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The Crystal Structure of Hydrated Potassium Tetraperoxyditungstate(VI), $\text{K}_2\text{W}_2\text{O}_{11} \cdot 4\text{H}_2\text{O}$

BY FREDERICK W. B. EINSTEIN AND BRUCE R. PENFOLD

Chemistry Department, University of Canterbury, Christchurch, New Zealand

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A three-dimensional crystal structure analysis of a hydrated potassium peroxytungstate has served to establish the composition of the compound as $\text{K}_2\text{W}_2\text{O}_{11} \cdot 4\text{H}_2\text{O}$, there being two formula units per unit cell in triclinic crystals of space group $P\bar{1}$. There are discrete tetraperoxyditungstate anions $[\text{W}_2\text{O}_{11} \cdot 2\text{H}_2\text{O}]^{2-}$ in which the two tungsten atoms are linked by a single non-linear oxygen bridge. Each tungsten atom is surrounded by a pentagonal bipyramidal arrangement of oxygen atoms, the equatorial planes of the two bipyramids being approximately at right angles. Each equatorial plane contains two laterally coordinated peroxide groups together with the shared bridge oxygen. Apical positions are occupied by a water molecule and a double-bonded oxygen. The tungsten atoms are displaced by 0.35 Å out of the equatorial plane towards the double-bonded oxygen atoms. Three-dimensional least-squares refinement led to mean interatomic distances $\text{W}-\text{O} = 1.93$, $\text{W}=\text{O} = 1.68$, $\text{W}-\text{H}_2\text{O} = 2.35$ and $\text{O}-\text{O}$ (peroxide) = 1.50 Å.

Introduction

The crystal structures of only four of the many known peroxy compounds of transition metals have so far been reported. These structures are of potassium tetraperoxychromate, containing the $[\text{CrO}_8]^{3-}$ anion (Stomberg & Brosset, 1960; Swalen & Ibers, 1962), triamminechromium diperoxide, $(\text{NH}_3)_3\text{CrO}_4$ (McLaren & Helmholz, 1959), chromium oxide diperoxide pyridine, $\text{CrO}_5 \cdot \text{Py}$ (Stomberg, 1962; Pedersen & Pedersen, 1963) and decamine- μ -peroxodicobalt pentanitrate, $[(\text{NH}_3)_{10}\text{Co}_2\text{O}_2](\text{NO}_3)_5$ (Vannerberg & Brosset, 1963).

A relatively stable class of salts, containing two peroxide groups per transition metal atom and for which the anion has been alternatively formulated as $[\text{HMO}_6]^-$ and $[\text{M}_2\text{O}_{11}]^{2-}$ ($\text{M} = \text{Mo}$ or W), has been the subject of much investigation (*e.g.* Jahr & Lothar, 1938; Jahr & Blanke, 1953; Souchay, 1949; Chauveau, Souchay & Tridot, 1955; Fergusson, Wilkins & Young, 1962). From salts of this class the potassium peroxy-

tungstate was chosen for structure analysis mainly because it was sufficiently stable for X-ray diffraction data to be collected at room temperature. It was realized also that the compound would provide a useful test of the ability of the X-ray diffraction method (with conventional techniques for intensity measurement) to define precisely an unknown oxygen skeleton in the presence of atoms of a third-row transition element. The results of this analysis were reported by us at the Sixth International Congress of the International Union of Crystallography in Rome (Einstein & Penfold, 1963).

Experimental

Following the method described by Fergusson *et al.* (1962) the salt was formed in cold aqueous solution from which colourless blade shaped crystals quickly separated. The crystals were triclinic and elongated along the *c* crystallographic axis.

Crystallographic data

Unit-cell parameters, assuming $\lambda=1.5418 \text{ \AA}$ for Cu $K\alpha$ radiation, are listed below both for a Delaunay reduced cell and also for the non-reduced cell on which the diffraction data were indexed and which is used in all subsequent discussion. Uncertainties are three times the estimated standard deviations.

