736. *The Structure of* $(PW_{12}O_{40})^{3-}$ *and Related Ions.*

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The structure of the ion $(PW_{12}O_{40})^{3-}$ is described, and it is shown that the oxygen atoms form a close-packed arrangement of nearly equal-sized spheres, the close-packing being an interesting mixture of cubic and hexagonal. The PO and WO bond lengths are discussed and, in particular, an electronic formula is suggested in which each tungsten atom participates in one one-electron, one three-electron, and four two-electron bonds. The structures of (and electronic binding in) the hydrates of phosphotungstic acids are also examined, as well as those of other related ions [*e.g.*, $(TeMo_6O_{24})^{6-}$ and $(MnMo_9O_{32})^{6-}$].

THE main object is the consideration of the structure of ions of the general formula $(NM_{12}O_{40})^{n-}$ where N is a non-metal (*e.g.*, boron, silicon, phosphorus, germanium, or arsenic) and M is either tungsten or molybdenum. For convenience, the phosphotungstate ion $(PW_{12}O_{40})^{3-}$ will be considered in particular.[1] The structure of this can be understood most easily by considering the arrangement of the oxygen atoms, regarding them as a collection of equal spheres adopting a close-packed arrangement. (Instructive models can be made very easily with table-tennis balls and " Seccotine.") The validity of treating the structure in this way will be demonstrated later.

Structure of the Ion.—The 40 oxygen atoms can be divided into five groups; a central " core " of 16 atoms and four other identical triangular planar groups of six atoms which fit on to the core in a way to be described. The central core of 16 atoms is cubic close-packed. It is best visualised in the following way. A cubic close-packed stack forming

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[1] Bradley and Illingworth, *Proc. Roy. Soc.*, 1936, *A*, **157**, 113.

a regular tetrahedron can be made by forming a triangle of 10 spheres as a close-packed layer, and then placing on this a second layer of six atoms (as a triangle), and on this a third layer of three, followed by a fourth layer of a single sphere at the apex. This regular tetrahedron contains 20 spheres and, if one is removed from each corner, the central core of 16 found in the phosphotungstate ion is produced. This is shown in Fig. 1 and can be seen to involve cubic close-packing. Each face of the core consists of seven atoms, six (O_b) forming a hexagon round a central seventh atom (O_c). The phosphorus atom is located in the tetrahedral hole formed by the four atoms (O_c) which are at the centres of these four faces. All the 12 tungsten atoms are in octahedral holes *outside* this central core; the four octahedral holes in the central core are empty.

The four planar groups of six atoms are now added to the four faces of the central core; one group to each face. These groups of six could be added so that the *whole* structure was cubic close-packed. However, though they are added in a close-packed manner, they are not added to form a wholly cubic close-packed system. They are added so that they each form, with the next two layers of the central core, a hexagonal close-packed pattern. This is illustrated in Fig. 2. In this diagram the six spheres are drawn with full lines, and the adjacent layer of the central core (which contains seven atoms) is shown with broken lines. The next layer in the central core consists of six atoms and is disposed in the same way as the outermost layer of six atoms (since the stacking of these three layers is hexagonal close-packed).

FIG. 1. *Diagram showing arrangement of* 16 *spheres* (i.e., *oxygen atoms*) *in the central core of* $(PW_{12}O_{40})^{3-}$.

