline{13}$		−126	85
$\overline{12}$		28	< 75
$\overline{11}$		−261	240
$\overline{10}$		−99	75
$\overline{9}$		−98	65
$\overline{8}$		80	76
$\overline{7}$		135	105
$\overline{6}$		−83	64
$\overline{5}$		−47	*80
$\overline{4}$		28	*50
$\overline{3}$		37	< 40
$\overline{2}$		209	242
$\overline{1}$		280	280
1		18	< 35
2		−35	*109
3		−342	324
4		−12	< 46
5		−17	< 48
6		−24	< 49
7		581	552
8		−402	364
9		95	64
10		95	70
11		90	70
12		138	120
13		− 6	< 75
14		−49	95
15		207	180
$\overline{15}$	2	8	< 70
$\overline{14}$		50	< 75
$\overline{13}$		−31	< 75
$\overline{12}$		−13	< 72
$\overline{11}$		95	121
$\overline{10}$		78	93
$\overline{9}$		−50	< 60
$\overline{8}$		195	142
$\overline{7}$		−114	128
$\overline{6}$		15	< 48
$\overline{5}$		−50	< 48
$\overline{4}$		−270	326
$\overline{3}$		−75	*83
$\overline{2}$	2	− 7	< 35
$\overline{1}$		13	< 30
1		−280	250
2		−20	< 40
3		20	< 45
4		133	125
5		80	87
6		240	190
7		294	250
8		−120	133
9		−73	93
10		−27	< 70
11		154	75
12		12	< 75
13		−25	< 75
14		− 6	< 70
15		−230	161
$\overline{15}$	3	−137	102
$\overline{14}$		−160	131
$\overline{13}$		110	107
$\overline{12}$		102	74
$\overline{11}$		−149	140
$\overline{10}$		175	161
$\overline{9}$		53	< 60
$\overline{8}$		50	76
$\overline{7}$		−178	191
$\overline{6}$		−40	*70
$\overline{5}$		10	< 45
$\overline{4}$		20	*45
$\overline{3}$		−230	227
$\overline{2}$		−130	171
$\overline{1}$		150	154
1		−133	137
2		−63	*87
3		90	106
4		73	68
5		75	50
6		−100	89
7		−200	146
8		35	< 60
9		22	< 65
10		−110	< 70
11		168	169
12		20	< 75
13		120	74
14		100	100
15		−235	127
$\overline{15}$	4	38	*73
$\overline{14}$		83	< 75
$\overline{13}$		78	107
$\overline{12}$		−115	148
$\overline{11}$		46	< 70
$\overline{10}$		103	130
$\overline{9}$		120	144
$\overline{8}$		−100	119
$\overline{7}$		223	220
$\overline{6}$		24	< 50
$\overline{5}$	4	121	106
$\overline{4}$		−200	211
$\overline{3}$		200	224
$\overline{2}$		−20	*57
$\overline{1}$		188	184
1		77	75
2		42	< 45
3		−76	68
4		−232	187
5		6	< 50
6		−57	< 52
7		−74	57
8		−200	163
9		18	< 65
10		70	< 70
11		8	< 75
12		8	< 75
13		11	< 70
14		2	< 65
$\overline{15}$	5	260	258
$\overline{14}$		−130	132
$\overline{13}$		25	< 75
$\overline{12}$		68	< 70
$\overline{11}$		−223	154
$\overline{10}$		34	< 65
$\overline{9}$		92	131
$\overline{8}$		5	*53
$\overline{7}$		110	113
$\overline{6}$		−53	< 45
$\overline{5}$		−166	218
$\overline{4}$		64	58
$\overline{3}$		234	234
$\overline{2}$		3	< 40
$\overline{1}$		27	< 40
1		42	*45
2		50	91
3		−109	180
4		81	101
5		− 6	< 50
6		118	< 55
7		−300	236
8		67	< 65
9		− 5	< 70
10		−22	< 75
11		−152	107
12		43	< 70
$\overline{15}$	6	−15	< 70
$\overline{14}$		−106	131
$\overline{13}$		−122	107
$\overline{12}$		−352	310
$\overline{11}$		166	180
$\overline{10}$		−156	215
$\overline{9}$		−132	144
$\overline{8}$		185	152
$\overline{7}$		−210	203
$\overline{6}$		60	< 50
$\overline{5}$		− 6	< 47
$\overline{4}$		−140	148
$\overline{3}$	6	420	570
$\overline{2}$		200	234
$\overline{1}$		23	< 45
1		−28	< 47
2		−50	< 48
3		−12	< 50
4		107	80
5		−92	< 55
6		94	91
7		−22	< 65
8		−56	< 68
9		− 4	< 70
10		−86	< 75
11		38	< 75
12		64	75
13		−11	< 70
14		−171	157
$\overline{14}$	7	−152	131
$\overline{13}$		−149	150
$\overline{12}$		−233	207
$\overline{11}$		350	354
$\overline{10}$		58	< 65
$\overline{9}$		23	*88
$\overline{8}$		−34	< 55
$\overline{7}$		−81	82
$\overline{6}$		23	< 50
$\overline{5}$		−110	99
$\overline{4}$		50	*67
$\overline{3}$		−36	< 45
$\overline{2}$		60	< 45
$\overline{1}$		−92	105
1		−50	< 50
2		−58	*50
3		100	109
4		307	274
5		−13	< 55
6		89	106
7		38	< 65
8		115	< 70
9		4	< 75
10		27	< 75
11		146	100
12		−61	< 70
13		7	< 65
$\overline{15}$	8	−123	145
$\overline{14}$		66	92
$\overline{13}$		151	129
$\overline{12}$		327	388
$\overline{11}$		−76	140
$\overline{10}$		72	< 65
$\overline{9}$		95	85
$\overline{8}$		−94	77
$\overline{7}$		−241	229
$\overline{6}$		−300	270
$\overline{5}$		−275	248
$\overline{4}$		460	443
$\overline{3}$		−500	470
$\overline{2}$		−200	173