(a) Reduced cell:

$$a=9.93 \pm 0.04, b=11.31 \pm 0.06, c=6.33 \pm 0.03 \text{ \AA}, \\ \alpha=100.0^\circ \pm 0.2^\circ, \beta=111.0^\circ \pm 0.2^\circ, \gamma=94.8^\circ \pm 0.2^\circ$$

(b) Non-reduced working cell:

$$a=9.68 \pm 0.04, b=11.31 \pm 0.06, c=6.33 \pm 0.03 \text{ \AA}, \\ \alpha=100.0^\circ \pm 0.2^\circ, \beta=73.3^\circ \pm 0.2^\circ, \gamma=101.5^\circ \pm 0.2^\circ.$$

Formula weight for $\text{K}_2\text{W}_2\text{O}_{11} \cdot 4\text{H}_2\text{O} = 694.1$, $U = 646.8 \text{ \AA}^3$, D_m (pycnometric) $= 3.58 \text{ g.cm}^{-3}$, $Z = 2$, $D_x = 3.56 \text{ g.cm}^{-3}$, $F(000) = 480$. The presence of a centre of symmetry, hence space group $P\bar{1}$, was strongly suggested by the results of statistical tests on zonal intensity data and was confirmed by the number and relative weights of inter-tungsten vectors in the Patterson function.

Reciprocal-lattice levels ($hk0$, 1, 2, 3) and ($0kl$) were recorded by the equi-inclination Weissenberg method using Cu $K\alpha$ radiation ($\mu = 398.3 \text{ cm}^{-1}$) and the levels ($h0l$) and (hkk) with the Buerger precession camera using Mo $K\alpha$ radiation ($\mu = 208.1 \text{ cm}^{-1}$). Within these levels and out to $\sin \theta/\lambda = 0.60$, intensities of 1721 independent reflexions were visually estimated, 223 were unobservably weak and a further 255 were not recorded.

The crystals, mounted in air, decomposed slowly on exposure to X-rays, and six different specimens were required to complete the data collection. Crystal dimensions ranged from 0.015 to 0.025 cm parallel to the c axis and from 0.003 to 0.010 cm at right angles to c . Absorption corrections were made to all Weissenberg data on the basis of a cylindrical shape and to precession data for spherical shape. Some specimens deviated considerably from ideal shape and the condition that the average angular fall-off of corrected intensities should be approximately the same for all crystals was used to aid choice of absorption parameters where the cylindrical or spherical approximations were particularly inadequate.

Structure determination*Heavy atom positions*

Approximate coordinates for the two tungsten and two potassium atoms in the asymmetric unit were derived from projections of sharpened Patterson functions on (001) and (100). With signs of Fourier coefficients determined by contributions from these four atoms only, successive electron density difference projections were evaluated. By this means preliminary refinement was made of all heavy atom coordinates

and approximate isotropic thermal parameters were assigned.

Oxygen atoms

Coordinates of oxygen atoms were sought from a three-dimensional electron-density function from which the contributions of heavy atoms had been subtracted. The coefficients used in evaluating this function were limited to those within a sphere of radius $\sin \theta/\lambda = 0.41$ at which distance (taking into account final average temperature factors) the oxygen/tungsten atomic scattering ratio is only $\frac{1}{20}$. Heavy atoms alone, based on final projection coordinates, gave an R index of 0.24 for this entire inner sphere.

Oxygen atoms were assigned to the 15 largest peaks on the first three-dimensional difference map and structure factors were recalculated. The next map led to the rejection of six oxygen atoms of the first set and their replacement by nine others, making 18 in all. It was not possible to reject any of these with confidence on the basis of the ensuing difference map.

So far no assumptions whatever had been made regarding the configuration of the peroxide anion although it had been apparent from the closeness of the tungsten atoms that it must be binuclear. At this stage the building of a model to include all 18 major peaks in the third difference map immediately indicated the general features of the anion. The retention of all necessary oxygen atoms meant that three of the 18 possibilities were in unacceptable

Table 1. *Atomic parameters*

	x	y	z	$B (\text{\AA}^2)$
W(1)	0.9731	0.7696	-0.1543	2.97
W(2)	0.6092	0.7955	0.1862	3.08
K(1)	0.1189	0.6309	0.2094	4.39
K(2)	0.2285	0.9926	0.2655	4.00
O(1)	0.882	0.615	-0.050	3.7
O(2)	1.032	0.609	-0.198	3.6
O(3)	1.130	0.809	-0.419	5.6
O(4)	1.023	0.902	-0.349	3.6
O(5)	1.052	0.834	0.046	4.5
O(6) (H ₂ O)	0.868	0.678	-0.442	3.9
O(7)	0.787	0.827	-0.038	3.6
O(1')	0.721	0.825	0.387	5.2
O(2')	0.564	0.822	0.487	4.5
O(3')	0.415	0.832	0.214	4.1
O(4')	0.509	0.831	-0.019	3.9
O(5')	0.581	0.640	0.141	3.9
O(6') (H ₂ O)	0.648	1.012	0.225	4.2
O(8) (H ₂ O)	0.638	0.389	0.168	5.4
O(9) (H ₂ O)	0.297	0.546	0.419	5.0
	0.150	0.190	0.150	
Spurious peaks	0.730	0.750	0.155	
	0.440	0.810	0.255	
	0.285	0.215	0.355	