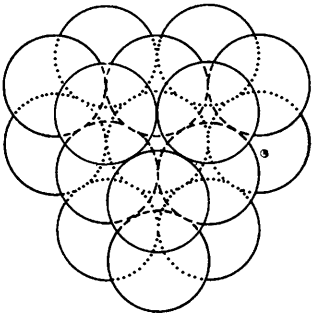
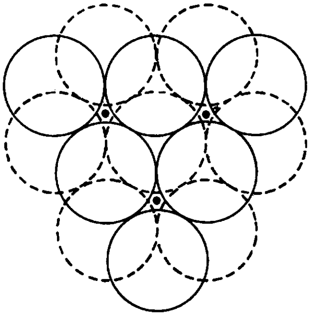


FIG. 2. *Diagram showing " attachment " of outer group of six oxygen atoms to a face of the central core. The dots mark the positions of the tungsten atoms.*



The mixing of cubic and hexagonal close-packing makes the structure a most fascinating one. The arrangement has, in a sense, the compactness of being fully close-packed, and yet there is no possibility of the pattern being extended indefinitely, because the four outermost groups of six atoms do not form part of a single cubic or hexagonal close-packed structure. Undoubtedly this feature must contribute to making this particular structure such a well-defined one so that it is found in several ions containing different atoms.

The location of the tungsten atoms is shown by the black dots in Fig. 2. They occupy the octahedral holes between the outermost groups of six spheres (*i.e.*, oxygen atoms) and the layers of seven spheres (*i.e.*, oxygen atoms) forming the faces of the central core. There are just twelve of these octahedral holes for the twelve tungsten atoms. From this it will be seen that the tungsten atoms occur in four sets of three which have the pattern with their accompanying oxygen atoms which is shown in Fig. 3.[2] The six oxygen atoms marked O_i and O_s form the outermost group of six, the other seven (O_c and O_b) form one of the faces of the central core (see above). The oxygen atoms labelled O_b in Fig. 3, of which there are six, form, in pairs, the bridges to the similar groups " attached " to the

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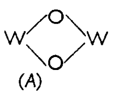
[2] Cf. Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 1043.

three other faces of the core. This is indicated by the broken lines. From Fig. 3 it is easily deduced that 24 oxygen atoms (O_b and O_i) are linking two tungsten atoms, twelve (O_s) are attached to one only, while four (O_c) are linked to three tungsten atoms and also to the central phosphorus atom.

If the outermost layers of oxygen atoms had been added in such a way that all the oxygen atoms formed part of a single cubic close-packed arrangement, the diagram analogous to Fig. 3 would be that shown in Fig. 4. This would require that the four W_3 sets were linked by groups of atoms of type *A* whereas the linkage is in fact by two separate W–O–W linkages. Wells[3] states that chains involving the grouping *A* do not exist in tungsten oxides, and this would appear to be a reason for preferring the arrangement shown in Fig. 3 (hexagonal close-packed, added layer) to that shown in Fig. 4 (cubic close-packed added layer). However this cannot be the complete explanation because the grouping *A* does in fact exist in the phosphotungstate ion (see Fig. 3). While this difference may contribute, a more likely reason for preferring the arrangement in Fig. 3 to that in Fig. 4 would seem to be that the latter brings together the oxygen atoms, from adjacent outermost groups of six, which are attached to only one tungsten atom, and which therefore probably carry a resultant negative charge. In order therefore that this negative charge may be spread less unevenly over the surface of the ion, the structure indicated in Fig. 3 (which keeps these oxygen atoms apart) is preferred. This can, of course, be done without changing any of the distances between bonded atoms. This would explain why the mixture of cubic and hexagonal close-packing is adopted. (The central core must have tetrahedral symmetry and be *cubic* close-packed, because of the tetrahedral disposition of the phosphorus valencies.)



(*A*)

FIG. 3. *Diagram of the inter-connections between the oxygen and tungsten atoms in one quarter-section of* $(PW_{12}O_{40})^{3-}$.