Table 4 (*cont.*)

k	l	F_c	F_o
$\bar{1}$	8	30	< 46
1		171	152
2		23	< 50
3		36	< 50
4		407	350
5		66	< 60
6		204	182
7		−90	110
8		106	80
9		17	< 75
10		96	< 75
11		−73	< 75
12		−87	< 70
$\overline{15}$	9	−95	128
$\overline{14}$		66	75
$\overline{13}$		82	130
$\overline{12}$		61	< 75
$\overline{11}$		74	< 70
$\overline{10}$		−100	93
$\bar{9}$		−171	161
$\bar{8}$		−21	< 55
$\bar{7}$		−65	106
$\bar{6}$		17	< 50
$\bar{5}$		183	177
$\bar{4}$		−100	159
$\bar{3}$		168	122
$\bar{2}$		85	110
$\bar{1}$		−230	269
1		−14	< 50
2		−36	*52
3		390	369
4		−692	609
5		−37	< 60
6		−87	< 65
7		−132	101
8		52	< 70
9		−33	< 75
10		20	< 75
11		334	289
12		−155	184
$\overline{15}$	10	44	73
$\overline{14}$		−89	75
$\overline{13}$		−164	167
$\overline{12}$		139	147
$\overline{11}$		−137	< 70
$\overline{10}$		97	70
$\bar{9}$		115	140
$\bar{8}$		−120	129
$\bar{7}$		305	274
$\bar{6}$		326	279
$\bar{5}$		93	51
$\bar{4}$		160	151
$\bar{3}$		−63	*50
$\bar{2}$		−18	< 50
$\bar{1}$		70	< 50
1		−100	83
2		42	< 55
3		−153	126
4		−180	143
5		−80	< 65
6		−95	99
7		280	233
8		−10	< 75
9		32	< 75
10		183	169
11		−235	196
12		166	147
$\overline{15}$	11	−201	193
$\overline{14}$	11	85	< 75
$\overline{13}$		15	< 75
$\overline{12}$		−15	< 75
$\overline{11}$		−31	< 70
$\overline{10}$		35	< 65
$\bar{9}$		188	137
$\bar{8}$		70	< 60
$\bar{7}$		−148	113
$\bar{6}$		−24	< 55
$\bar{5}$		216	187
$\bar{4}$		−159	140
$\bar{3}$		−25	< 50
$\bar{2}$		−81	< 50
$\bar{1}$		−23	< 50
1		24	< 55
2		−80	< 60
3		88	96
4		79	< 65
5		85	< 67
6		26	< 70
7		6	< 75
8		− 2	< 75
9		51	< 75
10		−127	102
11		−292	245
$\overline{15}$	12	−49	< 70
$\overline{14}$		25	< 75
$\overline{13}$		−28	< 77
$\overline{12}$		−144	141
$\overline{11}$		169	144
$\overline{10}$		−124	< 70
$\bar{9}$		−36	< 65
$\bar{8}$		−244	221
$\bar{7}$		80	84
$\bar{6}$		−104	79
$\bar{5}$		74	85
$\bar{4}$		−147	131
$\bar{3}$		157	118
$\bar{2}$		163	127
$\bar{1}$		−12	< 55
1		266	251
2		119	105
3		14	< 65
4		−37	< 70
5		31	< 70
6		110	< 75
7		−74	< 75
8		−134	107
9		−76	< 75
10		− 7	< 70
11		− 4	< 65
$\overline{15}$	13	−131	125
$\overline{14}$		80	< 70
$\overline{13}$		65	< 70
$\overline{12}$		51	92
$\overline{11}$		30	< 75
$\overline{10}$		−72	< 70
$\bar{9}$		−218	187
$\bar{8}$		−34	< 65
$\bar{7}$		73	76
$\bar{6}$		−92	83
$\bar{5}$		−49	< 55
$\bar{4}$		96	78
$\bar{3}$		−114	110
$\bar{2}$		29	< 55
$\bar{1}$		−212	180
1		34	*63
2		156	140
3		−217	176
4	13	140	142
5		33	< 70
6		−25	< 75
7		− 6	< 75
8		142	131
9		− 9	< 70
$\overline{15}$	14	330	383