Mean standard errors

	W	K	O
x	0.0013 \AA	0.0073 \AA	0.027 \AA
y	0.0011 \AA	0.0065 \AA	0.024 \AA
z	0.0018 \AA	0.0096 \AA	0.032 \AA
B	0.046 \AA ²	0.13 \AA ²	0.49 \AA ²

chemical environments and these were rejected. (In a further difference map following the least-squares refinement these peaks disappeared almost completely.) There remained 15 oxygen atoms of which 13 were associated with the binuclear anion.

Refinement of atomic parameters

Following the location of oxygen atoms, adjustments were made to the positional and isotropic thermal parameters of all atoms in the course of three further difference cycles. There were no indications of significant thermal anisotropy. At this stage the R index for all reflexions was 0.18 and for the inner sphere only it was 0.17. The refinement was then completed in the course of two three-dimensional least-squares cycles. The program used was ORFLS written by Busing, Martin & Levy (1962) and the computations were performed on the IBM 7090 installation at the Weapons Research Establishment, Salisbury, South Australia. All observed data were included in the refinement, and 81 parameters were adjusted, four for each atom and five scale factors. The ratio of observations to parameters was therefore about 21:1. The weighting scheme chosen was similar to that described by Hughes (1941) except that a number of intense low angle reflexions for which $|F_o - F_c|$ was greater than $0.3|F_c|$ were assigned nearly zero weights. These large errors could be attributed to the lack of precise corrections for absorption and they were clearly the cause of the relatively small decrease in R to its final figure of 0.159 for all observed reflexions. (The error of fit function $\sqrt{(\sum w(F_o - |F_c|)^2)/(m - n)}$ was finally 1.98.) The most obvious indications that the structure had refined were the considerable shifts in oxygen coordinates leading to striking improvement in the internal consistency of bond distances and angles. In the first cycle, mean and maximum shifts in individual oxygen coordinates were 0.08 Å and 0.22 Å respectively while corresponding values for the second cycle were 0.03 Å and 0.10 Å. Among the final oxygen thermal parameters, none is significantly higher than the mean value of 4.3 Å^2 .

In Table 1 are listed final parameters for all atoms together with mean values of the standard errors given by the inverse least-squares matrix. Inspection of the correlation matrix put out by ORFLS showed that the only strong parameter interactions were between individual scale factors and between some scale factors and tungsten thermal parameters. Among these interactions, the maximum value for the correlation coefficient ρ_{ij} was 0.66. Such interactions will not be expected to contribute to errors in positional parameters (Geller, 1961). Also listed in Table 1 are the only four spurious peaks in a final difference map which were greater than one third the mean height of a true oxygen peak. The highest of these peaks is less than half the mean oxygen height and all are in impossible chemical environments. In Table 2 are

listed about half of the observed and calculated structure amplitudes. All values of l are included in the selection and within each group of constant l there are listed reflexions with both low and high values of h and k . The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962), the Thomas, Fermi and Dirac statistical model being used for the tungsten atom, and the self-consistent field model for potassium (K^+) and oxygen. Anomalous dispersion corrections for the appropriate radiation were made for W and K, the actual scattering factor used being $f = \sqrt{\{(f_o + \Delta f')^2 + (\Delta f'')^2\}}$ (Templeton, 1955).

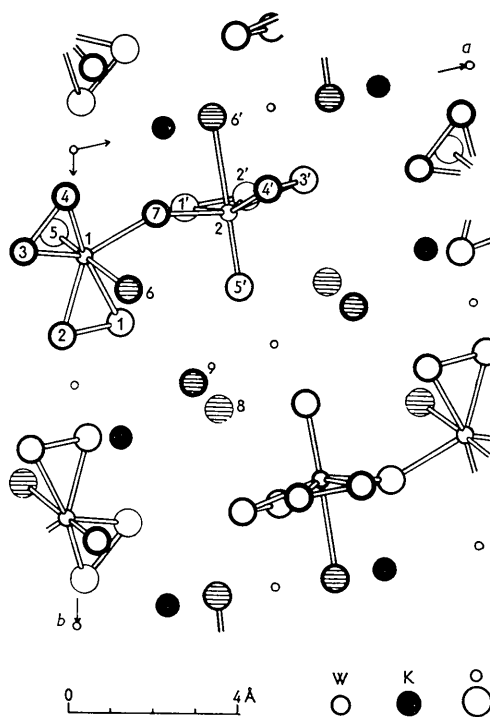


Fig. 1. The crystal structure viewed down the c axis. Shaded circles represent oxygen atoms from water molecules.