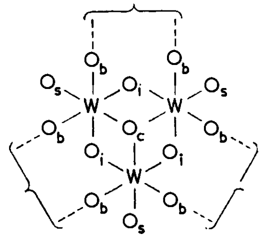
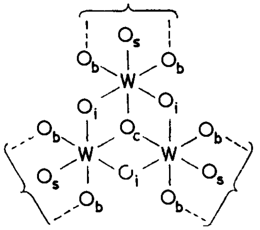


FIG. 4. *Diagram showing what the inter-connection between the oxygen and tungsten atoms would be if* $(PW_{12}O_{40})^{3-}$ *were a fully cubic close-packed structure.*



Another contributory reason to the preference for the arrangement shown in Fig. 3 may be that the oxygen atoms (O_s), which are attached to only one tungsten atom, behave as if they are bigger than the other oxygen atoms so that, if they were close to one another, there would be a serious increase of energy because of steric hindrance. In fact, this probably amounts, in part, to putting the first reason in other words since the larger size of these oxygen atoms is a consequence of the negative charge they carry.

Dimensions of the Ion.—The question mentioned earlier may now be asked: How satisfactory is it to visualise the structure of the phosphotungstate ion in terms of a close-packed array of equal spheres? Let us consider the core first. There are four separate distances which are listed in Table 1. (Bradley and Illingworth's data[1] are used.) These are all approximately equal, being within 3% of 2·72 Å. It is surprising to find the two different O_b–O_b distances so nearly equal. (Bradley and Illingworth list only one O_b–O_b distance.) Thus the face of the central core (which contains six atoms O_b round a central O_c atom) has only a three-fold axis of symmetry, this being all that is required by the symmetry of the core; nevertheless, it is very close to having six-fold symmetry which

[3] Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, 1945, p. 327.

it would have if the core were made up of spheres of exactly equal size. Hence it is undoubtedly an extremely good approximation to treat the core as made up of close-packed spheres, all of radius 1·36 Å. In the outer triangular groups of six atoms there are two O–O distances, which are listed in the second part of Table 1. So these, in themselves, behave as a group of equal spheres but the size (one to another) is a little bigger than those in the central core; though only by about 5%. The distances between the oxygen centres in the outer layer of six and those in the adjacent face of the core are given in the third section of Table 4. The first two distances are within about 4% of 2·72 Å, but the O_s–O_b distance is much greater (about 10%). The O_s atoms are linked to only one tungsten atom, and, as stated above, probably carry a negative charge. This may be, in part, the cause of the large O_s–O_b distance (but see later).

TABLE 1. *Interatomic distances in the* $(PW_{12}O_{40})^{3-}$ *ion.*[1]

	Atom pair	Distance between centres		Atom pair	Distance between centres
Central core	O_c–O_c	2·80	*Between core and outer groups*	O_i–O_c	2·65
	O_c–O_b	2·70		O_i–O_b	2·61
	O_b–O_b *	2·64		O_s–O_b	3·10
	O_b–O_b †	2·74	*Phosphorus to oxygen*	P–O_c	1·71
Outer groups	O_i–O_i	2·90	*Tungsten to oxygen*	W–O_c	2·29
	O_i–O_s	2·81		W–O_b	1·93
				W–O_i	1·97
				W–O_s	1·84

* Bonded to same tungsten atom; † bonded to different tungsten atoms.

In Table 2, the co-ordinates of the various types of atoms (phosphorus being placed at the origin) as determined by Bradley and Illingworth are listed (Keggin's results[4] are very similar). The calculated co-ordinates for spheres of radius R are listed in the third column, and corresponding numerical values for $R = 1{\cdot}36$ Å in the fourth. It will be seen that O_c, O_b, and O_i are close to their expected positions but that the O_s atoms and the tungsten atoms are further from the centre than would be expected. This is a consequence of the large W–O_c distance (Table 1). However, broadly speaking, Table 2 shows that the packing of the oxygen atoms is close to that to be expected for equal close-packed spheres.

