

The Crystal Structure of Potassium μ -Carbonato-octaoxohexaperoxtetratungstate(VI)-6-water, $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$, a New Type of Polytungstate

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The crystal structure of the title compound has been determined from single-crystal X-ray diffractometer data. $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$ crystallizes, as colourless needles, in space group $P2_1/n$ with $a=18.904(10)$, $b=13.193(3)$, $c=10.538(4)$ Å, $\beta=94.92(4)^\circ$ and $Z=4$. Full-matrix least-squares refinement of 361 structural parameters gave $R_F=0.045$ for 2108 observed [$I > 3\sigma(I)$] reflexions. The anion is a new type of polytungstate, viz. a tetratungstate with the four tungsten atoms forming a slightly distorted parallelogram, stabilized by a bidentate carbonate ligand bridging two *trans* tungsten atoms. The lengths of the sides of the tungsten parallelogram are 3.27 and 4.08 Å, respectively, corresponding to edge- and corner-sharing polyhedra. The largest deviation of the tungsten atoms from the best plane through them is 0.08 Å. All four tungsten atoms are pentagonal-bipyramidally coordinated with an unshared double-bonded oxygen atom in one apical position and a shared oxygen atom in the other. Two of the tungsten atoms are each coordinated by one peroxo group while the two other tungsten atoms are each coordinated by two peroxo groups; the peroxo groups form part of the pentagonal equatorial planes. The tungsten atoms are displaced 0.27–0.31 Å from the respective equatorial plane in the direction of the double-bonded oxygen atoms. The anion has approximately C_2 symmetry. The structure is further stabilized by extensive hydrogen bonding.

Average bond distances are: W–O 1.70(4), W–O_{apical} 2.21(3), W–O_{peroxo} 1.95(5), W–O 1.98(3), (O–O)_{peroxo} 1.48(2) and C–O 1.28(3) Å.

Polymolybdates and polytungstates are numerous and of great complexity. Those of similar formula-type often have different structures; often the structure depends on the cation. An extensive investigation at this department of peroxomolybdates crystallizing from solution at different pH and different peroxide: molybdenum ratios has shown this system to be no less complex than the molybdate system. Peroxomono-, di-, tri-, tetra-, penta-, hepta-, octa- and decamolybdates have been characterized. The situation might be expected to be equally complex among the peroxotungstates.

While peroxo compounds of both chromium and molybdenum have been investigated rather extensively by X-ray crystallographic methods (see, e.g., Refs. 1–12) only few structural studies have been performed on peroxotungstates.^{13–15} Preparative and structural studies on peroxotungstates have, therefore, also begun at this department. The first system

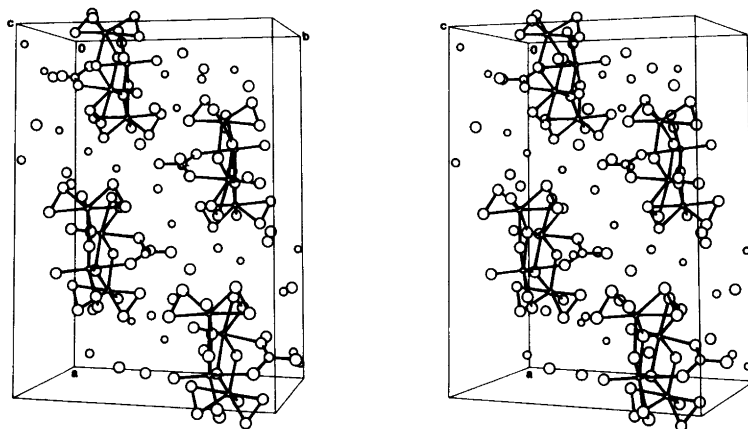


Fig. 1. Stereoscopic drawing of the unit cell of $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$, omitting the hydrogen atoms.