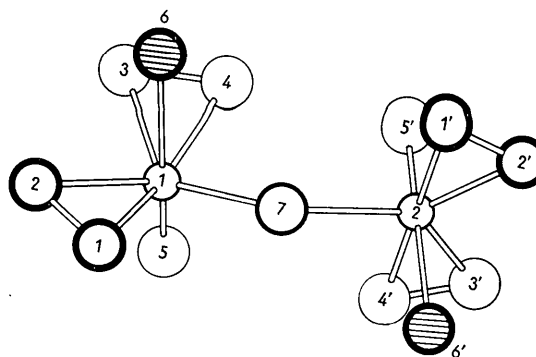


Fig. 2. The dihydrated tetraperoxyditungstate anion $[W_2O_{11}.2H_2O]^{2-}$. Large circles represent oxygen atoms, those from water molecules being shaded.

Discussion

As can be seen from the projection of the unit cell contents shown in Fig. 1, the main feature of the crystal structure is the existence of discrete binuclear anions which may be described as dihydrated tetra-peroxytungstate ions. To balance the double negative charge on each anion are two potassium ions and, in addition, there are two water molecules not associated with the anion. A view of a single anion is given in Fig. 2 and all interatomic distances and some angles within the ion are listed in Table 3. As an essential preliminary to a discussion of the features of this ion we shall consider the assignment of errors to individual distances and angles.

Table 3. Distances and angles within the hydrated peroxytungstate anion

W(1)-O(1)	1.93 Å	W(2)-O(1')	1.84 Å
W(1)-O(2)	1.96	W(2)-O(2')	1.81
W(1)-O(3)	1.96	W(2)-O(3')	1.96
W(1)-O(4)	2.00	W(2)-O(4')	1.96
W(1)-O(7)	1.94	W(2)-O(7)	1.91
W(1)-O(5)	1.66	W(2)-O(5')	1.71
W(1)-O(6)	2.33	W(2)-O(6')	2.38
O(1)-O(2)	1.50	O(1')-O(2')	1.46
O(3)-O(4)	1.54	O(3')-O(4')	1.50
∠ W(1)-O(7)-W(2) 139°			
∠ O(1)-W(1)-O(2)	45°	∠ O(1')-W(2)-O(2')	47°
O(3)-W(1)-O(4)	46	O(3')-W(2)-O(4')	45
O(5)-W(1)-O(1)	101	O(5')-W(2)-O(1')	102
O(5)-W(1)-O(2)	98	O(5')-W(2)-O(2')	101
O(5)-W(1)-O(3)	101	O(5')-W(2)-O(3')	102
O(5)-W(1)-O(4)	102	O(5')-W(2)-O(4')	100
O(5)-W(1)-O(7)	100	O(5')-W(2)-O(7)	99
O(6)-W(1)-O(1)	80	O(6')-W(2)-O(1')	81
O(6)-W(1)-O(2)	81	O(6')-W(2)-O(2')	82
O(6)-W(1)-O(3)	78	O(6')-W(2)-O(3')	77
O(6)-W(1)-O(4)	78	O(6')-W(2)-O(4')	77
O(6)-W(1)-O(7)	82	O(6')-W(2)-O(7)	79
O(2)-W(1)-O(3)	88	O(2')-W(2)-O(3')	86
O(1)-W(1)-O(7)	89	O(1')-W(2)-O(7)	87
O(4)-W(1)-O(7)	85	O(4')-W(2)-O(7)	87

Errors in distances and angles

Coordinate standard error indications from the inverse least-squares matrix will provide a useful lower limit but for a better indication we may turn to the internal consistency of the lengths of chemically equivalent bonds. There is no evidence that the tungsten atoms are nearer to one oxygen atom than to the other in any of the peroxide groups with which they are associated. It is also observed that the mean W-O (bridge) length is the same as the mean W-O (peroxy) length. We shall therefore regard the ten crystallographically distinct bonds linking tungsten to peroxy and bridge oxygen atoms as being of a single population. We find then that the standard error of an individual bond length is 0.056 Å while the mean length of 1.93 Å has a standard error of 0.02 Å.