TABLE 2. *Co-ordinates of atoms in the* $(PW_{12}O_{40})^{3-}$ *ion, observed and calculated.*

Atom	Obs. Co-ord. (typical)	Calc. Co-ord. (Radius R)	Calc. Co-ord. ($R = 1{\cdot}36$ Å)
P	(0,0,0)	(0,0,0)	(0,0,0)
W	(0·15, 2·495, 2·495)	$\left(\frac{R}{3\sqrt{2}}, \frac{7R}{3\sqrt{2}}, \frac{7R}{3\sqrt{2}}\right)$	(0·31, 2·25, 2·25)
O_c	(0·99, 0·99, 0·99)	$\left(\frac{R}{\sqrt{2}}, \frac{R}{\sqrt{2}}, \frac{R}{\sqrt{2}}\right)$	(0·96, 0·96, 0·96)
O_b	(0·97, −0·97, 2·84)	$\left(\frac{R}{\sqrt{2}}, \frac{-R}{\sqrt{2}}, \frac{3R}{\sqrt{2}}\right)$	(0·96, −0·96, 2·89)
O_i	(1·49, 1·49, 3·54)	$\left(\frac{5R}{3\sqrt{2}}, \frac{5R}{3\sqrt{2}}, \frac{11R}{3\sqrt{2}}\right)$	(1·60, 1·60, 3·53)
O_s	(−0·1, 3·79, 3·79)	$\left(-\frac{1}{3\sqrt{2}}, \frac{11R}{3\sqrt{2}}, \frac{11R}{3\sqrt{2}}\right)$	(−0·31, 3·53, 3·53)

How do the PO and WO distances in other compounds compare with the values 1·71 (for PO) and 1·84, 1·93 (two), 1·97 (two), and 2·29 Å (for WO) found in the phosphotungstate ion? In the HPO_4^{2-} ion in $GaHPO_4$ the PO distance is 1·54,[5] in the $H_2PO_4^-$ ion in

[4] Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75.

[5] Maclennan and Beevers, *Acta Cryst.*, 1955, **8**, 579.

KH_2PO_4 it is 1·54 also,[6] and those in the $P_2O_7^{4-}$ ion in ZrP_2O_7 are 1·52 and 1·56.[7] Therefore the PO distance is a little greater in the phosphotungstate ion. In the WO_4^{2-} ion the WO distance is [8] about 1·8 Å, so that again the distances are a little greater in the phosphotungstate (and one is 20% greater). The increase from 1·54 to 1·71 Å (Table 2) in the PO distance is about 10%, and that from 1·8 to about 1·95 Å in the WO distance is about 8%, so that one might say that the oxygen atoms behave uniformly as being 5—10% bigger in the phosphotungstate ion. The size of the MoO_4^{2-} ion is virtually the same (MoO, 1·83 Å) as that of the WO_4^{2-} ion,[9] so that it is not surprising that molybdenum can replace tungsten in the structure very easily.

As regards the replacement of phosphorus by silicon, the SiO distance in α-quartz [10] is 1·61 Å which corresponds to an OO distance of 2·6 Å which is close to, but again slightly less than, the separation in the phosphotungstate ion. Therefore it is to be expected (as far as size is concerned) that silicon would be able to replace phosphorus. With boron, it is difficult to know what value to assume as a probable BO distance in borotungstates and boromolybdates. In Me_2O,BF_3, in which boron is linked to four atoms (approximately tetrahedrally), the BO distance [11] is 1·50 ± 0·06, which is close to the PO distance in $H_2PO_4^{2-}$ and HPO_4^{-}. So again (as far as size is concerned) it is not surprising that boron can replace phosphorus.

In the arsenic and germanium compounds, however, the AsO and GeO distances are about 1/4 Å greater than the corresponding ones in the boron, silicon, and phosphorus compounds [12] As a result of this it must be supposed that, with these atoms, there will be some distortion of the close-packing; the central atoms of each face of the core (O_c in Fig. 3) will be forced outward from the centre, and, with them, the central three atoms (O_i) of each of the four outer triangular groups of six atoms. It seems, from the stability of the ions concerned, that this distortion can be accommodated, even though some slight modification of the interbond angles is involved; and certainly, from the model that has been described, there is no apparent reason why this small outward distortion should not be possible. It would be valuable to have data on this.