studied was $K^+ - WO_4^{2-} - C_2O_4^{2-} - H_2O_2$, and the structure of $K_2[WO(O_2)_2(C_2O_4)]$ has recently been determined.¹⁵ Crystals of this compound are formed easily in a wide concentration and pH range. It was noticed that the crystals, while in contact with their mother liquor at 5 °C for several days, changed into other products. Of these the first crystalline one was the very unstable, explosive, light-yellow $K_2[W(O_2)_4]$. Ultimately, a considerable amount of colourless, prismatic (needles), rather stable crystals of the title compound appeared at pH 9. The compound contained no oxalate but peroxide and, as shown by the structure investigation, unexpectedly, carbonate. Oxalate might have been oxidized to carbonate by peroxide, catalytically or by the intermediate $K_2[W(O_2)_4]$, or carbonate might have been present as impurities. Since the peroxide content indicated a new compound it was thought worthwhile to perform a structural investigation.

EXPERIMENTAL

Preparation. Crystals used for the X-ray work were obtained in the manner described in the preceding section. The compound is synthesized in a more straight-forward way by mixing solutions of 0.82 g K_2WO_4 in 20 ml H_2O and 0.35 g K_2CO_3 in 10 ml H_2O and then adding 2.5 ml 30 % H_2O_2 and maintaining the resulting solution at 5 °C. When crystals appeared pH was 10. The amount of peroxide was determined by permanganate titration as well as by iodometric titration (Found: O_2^{2-} 13.1. Calc. for $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$: 13.17).

X-Ray method. Intensity data were collected at 18 °C for $3.5^\circ \leq 2\theta \leq 50^\circ$ using a SYNTEX P2₁ X-ray diffractometer (graphite-monochromated $MoK\alpha$ radiation, crystal size $0.05 \times 0.09 \times 0.10$ mm, $\theta - 2\theta$ scan method, 2θ scan speed $3.5 - 29.3^\circ/\text{min}$). Integrated intensity values were obtained with the Lehmann-Larsen profile analysis method.¹⁶ Two test reflexions (020 and 511) showed only a minor drop in intensity during the collection of the data. A total of 4847 independent reflexions were measured and 2108 of these, having $I \geq 3\sigma(I)$, were used in the subsequent calculations. The intensities were corrected for Lorentz, polarization and absorption effects. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters for $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$.

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Atom	x	y	z	B_{eq}
W1	0.07658(6)	0.25019(8)	0.0750(1)	1.85(3)
W2	0.23997(7)	0.23725(9)	-0.0031(1)	2.17(3)
W3	0.16368(6)	0.23865(9)	0.3485(1)	1.63(3)
W4	-0.00053(7)	0.22789(9)	0.4220(1)	2.14(3)
K1	0.2843(5)	-0.0033(5)	0.2922(8)	3.8(2)
K2	0.3726(5)	0.0093(6)	-0.0466(10)	4.7(3)
K3	0.0518(5)	-0.0039(7)	0.8708(9)	4.4(3)
K4	0.1135(5)	-0.0184(6)	0.4977(8)	3.9(2)
K5	0.3950(4)	0.2476(5)	0.2775(7)	3.0(2)
K6	0.3470(5)	0.2111(7)	0.6482(8)	4.1(2)
O1	-0.025(1)	0.210(2)	0.063(2)	2.4(5)
O2	0.004(1)	0.198(2)	-0.059(2)	3.4(6)
O3	0.138(1)	0.229(2)	-0.063(2)	2.3(5)
O4	0.176(1)	0.253(1)	0.162(2)	2.1(5)
O5	0.066(1)	0.250(1)	0.257(2)	1.4(4)
O6	0.084(1)	0.086(2)	0.099(2)	2.1(5)
O7	0.067(1)	0.380(2)	0.055(2)	2.7(6)
O8	0.269(1)	0.224(2)	-0.145(2)	4.1(7)
O9	0.241(2)	0.091(2)	0.044(4)	7.0(7)
O10	0.303(2)	0.151(2)	0.097(3)	4.4(8)
O11	0.293(2)	0.349(2)	0.070(3)	5.0(8)
O12	0.228(2)	0.390(2)	-0.004(4)	7.0(8)
O13	0.264(1)	0.198(2)	0.356(2)	3.2(6)
O14	0.227(2)	0.177(2)	0.475(2)	4.6(8)
O15	0.098(1)	0.204(2)	0.482(2)	3.2(7)
O16	0.149(1)	0.081(1)	0.289(2)	2.4(6)
O17	0.176(1)	0.361(2)	0.389(2)	2.6(6)
O18	-0.035(1)	0.213(2)	0.569(2)	3.9(7)
O19	-0.004(1)	0.086(2)	0.371(2)	3.5(7)
O20	-0.065(2)	0.148(2)	0.317(2)	3.9(7)
O21	-0.053(1)	0.342(2)	0.355(3)	3.8(8)
O22	0.011(2)	0.377(2)	0.430(4)	7.0(8)
O23	0.119(2)	-0.058(2)	0.188(3)	7.0(8)
C	0.122(2)	0.038(2)	0.192(3)	2.3(8)
Ow1	0.272(2)	0.012(3)	0.730(3)	8.0(8)
Ow2	0.446(2)	0.037(3)	0.221(4)	9.0(8)
Ow3	0.408(2)	0.081(2)	0.495(4)	7.0(8)
Ow4	0.825(2)	0.095(3)	0.053(4)	9.0(8)
Ow5	0.136(2)	0.116(2)	0.713(4)	6.0(8)
Ow6	0.584(3)	0.126(3)	0.229(4)	9.0(8)