$\overline{14}$		− 8	< 75
$\overline{13}$		46	< 75
$\overline{12}$		231	198
$\overline{11}$		−230	179
$\overline{10}$		9	< 70
$\bar{9}$		−101	121
$\bar{8}$		−167	135
$\bar{7}$		218	201
$\bar{6}$		−37	< 60
$\bar{5}$		−100	123
$\bar{4}$		− 5	< 60
$\bar{3}$		−125	94
$\bar{2}$		−133	120
$\bar{1}$		34	< 60
1		−85	66
2		60	120
3		−70	< 70
4		−74	90
5		38	< 75
6		−87	< 75
7		129	92
8		109	75
$\overline{15}$	15	163	152
$\overline{14}$		−11	< 75
$\overline{13}$		− 8	< 75
$\overline{12}$		−160	130
$\overline{11}$		6	< 75
$\overline{10}$		58	< 75
$\bar{9}$		−127	142
$\bar{8}$		301	289
$\bar{7}$		16	< 70
$\bar{6}$		181	156
$\bar{5}$		87	< 65
$\bar{4}$		−240	205
$\bar{3}$		84	78
$\bar{2}$		−31	< 65
$\bar{1}$		−12	*65
1		−239	242
2		−107	90
3		−92	138
4		−117	95
5		−79	< 75
6		47	< 75
$\overline{15}$	16	−116	170
$\overline{14}$		−17	< 70
$\overline{13}$		29	< 75
$\overline{12}$		152	119
$\overline{11}$		−153	92
$\overline{10}$		84	< 75
$\bar{9}$		213	183
$\bar{8}$		438	380
$\bar{7}$		189	210
$\bar{6}$		2	< 70
$\bar{5}$		−77	< 65
$\bar{4}$		66	< 65
$\bar{3}$		−31	*83
$\bar{2}$		−184	168
$\bar{1}$		94	112
1		−51	< 70
2		−213	218
3		−100	< 75
4	16	188	169
5		44	< 75
6		62	< 70
$\overline{15}$	17	22	< 70
$\overline{14}$		−17	< 75
$\overline{13}$		− 6	< 75
$\overline{12}$		16	< 75
$\overline{11}$		47	< 75
$\overline{10}$		−80	< 75
$\bar{9}$		56	< 75
$\bar{8}$		−109	105
$\bar{7}$		−44	< 70
$\bar{6}$		−109	< 70
$\bar{5}$		−128	100
$\bar{4}$		−11	< 70
$\bar{3}$		135	79
$\bar{2}$		125	82
$\bar{1}$		338	322
1		234	212
2		72	< 75
3		72	< 75
4		49	< 75
5		−31	< 75
$\overline{15}$	18	−90	75
$\overline{14}$		19	< 75
$\overline{13}$		−65	< 75
$\overline{12}$		−298	250
$\overline{11}$		52	< 75
$\overline{10}$		−18	< 75
$\bar{9}$		−213	181
$\bar{8}$		−39	< 75
$\bar{7}$		−82	< 75
$\bar{6}$		41	< 75
$\bar{5}$		202	183
$\bar{4}$		−75	< 75
$\bar{3}$		112	103
$\bar{2}$		296	257
$\bar{1}$		−32	< 75
1		−46	< 75
2		−45	< 75
3		188	167
4		−112	100
5		−96	70
$\overline{15}$	19	−18	< 65
$\overline{14}$		−30	< 70
$\overline{13}$		92	< 75
$\overline{12}$		−46	< 75
$\overline{11}$		−142	126
$\overline{10}$		60	< 75
$\bar{9}$		223	199
$\bar{8}$		−134	158
$\bar{7}$		74	< 75
$\bar{6}$		−23	< 75
$\bar{5}$		−47	< 75
$\bar{4}$		150	155
$\bar{3}$		−159	141
$\bar{2}$		−247	200
$\bar{1}$		78	106
1		−40	< 75
2		35	< 75
3		−125	75
4		172	150
$\overline{15}$	20	126	186
$\overline{14}$		−36	< 65
$\overline{13}$		89	70
$\overline{12}$		−93	103
$\overline{11}$		187	166