Why are no sulpho-, seleno- or telluro-tungstate or -molybdate ions of this formula known? It is difficult to believe that this is an effect of size because, surely, with one or other of the three atoms, the size would be satisfactory. The reason must therefore be that the valency of these Group VI elements is not suitable (see later).

Two further remarkable features of the structure of the phosphotungstate ion are the length of the WO_c bond (2·29 Å) and the shortness of the WO_s bond (1·84 Å). The electronic structure could be written with electron-pair bonds between the phosphorus atom and the four O_c atoms and between each tungsten and its six near neighbours. With this formula, the formal charges on the various atoms would be: P, +1; O_c, +2; W, 0; O_i, 0; O_b, 0; O_s, −1. This is a most unsatisfactory charge distribution as regards both the +2 on the four O_c atoms and the formal presence of +9 on the central five atoms ($P + 4O_c$). As an alternative, in a single electronic structure, one can make the W–O_c linkages one-electron bonds and the W–O_s linkages three-electron bonds; [13] the charges become P, +1; O_c, $+\frac{1}{2}$; W, 0; O_i, 0; O_c, 0; O_b, 0; O_s, $-\frac{1}{2}$. This is a more satisfactory formula. (Of course the same ***mean*** charge distribution could also be achieved by resonance between a multitude of forms.) In this formula, each oxygen and the phosphorus atom have an octet made up of four electrons of each spin, and every tungsten atom has a valency shell of 12 electrons, 6 of each spin, all shared. This also concentrates positive charge at

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[6] Bacon and Pease, *Proc. Roy. Soc.*, 1955, *A*, **230**, 359.
[7] Levi and Peyronel, *Z. Kryst.*, 1935, **92**, 190.
[8] Sillén and Nylander, *Arkiv Kemi, Min., Geol.*, 1943, **17**, *A*, No. 4.
[9] Donohue and Shand, *J. Amer. Chem. Soc.*, 1947, **69**, 222.
[10] Driel and Verweel, *Z. Kryst.*, 1936, **95**, 308.
[11] Bauer, Findlay, and Laubengayer, *J. Amer. Chem. Soc.*, 1945, **67**, 339.
[12] Sutton, " Tables of Interatomic Distances," *Chem. Soc. Spec. Publ. No.* 11, 1958.
[13] Linnett, *Nature*, 1960, **187**, 859; *J. Amer. Chem. Soc.*, 1961, in the press.

the centre (+3 on the central five atoms), and suggests that there is a tendency for negative charge to be on the outer oxygen atoms (O_s). In the silicotungstates there would be formally +2 (Si, 0) on the central five atoms, and in the borotungstates +1 (B, −1). However, if the central atom were from Group VI, the formal charge on the central five atoms would be +4, and it is possible that this high density of positive charge accounts for the non-existence of corresponding selenotungstates, etc. Therefore, the electronic formula suggested above does account for the observed W–O_c (long) and W–O_s (short) bond lengths. It also offers a reasonable explanation of the non-existence of Group VI compounds having this structure. The telluromolybdates adopt a structure having the formula $(TeMo_6O_{24})^{6-}$ in which the tellurium and molybdenum atoms are all surrounded by six oxygen atoms.[14] There are three types of oxygen atom: those linked to the tellurium and two molybdenum atoms (six O_α); those linked to two molybdenum atoms (six O_β); and those linked to only one molybdenum atom (twelve O_γ). If the TeO bonds are two-electron, the MoO_α one electron, the MoO_β two-electron, and the MoO_γ three-electron, then the formal charges are as follows: Te, 0; Mo 0; O_α, 0; O_β, 0; O_γ, $-\frac{1}{2}$. This is a most satisfactory charge distribution. It would be interesting to know the various interatomic distances in the $(TeMo_6O_{24})^{6-}$ ion, since the above formula would suggest that MoO_α should be about 2·3, MoO_β about 1·95, and MoO_γ about 1·85 Å. The tellurium atom in this structure can be replaced by iodine, which would have a formal charge of +1, molybdenum, and other metals. In all these the positive charge at the centre is not excessive, which it would be with these central atoms in an $(NM_{12}O_{40})^{n-}$ ion.