CRYSTAL DATA

$K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$ F.W.=1458.10. Space group $P2_1/n$ (No. 14; non-standard setting). $a=18.904(10)$ Å, $b=13.193(3)$ Å, $c=10.538(4)$ Å, $\beta=94.92(4)^\circ$, $V=2619(2)$ Å³, $Z=4$, $D_x=3.699$ g cm⁻³, $\mu(MoK\alpha)=19.6$ mm⁻¹.

STRUCTURE DETERMINATION

The four tungsten positions were derived from the Patterson function (the multi-solution programme MULTAN¹⁷ could not be applied successfully). All other non-hydrogen atoms were located in a series of electron density maps. Block-diagonal least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms and application of an empirical method for correcting diffractometer data for absorption effects due to Walker and Stuart,¹⁸ led to an *R*-value of 0.063 (0.071 before absorption correction) ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$). Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms reduced the *R*-value to 0.045 for all observed reflexions. The scattering factors for W, K, O and C were taken from Ref. 19. The hydrogen atoms could not be located. Weights were used according to $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$ with $a=200$, $c=0.0005$ and $d=0$.²⁰ The final electron density difference map showed a maximum peak height of 1.9 e/Å³. Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Ref. 21.

RESULTS AND DISCUSSION

Positional parameters and B_{eq} are listed in Table 1 and distances and angles within the anion in Table 2. Fig. 1 shows the positions of the non-hydrogen atoms in the unit cell and Fig. 2 the complex anion.

The investigation has shown the existence of a hexaperoxotetrate(VI), stabilized by a bridging carbonato group, with the formula $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$. The crystals

Table 2a. Bond distances (Å) within the $[W_4O_8(O_2)_6(CO_3)]^{6-}$ anion. (W(1), W(2), O(4), O(1)–O(3) and O(6)–O(12) are related to W(3), W(4), O(5) and O(13)–O(22) in that order by an approximate two-fold axis almost parallel to *b* through the center of the anion. The first five oxygen atoms within each group are the equatorial oxygen atoms and the last two the apical oxygen atoms.

W(1)–O(1)	1.99(2)	W(3)–O(13)	1.96(2)
W(1)–O(2)	2.00(2)	W(3)–O(14)	1.90(3)
W(1)–O(3)	1.95(2)	W(3)–O(15)	2.01(2)
W(1)–O(4)	2.02(2)	W(3)–O(5)	2.02(2)
W(1)–O(5)	1.96(2)	W(3)–O(4)	2.00(2)
W(1)–O(6)	2.18(2)	W(3)–O(16)	2.18(2)
W(1)–O(7)	1.73(2)	W(3)–O(17)	1.68(2)
W(2)–O(3)	1.97(2)	W(4)–O(15)	1.94(2)
W(2)–O(9)	1.99(3)	W(4)–O(19)	1.94(2)
W(2)–O(10)	1.89(3)	W(4)–O(20)	1.90(3)
W(2)–O(11)	1.91(3)	W(4)–O(21)	1.91(3)
W(2)–O(12)	2.03(3)	W(4)–O(22)	1.98(3)
W(2)–O(4)	2.21(2)	W(4)–O(5)	2.25(2)
W(2)–O(8)	1.64(3)	W(4)–O(18)	1.74(3)
O(1)–O(2)	1.45(3)	O(13)–O(14)	1.50(4)
O(9)–O(10)	1.47(4)	O(19)–O(20)	1.48(4)
O(11)–O(12)	1.51(5)	O(21)–O(22)	1.46(5)
C–O(6)	1.31(4)	C–O(16)	1.24(4)
C–O(23)	1.28(3)		