The self-consistency approach is not appropriate for

the O-O bonds as there are not enough independent observations. Turning to the results of the inverse matrix we find that the mean standard error in an individual oxygen coordinate is 0.028 Å indicating a mean standard error of 0.04 Å in the length of an O-O bond and hence a standard error in the mean of four such bonds of about 0.025 Å. This will be an underestimate and we shall assign 0.030 Å as the standard error of the mean peroxide bond length which is 1.50 Å. The fact that the internal consistency of the four O-O lengths is much better than these figures would indicate is fortuitous. The standard error in an individual angle subtended at a tungsten atom is 2.6° from the treatment of Cruickshank & Robertson (1953).

The peroxytungstate anion

Linking the two tungsten atoms of the anion is a non-linear (139°) oxygen bridge. Each tungsten is 7-coordinate, being surrounded by a pentagonal bipyramidal arrangement of oxygen atoms. Each equatorial group is planar within limits of error. Equations of the least-squares planes through the pentagonal groups associated with W(1) and W(2) respectively are:

$$0.176x + 10.936y + 0.147z = 9.187$$

$$\text{and } 5.759x + 2.642y + 5.147z = 6.494$$

where the plane constants refer to the crystallographic axes and were determined by the method of Schomaker, Waser, Marsh & Bergman (1959). For the first plane, mean and maximum deviations are 0.018 Å and 0.027 Å while for the second plane the corresponding deviations are 0.032 Å and 0.048 Å. These two planes are approximately at right angles. Mean dimensions within them are shown in Fig. 3. Each coordina-

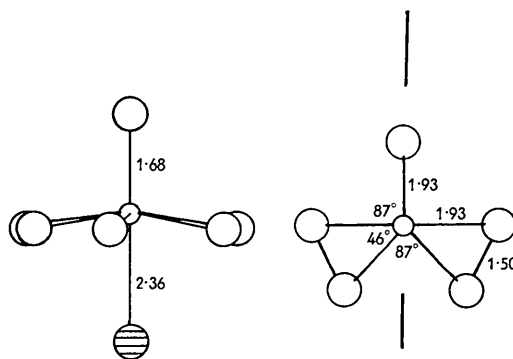


Fig. 3. The coordination group about tungsten viewed (a) parallel to the equatorial plane and (b) normal to the equatorial plane.

tion group possesses a mirror plane within limits of error. This plane is defined by the tungsten, the two apical oxygen atoms and the bridge oxygen, and it relates pairs of peroxide groups.

Each tungsten is displaced by 0.35 Å out of the equatorial plane of its surrounding bipyramid in the direction of the close apical oxygen atoms (O(5) and O(5')). This recalls a similar displacement of the tungsten atom in WO_3 from its position at the centre of an octahedral group of oxygen atoms, a feature related to the ferroelectric transition which this compound undergoes. (e.g. Megaw, 1957).

The observations that the bonds W(1)–O(5) and W(2)–O(5') are significantly shorter (1% level) than the mean W–O (peroxy) distance, and that bonds W(1)–O(6) and W(2)–O(6') are significantly longer (0.1% level) than this distance, establish that the two types of apical bond are chemically distinct from all other W–O bonds. We first assume, on the grounds of their extreme length that the long bonds are not covalencies but are loose electrostatic bonds to neutral water molecules. The short apical bonds must then possess a bond order considerably greater than one if O(5) and O(5') are not to carry a high proportion of the double negative charge on the anion (W is in oxidation state +6). As a negative charge would not be expected to lead to the observed bond shortening, it would appear that W(1)–O(5) and W(2)–O(5') do indeed possess considerable double-bond character and contain π components.

Of the various reported values for the lengths of W–O bonds only those in the structure of Li_2WO_4 (Zachariasen & Plettinger, 1961) are known with precision. The mean W–O distance reported in Li_2WO_4 is 1.79 Å (standard error 0.015 Å) which is about mid way between the short and the long bonds of the peroxytungstate. The bonds in the two compounds are however not directly comparable. Li_2WO_4 has the phenacite structure in which there are discrete tetrahedral $[\text{WO}_4]^{2-}$ ions packed intimately with Li^+ ions. The peroxide bond length does not appear to be known with sufficient precision in any of the transition metal compounds to justify a detailed discussion. Values reported range from 1.31 Å to 1.50 Å and individual differences are not significant. The value of 1.50 Å found in this analysis is in agreement with the value of 1.49 Å reported for hydrogen peroxide by Abrahams, Collin & Lipscomb (1951) and there is nothing to suggest that the oxygen atoms are not connected by normal peroxide linkages of bond order unity.