Structure of $H_3PW_{12}O_{40},29H_2O$.—Bradley and Illingworth's diagrams[1] present the atomic locations in crystals of this substance most clearly, but they tend to be somewhat misleading regarding bonding, and therefore this aspect of this structure will be discussed. For instance they refer to the ion $(H_3,29H_2O)^{3+}$. However, in their structure 12 of the water molecules in their group of 29 are not bound (or only very loosely so) to the other 17 (judged from interatomic distances given by them.) * It seems best to treat the 17 water molecules as made up of a group of 11 and six other separate water molecules which link the $(11H_2O)$ units to adjacent $(PO_{12}O_{40}{}^{3-})$ units. The $11H_2O$ unit is made up in the following way: There is a central oxygen (O_e') which is linked tetrahedrally to four other oxygen atoms, O_t' (O–O distance 2·91 Å). These four are linked to one another through six other oxygen atoms, O_e' (across the six edges of the tetrahedron). Again, the O–O distance is 2·91 Å. (The O–O distances given by Bradley and Illingworth do not quite agree with the atomic co-ordinates they list; I have accepted that the co-ordinates are correct.) This construction means that the outer six oxygen atoms are mutually along six cartesian directions from the central atom. These six are linked to six further water molecules, O_a' (O–O separation 2·95 Å). These form the group of $17H_2O$. The six O_a' are each close to oxygen atoms in $PW_{12}O_{40}{}^{3-}$ ions. With respect to the co-ordinate system of the $PW_{12}O_{40}{}^{3-}$ unit used in Table 2 there are six O_a' atoms at (5·33,0,0), (−5·33,0,0), (0,5·33,0) . . . (0,0,−5·33). Their distances from the O_b and O_i atoms are 2·84 and 2·77 Å, respectively. So, by this means, the $17H_2O$ units serve to bind the different $(PW_{12}O_{40})^{3-}$ units together. But, further, the O_a' atoms are not only linked to two O_b and two O_i atoms of one $(PW_{12}O_{40})^{3-}$ ion, but also to two O_s atoms of two other $(PW_{12}O_{40})^{3-}$ ions (one from each). The O_a'–O_s distances are 2·90 Å. This adds further binding between the phosphotungstate ions. Moreover, it seems that the attraction between O_a' and O_s atoms contributes to the displacement of the O_s atoms so that the O_s–O_b separations are unexpectedly long (see Table 1). It is interesting that the O_a' atom is close to two O_s, two O_i, two O_b, and one O_e' atom, only the last being the oxygen of a water molecule.

The remaining 12 water molecules of Bradley and Illingworth's group of 29 participate

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* These are Bradley and Illingworth's[1] 12 O_7 which are 2·92 Å from other O_7 atoms (though not of the same set drawn by them in their Fig. 6). Each O_7 is also 2·85 Å from one O_i of an adjacent $PW_{12}O_{40}{}^{3-}$ unit. They are much farther from any other members of the $(H_3,29H_2O)^{3+}$ group.

[14] Evans, *J. Amer. Chem. Soc.*, 1948, **70**, 1291.

in four six-membered rings. That is, three of the twelve, with a similar three from an adjacent $29H_2O$ set, form a slightly puckered but almost planar ring of six in which the O–O separations are 2·92 Å. Each oxygen atom of the six-membered ring is 2·90 Å from one O_i atom of a phosphotungstate ion. The six oxygen atoms in any given ring are linked to six different phosphotungstate ions, so that this provides further cross linking between the negative ions.