Table 2b. Bond angles ($^\circ$) in $[W_4O_8(O_2)_6(CO_3)]^{6-}$.

O(1)–W(1)–O(2)	42.7(9)	O(13)–W(3)–O(14)	45.7(11)
O(1)–W(1)–O(5)	83.1(8)	O(13)–W(3)–O(4)	82.8(9)
O(1)–W(1)–O(6)	78.5(8)	O(13)–W(3)–O(16)	81.5(8)
O(1)–W(1)–O(7)	99.2(10)	O(13)–W(3)–O(17)	98.1(9)
O(2)–W(1)–O(3)	80.7(9)	O(14)–W(3)–O(15)	78.8(11)
O(2)–W(1)–O(6)	77.2(8)	O(14)–W(3)–O(16)	81.7(10)
O(2)–W(1)–O(7)	101.1(10)	O(14)–W(3)–O(17)	99.5(11)
O(3)–W(1)–O(4)	75.6(8)	O(15)–W(3)–O(5)	75.8(8)
O(3)–W(1)–O(6)	84.5(8)	O(15)–W(3)–O(16)	85.0(8)
O(3)–W(1)–O(7)	96.8(10)	O(15)–W(3)–O(17)	96.7(10)
O(4)–W(1)–O(5)	74.0(8)	O(5)–W(3)–O(4)	72.9(7)
O(4)–W(1)–O(6)	85.1(7)	O(5)–W(3)–O(16)	80.7(7)
O(4)–W(1)–O(7)	97.1(10)	O(5)–W(3)–O(17)	98.9(8)
O(5)–W(1)–O(6)	83.8(7)	O(4)–W(3)–O(16)	80.4(8)
O(5)–W(1)–O(7)	96.0(8)	O(4)–W(3)–O(17)	97.7(10)
O(6)–W(1)–O(7)	177.7(10)	O(16)–W(3)–O(17)	178.0(10)
O(3)–W(2)–O(9)	90.8(12)	O(15)–W(4)–O(19)	87.0(10)
O(3)–W(2)–O(12)	87.0(13)	O(15)–W(4)–O(22)	92.6(13)
O(3)–W(2)–O(4)	71.1(7)	O(15)–W(4)–O(5)	72.0(9)
O(3)–W(2)–O(8)	95.2(9)	O(15)–W(4)–O(18)	96.4(11)
O(9)–W(2)–O(10)	44.6(13)	O(19)–W(4)–O(20)	45.3(11)
O(9)–W(2)–O(4)	83.8(12)	O(19)–W(4)–O(5)	85.4(8)
O(9)–W(2)–O(8)	97.2(15)	O(19)–W(4)–O(18)	97.2(11)
O(10)–W(2)–O(11)	87.3(12)	O(20)–W(4)–O(21)	86.5(11)
O(10)–W(2)–O(4)	88.6(10)	O(20)–W(4)–O(5)	89.8(9)
O(10)–W(2)–O(8)	101.8(13)	O(20)–W(4)–O(18)	100.4(11)
O(11)–W(2)–O(12)	45.0(14)	O(21)–W(4)–O(22)	44.0(14)
O(11)–W(2)–O(4)	85.0(12)	O(21)–W(4)–O(5)	85.3(9)
O(11)–W(2)–O(8)	104.3(14)	O(21)–W(4)–O(18)	101.5(12)
O(12)–W(2)–O(4)	80.8(12)	O(22)–W(4)–O(5)	80.7(13)
O(12)–W(2)–O(8)	98.5(14)	O(22)–W(4)–O(18)	97.2(15)
O(4)–W(2)–O(8)	166.3(9)	O(5)–W(4)–O(18)	168.0(9)
O(6)–C–O(23)	116.2(28)	O(16)–C–O(23)	119.4(28)
O(6)–C–O(16)	123.4(23)		