Table 4 (*cont.*)

k	l	F_c	F_o	k	l	F_c	F_o	k	l	F_c	F_o	k	l	F_c	F_o
$\bar{10}$	20	4	< 75	$\bar{8}$	21	106	85	$\bar{2}$	22	68	< 75	$\bar{11}$	24	−185	205
$\bar{9}$		46	< 75	$\bar{7}$		−101	80	$\bar{1}$		−34	70	$\bar{10}$		− 2	< 65
$\bar{8}$		−32	< 75	$\bar{6}$		64	< 75	1		15	< 70	$\bar{9}$		−110	145
$\bar{7}$		12	< 75	$\bar{5}$		−174	152	2		−152	110	$\bar{8}$		152	136
$\bar{6}$		−27	< 75	$\bar{4}$		160	165					$\bar{7}$		−35	< 70
$\bar{5}$		−201	180	$\bar{3}$		36	< 75	$\bar{13}$	23	−209	170	$\bar{6}$		−111	97
$\bar{4}$		−194	180	$\bar{2}$		121	< 75	$\bar{12}$		175	170	$\bar{5}$		268	291
$\bar{3}$		85	70	$\bar{1}$		−142	160	$\bar{11}$		−102	131	$\bar{4}$		−11	< 70
$\bar{2}$		−23	< 70	1		−36	< 75	$\bar{10}$		13	< 65	$\bar{3}$		−48	70
$\bar{1}$		−156	120					$\bar{9}$		−53	< 70	$\bar{2}$		−140	123
1		23	< 75	$\bar{13}$	22	−70	< 65	$\bar{8}$		−232	196	$\bar{1}$		−94	< 65
2		89	< 75	$\bar{12}$		9	< 70	$\bar{7}$		86	< 75				
3		19	< 75	$\bar{11}$		187	208	$\bar{6}$		21	< 75	$\bar{10}$	25	−27	< 60
4		−72	75	$\bar{10}$		− 8	< 75	$\bar{5}$		86	< 75	$\bar{9}$		65	< 65
				$\bar{9}$		42	< 75	$\bar{4}$		209	221	$\bar{8}$		−153	120
$\bar{14}$	21	− 4	< 65	$\bar{8}$		17	< 75	$\bar{3}$		−83	102	$\bar{7}$		90	< 65
$\bar{13}$		−120	111	$\bar{7}$		−66	< 75	$\bar{2}$		28	< 75	$\bar{6}$		−22	< 65
$\bar{12}$		48	98	$\bar{6}$		−41	< 75	$\bar{1}$		20	< 70	$\bar{5}$		−69	< 65
$\bar{11}$		144	103	$\bar{5}$		115	76					$\bar{4}$		−295	285
$\bar{10}$		− 6	< 75	$\bar{4}$		150	100	$\bar{12}$	24	20	< 60	$\bar{3}$		14	< 60
$\bar{9}$		21	< 75	$\bar{3}$		−21	< 75								

necessary, but it has not been made here as the experimental data are not sufficiently accurate to detect the slight distortion that may be present.

5. Discussion

The relationship of the 9(18)-tungstophosphate anion to the 12-tungstophosphate anion may be seen from a comparison of Figs. 12 and 13. Although the orientations of the two anions are different the similarity of octahedra arrangements is obvious. It can be seen that the 'half-unit' of the 9(18)-anion is equivalent to the residue obtained by removing three WO_6 octahedra from the base of the 12-anion as drawn. The two relevant octahedra visible in Fig. 13 have been shaded. The 9(18)-anion is then formed by two such residues sharing the six corners exposed by the removal of the octahedra. These six corners are related by trigonal, not hexagonal, symmetry, i.e. the distance AB is not equal to the distance BC (Fig. 13): because of this, these corners can be shared only when the two 12-residues are orientated so that they are related by a plane of symmetry. It is in this respect that the 9(18)-anion differs from Wells's proposed structure which also has the formula $(P_2W_{18}O_{62})^{6-}$ (Wells, 1945, p. 344). In this structure two 'half-units' similar in form to Fig. 11 were joined in opposite orientations, so that the complete unit possessed a centre of symmetry. Such a union would be possible, however, only if the six connecting atoms were related by hexagonal symmetry, and it has been shown above that this condition is not satisfied in the 12-anion residues which produce the 9(18)-anion.