A tempting question is: Where are the hydrogen atoms and particularly the three H_3O^+ units (if there are such units)? It does not seem to the author that an answer can be given to this, though it appears improbable that the $3H^+$ are associated with the unit of 11 water molecules. It is more likely that they are associated with the O_s atoms, since these have a tendency to be negatively charged (see earlier).

It seems from the above discussion that the best formulation of the structure of this hydrated acid is not $(H_3,29H_2O)^{+3}(PW_{12}O_{40})^{-3}$ but either $3H^+(PW_{12}O_{40})^{-3}(17H_2O)$-$\{4[\frac{1}{2}(6H_2O)]\}$ or $3H^+(PW_{12}O_{40})^{-3}$ $\{(11H_2O),6H_2O\}$ $\{4[\frac{1}{2}(6H_2O)]\}$. These formulæ are perhaps unduly complex but they are less misleading than the first, and there seems to be some advantage in specifying the $11H_2O$ group in the formula.

Other Structures.—Keggin [4] determined the structure of the lower hydrate of phosphotungstic acid, probably $H_3PW_{12}O_{40},5H_2O$. He concluded that, in the cubic unit cell, there were anions at the corners, orientated similarly, and also at the cube-centres, orientated differently. The anions at the cube-centres "interlock" with four of those at the cube corners through the four groups of three projecting O_s atoms, the three on one anion "interlocking" with three on the other anion. There is a water molecule situated between them which contributes to the binding. An anion is also linked to the six anions, in the cartesian directions from it, *via* six water molecules which are close to two O_b and two O_i atoms on each anion. Thus each anion is hydrogen-bonded to ten water molecules, each water molecule being shared between two anions. (In considering the above description it is important to recognise that the corners and centres of the cubes are equivalent positions.)

Dawson [15] has determined the structure of the ion $(P_2W_{18}O_{62})^{6-}$ and has shown how closely it is related to the $PW_{12}O_{40}{}^{3-}$ anion. It is clear therefore that that structure can also be considered satisfactorily in terms of a close-packed arrangement of oxygen atoms. However Dawson could not, unfortunately, place the oxygen atoms precisely so that the details of the binding cannot be determined.

Another interesting anion is $(MnMo_9O_{32})^{6-}$ which is found in $(NH_4)_6MnMo_9O_{32},8H_2O$, and has a central manganese atom surrounded by nine molybdenum atoms; three of these molybdenum atoms are coplanar with the manganese atom, and three are in a plane on one side of the central plane and three in a plane on the other. The structure appears to involve a close-packing of the oxygen atoms, the manganese and molybdenum atoms occupying octahedral holes.[16] Fig. 5 shows the structure suggested for this ion. There are four layers of oxygen atoms which are arranged in a fully cubic close-packed manner. The two middle layers are shown in Fig. 5a; there is a manganese atom in the central octahedral hole and three molybdenum atoms in the other three octahedral holes. Two outer layers of seven oxygen atoms (six round a central seventh) are added in the manner shown in Fig. 5b; the three octahedral holes produced by each of these layers are occupied by molybdenum atoms. There are six sets of oxygen atoms: the six round the central Mn(O_c''), the six touching three of these in the central layers (O_i''), the outer six of the central layers (O_o''). In the outer layers there are the two at the centres of the hexagon (O_h''), the six which "touch" the O_o'' of the central layers (O_x'') and the remaining six which do not (O_y''). There are two sets of molybdenum atoms: the three in the central plane, Mo_i, and the outer six, Mo_o. A satisfactory single electronic formula can be written

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[15] Dawson, *Acta Cryst.*, 1953, **6**, 113.