are composed of potassium ions, μ -carbonatooctaohexaperoxo-tungstate(VI) ions and water of crystallization. The four tungsten atoms and two of the six potassium ions in the asymmetric unit are situated near $y = \frac{1}{2}$, and the four remaining potassium ions near $y = 0$.

Each anion is built about a slightly bent parallelogram of four tungsten atoms and can be considered to be composed of two $WO_5(O_2)$ units, two $WO_3(O_2)_2$ units and a bridging CO_3^{2-} group. The monoperoxo- and diperoxo-tungstate units have pentagonal-bipyramidal geometry with the peroxo group(s) in the equatorial planes. Each $WO_5(O_2)$ group shares two neighbouring, equatorial edges with one $WO_3(O_2)_2$ group and the other $WO_5(O_2)$ group and a corner with the other $WO_3(O_2)_2$ group. The $WO_5(O_2)$ groups are further connected by a bridging carbonato ligand, two oxygen atoms of which occupy one apical position in each $WO_5(O_2)$ group. The anion has approximately C_2 symmetry with the twofold axis through the uncoordinated carbonato oxygen atom, the carbon atom and the midpoint of the tungsten parallelogram. The two $WO_3(O_2)_2$ groups are related by the approximate twofold axis as are the $WO_5(O_2)$ groups.

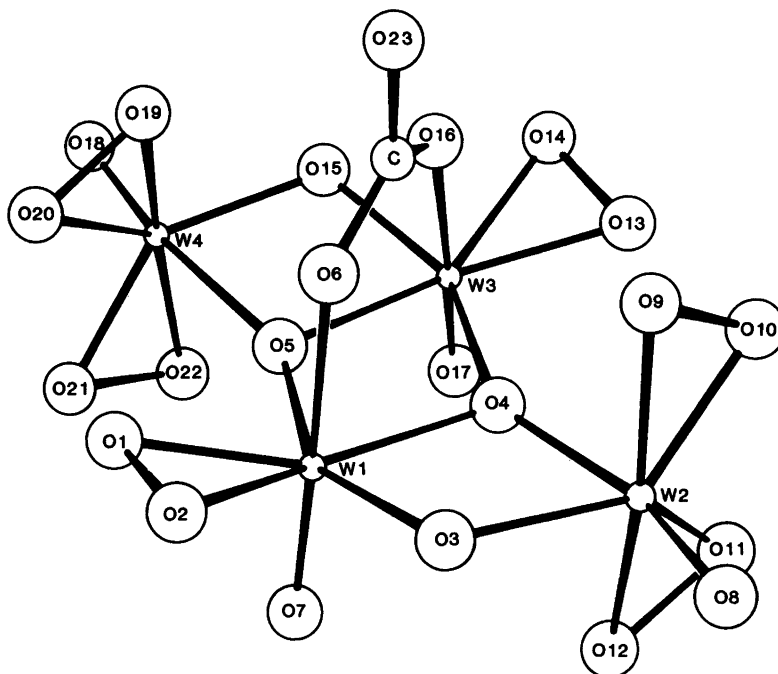


Fig. 2. The anion $[W_4O_8(O_2)_6(CO_3)]^{6-}$. An approximate twofold axis runs through O(23), C and the midpoint of the tungsten parallelogram.

Only few tetratungstates(VI) have been reported hitherto, *viz.* $W_4O_{16}^{8-}$ in $Li_{14}(WO_4)_3W_4O_{16} \cdot 4H_2O$,²² $Ag_8W_4O_{16}$,²³ and $Ag_{26}I_{18}W_4O_{16}$, while the tetratungstate complexes $[W_4O_8Cl_8(H_2O)_4]^{2-}$ and $[W_4O_8(NCS)_{12}]^{6-}$ contain both tungsten(V) and tungsten(VI) atoms.^{25,26} The only peroxotetrametallate reported hitherto is $K_4[Mo_4O_{12}(O_2)_2] \cdot 9K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$ is, therefore, not only a new type of transition metal peroxo compound but also a new type of tungstate(VI).