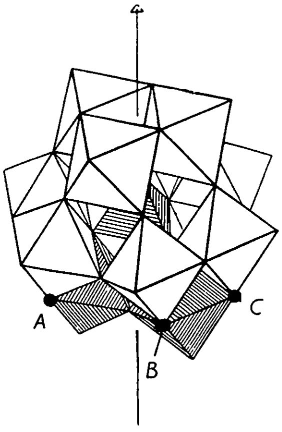

Fig. 13. The 12-tungstophosphate anion $(PW_{12}O_{40})^{3-}$.

The interatomic distances assumed in constructing the anion, and given in Table 3, are identical with those found previously in $(PW_{12}O_{40})^{3-}$. As stated earlier, the close agreement of the tungsten frameworks shown in Fig. 9(*a*) and (*b*) had suggested that the 9(18)-'half-unit' and the 12-anion residue were similar not merely in the arrangement of the WO_6 octahedra but also in the degree of distortion of these octahedra. The adoption of the 12-anion interatomic distances for the distorted octahedra in the present investigation was confirmed by comparing, in the following manner, the separation of the hexagonal rings of tungsten atoms in the 9(18)-anion and in the anion formed by the direct combination of two 12-anion residues. If it were assumed that the removal of three WO_6 octahedra from $(PW_{12}O_{40})^{3-}$ did not change any dimensions in the residue remaining, then the separation in the 'direct combination' anion was calculated to be 3·90 Å. However, the separation of the hexagonal rings in the 9(18)-anion was 3·75 Å (Fig. 9(*a*)). While the actual magnitude of the difference in ring-spacings in the two anions was subject to experimental error, the contraction observed in the 9(18)-anion was nevertheless a significant one, and to be expected if W–O and O–O distances in $(P_2W_{18}O_{62})^{6-}$

were similar to those in $(PW_{12}O_{40})^{3-}$. Thus, in the complete 12-anion the oxygen atoms marked as black dots (Fig. 13) were O_3 atoms, forming part of the shared edges O_1–O_3. However, in the 12-residue they were no longer in shared edges; and, when two residues combined to form the 9(18)-anion, these atoms became O_2 atoms, being in fact the atoms linking the two halves of the anion together (Fig. 11). Because of the different spacings W–O_3 = 2·0 Å and W–O_2 = 1·85 Å, the 9(18)-framework contracted slightly (as compared with the 'direct combination' framework) so as to make the W–new O_2 distances equal to 1·85 Å.

It might be expected that the trigonal anions would arrange themselves on a trigonal lattice. A trigonal form of potassium 9(18)-tungstophosphate, $K_6(P_2W_{18}O_{62}).28H_2O$, does in fact exist (Duparc & Pearce, 1899) but this form is difficult to prepare and changes readily into the triclinic form $K_6(P_2W_{18}O_{62}).14H_2O$ investigated here. The stability of the latter form must be ascribed to the closer packing which is possible when the anions are arranged on a triclinic lattice. Despite the closer packing, however, there is still a considerable volume of unoccupied space because of the shape of the anions. The water of crystallization presumably packs into these spaces so as to make the whole structure as homogeneous as possible.

The fact that the crystal arrangement is governed by packing conditions indicates that the negative charge of the 9(18)-anion is distributed uniformly over its whole surface. Because of the large surface area of the anion the charge density is therefore small. A similar charge distribution and charge density also exists in the 12-anion (Keggin, 1934), and this characteristic is doubtless the explanation of the extreme solubility in water and the ability to form insoluble precipitates with organic compounds such as alkaloids and basic dyes, which are properties common to both series of heteropoly-compounds.

It is probable that the structural form found for the 9(18)-tungstophosphate anion also exists in the other 9(18)-anions, namely the tungstoarsenate, molybdophosphate and molybdoarsenate anions. This has already been discussed in § 3(v). Whether or not this generalization is valid will be reported later.

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