[16] Waugh, Schoemaker, and Pauling, *Acta Cryst.*, 1954, **7**, 438.

for this ion in which the electrons are disposed as follows. Bonds: one-electron: MnO_c'', Mo_iO_c'', Mo_oO_c'', Mo_oO_h'': two-electron: Mo_iO_i'', Mo_oO_i''; three-electron: Mo_iO_o'', Mo_oO_y''; four-electron: Mo_oO_x''; unshared electrons: Mn: 3; O_c'', 4; O_i'', 4; O_o'', 5; O_x'', 4; O_y'', 5; O_h'', 5; Mo_c, and Mo_o, none. This places formal charges as follows: Mn, +1; O_o'', $-\frac{1}{2}$; O_y'', $-\frac{1}{2}$; O_h'', $-\frac{1}{2}$; O_c'', 0; O_i'', 0; O_x'', 0; Mo_i, 0; Mo_o, 0, all of which are entirely reasonable. This accounts for the charge of −6 on the ion and for its 259 valency-shell electrons. Waugh, Schoemaker, and Pauling[16] give the following bond orders: for the above one-electron bonds $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{2}$, and $\frac{2}{3}$, respectively; for the two-electron bonds, 1 for each; for the three-electron bonds, $1\frac{2}{3}$ for each; for the four-electron bond, $1\frac{2}{3}$. The correspondence is therefore fairly good. However, the orders given by Waugh, Schoemaker, and Pauling[16] would require a representation involving resonance between a multitude of structures. From a diagram of the bond orders it will be seen that the Mo_iO bonds which are directed mostly towards the central axis (MnO_h'') have low order (Mo_iO_c'' also) while those directed away have high order (Mo_iO_o''). The same is true for the outer molybdenum atoms, the three inwardly directed bonds being one-electron bonds and the outwardly directed bonds being of higher order (2, 1, and $1\frac{1}{2}$). This suggests that, in the actual structure, all the atoms will be somewhat further from the central axis than would be expected from " normal " radii. Unfortunately, the structure is not known with this detail. It is to be hoped that a more complete structure analysis may be possible; the length of the one-electron bonds would be expected to be about 2·3, the two-electron about 1·95, the three-electron 1·85, and the four-electron perhaps 1·75—1·8 Å. An interesting point is that this ion should be capable of showing optical activity (a ball model is extraordinarily like the section of a screw, having three sloping grooves running down the side; the screw can be right- or left-handed).

FIG. 5a. *Diagram showing two central layers of oxygen atoms in* $(MnMo_9O_{32})^{6-}$.

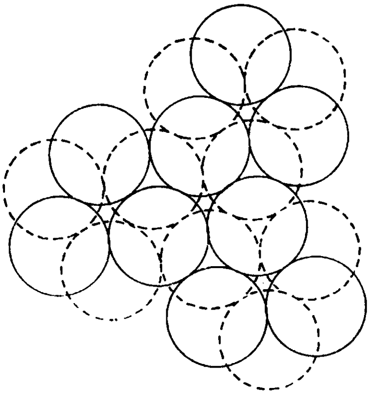
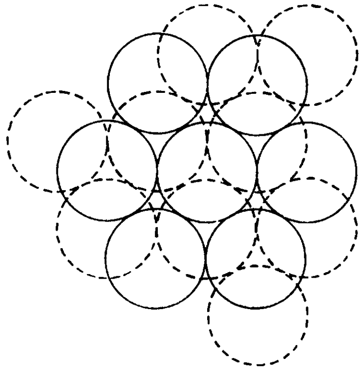


FIG. 5b. *Diagram showing one central and one outer layer of oxygen atoms in* $(MnMo_9O_{32})^{6-}$.



The above structure involves a greater unevenness of bond order than do such anions as phosphomolybdate, and this may be the reason why this is not so prevalent and formed by a variety of atoms. However, there is no high concentration of formal positive charge at the centre.

I thank M. J. Woolven for the challenging remark he made in a tutorial which stimulated my interest in the structure of these compounds and also to Messrs. Read, Ward, Williams, and Goodall for the lively assistance they gave me.

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[*Received, March 2nd,* 1961.]