The coordination mode about tungsten in the peroxytungstate ion is strikingly similar to that found in $(\text{NH}_3)_3\text{CrO}_4$. In this mononuclear complex of Cr(IV) there is the same pentagonal bipyramidal arrangement, three nitrogens having replaced three oxygens. It would appear that the steric requirement of the peroxide groups largely determines the nature of the coordination.

It has been suggested by Tuck & Walters (1963) that in CrO_5 and $\text{CrO}_5 \cdot \text{Py}$ the linkage of Cr (in oxidation state +6) with peroxide groups is by donation of π electrons in the O–O bonding system into the vacant

Cr d orbitals and that the coordination about Cr is effectively tetrahedral. They have also suggested that this type of bonding may be of general occurrence where peroxide groups are coordinated to transition metals in high oxidation states. Such π -donation from O_2^{2-} does not seem an attractive postulate for the peroxytungstate ion however. The disposition of oxygen atoms and O_2^{2-} groups is far from tetrahedral and there is no evidence of a shortening of the O–O bonds which might be expected to accompany such donation (Tuck, 1963). Although no alternative simple bonding scheme is suggested here, we note that all $5d$ orbitals of tungsten are available for formation of hybrid bonding orbitals. As has been pointed out by Fergusson *et al.* (1962) any hybrid orbitals provided by the tungsten would have to possess high d character with possibly some admixture of f character so that the valence angles would be sufficiently small to overlap with σ -bonding electron pairs provided by each of the peroxide oxygen atoms.

Cation environment and bonding

The environments of the two independent potassium ions are similar. Atom K(1) has ten oxygen neighbours in the range 2.79 Å to 3.29 Å of which six are peroxide oxygen atoms, one is a double-bonded oxygen and three are from water molecules, only one of which is associated with the anion. The ten oxygen neighbours of atom K(2) are within the range 2.71 to 3.14 Å. Of these, seven are peroxide oxygen atoms, one is double-bonded, one is a bridge oxygen atom and one is from a water molecule attached to the anion.

There are many possibilities for hydrogen bonds involving water molecules of both types, as well as peroxide oxygen atoms. Up to eight bonds may be associated with each asymmetric unit. However, in view of the relatively low precision of oxygen coordinates, any proposed scheme in detail would be somewhat speculative. All that seems certain is that the two independent water molecules O(8) and O(9) are connected by a bond of length 2.81 Å and that O(9) is connected by a bond of length 2.71 Å to the atom O(6) of a water molecule attached to the anion. These are the only oxygen contacts under 2.9 Å which are made by the free water molecules. The angle between the bonds is 99°.

This structure analysis is of interest in that it has demonstrated the possibility of determining a large unknown oxygen skeleton in detail in the presence of atoms of the third transition series elements and with the minimum of chemical assumptions. This was achieved with intensity data based on the visual estimation of photographs at room temperature and making only approximate absorption corrections. Ibers & Snyder (1962) have discussed at some length the determination of the details of carbon ring geometry in the presence of second row transition metals (in their case rhodium), a comparable case. The quality

of their data and their method of refinement were very similar to ours. The precision of our oxygen coordinates appears, however, to be significantly greater than that of their carbon coordinates. This could be attributed to the greater completeness of our data (our ratio of observations to parameters is about twice as big as theirs) and the fact that the thermal vibrations of all the heavy atoms could be well represented by a single isotropic parameter for each.

We are grateful to Dr. C. J. Wilkins of this department who first drew our attention to this problem. All computations apart from the least-squares refinement were carried out on the IBM 1620 in the Mobil Computer Laboratory of the University of Canterbury. We have pleasure in acknowledging the excellent cooperation we have received from the laboratory director, Mr. B. A. M. Moon, and also from Mrs J.M. Lester. We are grateful to a number of suppliers of programs, particularly Dr. D. van der Helm of the Institute for Cancer Research, Philadelphia. The New Zealand Universities Research Committee supported the work with grants for equipment and computing time, and F. W. B. E. was the holder of a bursary from the Colonial Sugar Refining Company.

Note added in proof.— Since submission of this paper, Griffith (1963) has described molecular weight measurements and infrared and Raman spectroscopic studies on compounds containing both the tetraperoxydimolybdate and tetraperoxyditungstate anions. He has shown that this evidence supports a binuclear structure with a non-linear oxygen bridge, but reports the potassium salts as containing only three molecules of water of crystallization instead of the four molecules found in this structure analysis.

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