The opposite sides of the tungsten parallelogram are 3.268 and 3.266 Å, and 4.062 and 4.089 Å, respectively. The tungsten atoms are situated 0.08 Å from their mean plane, two above and two below in such a way that the parallelogram can be described as being bent 2.7° about its shorter diagonal [W(1)⋯W(3); 3.198(2) Å].

The deviations of the ligand atoms from their respective pentagonal equatorial plane, which they define, are all less than 0.047 Å and the r.m.s. deviation is 0.031 Å. The tungsten atoms W(1)–W(4) are displaced 0.273, 0.306, 0.281 and 0.279 Å from the respective pentagonal equatorial plane towards the apical terminal oxygen atoms. This is slightly less than the displacements 0.358 Å, observed in $K_2[WO(O_2)_2(C_2O_4)]$,¹⁵ and 0.35 Å found in $K_2[O\{WO(O_2)_2(H_2O)\}_2] \cdot 2H_2O$.¹³ For further comparison, see the compilation of observed displacements of the metal atoms from the equatorial planes in peroxometallates given in Table V in Ref. 27. The equatorial planes in the $WO_5(O_2)$ groups form an angle of 27° with each other and 76–90° with those in the $WO_3(O_2)_2$ groups, which in turn form an angle of 11° with each other.

It has been observed in the two peroxomolybdates $(NH_4)_4[Mo_3O_7(O_2)_4] \cdot 2H_2O$,¹¹ and $K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$,²⁸ that one of the building units can be considered to be the tetraperoxodimolybdate ion $[O\{MoO(O_2)_2(H_2O)\}_2]^{2-}$, whose structure was determined by

the author.⁵ In $K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$ the corresponding tungsten analogue $[O\{WO(O_2)_2(H_2O)\}_2]^{2-}$ is, however, not encountered. Instead, the complex can be thought of as two edge-sharing $W_2O_6(O_2)_3$ units, related by an approximate twofold axis, and further coupled together by a bidentate carbonate bridging ligand.

The average W=O bond length is 1.70(4) Å (the r.m.s. deviation is given in parenthesis) and is comparable to W=O distances found in other polytungstates, where mean W=O bond lengths have been observed in the range 1.69 to 1.74 Å (see, e.g., Table 4 in Ref. 29), as well as in peroxotungstates; in $K_2[WO(O_2)_2(C_2O_4)]$ the W=O bond length is 1.716(7) Å,¹⁵ and in $K_2[O\{WO(O_2)_2(H_2O)\}_2] \cdot 2H_2O$ the mean W=O distance is 1.68(3) Å.¹³

The W–O_{apical} bonds *trans* to the W=O_{apical} bonds are considerably elongated, the mean value being 2.21(3) Å, comparable to the value 2.245(6) Å observed in $K_2[WO(O_2)_2(C_2O_4)]$,¹⁵ and to values between 2.19 and 2.34 Å found in polytungstates (Table 4, Ref. 29). This type of bond-weakening has been observed in numerous peroxometallates. With a water molecule *trans* to W=O the bond weakening is further enhanced as exemplified by $[O\{WO(O_2)_2(H_2O)\}_2]^{2-}$ (2.36 Å),¹³ and $[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]^{10-}$ (2.48 and 2.55 Å).³⁰ A completely missing atom *trans* to the double-bonded oxygen atom, thus resulting in pentagonal-pyramidal six-coordination, has not been observed in peroxotungstates. It was, however, observed for the first time for a peroxochromate, *viz.* $[CrO(O_2)_2(C_5H_5N)]$.^{31,32} Recently, the author has also shown the existence of a transition from six- to seven-coordination among peroxovanadates (see the discussion in Ref. 33).^{33–37}

Despite the large difference in the W=O_{apical} and W–O_{apical} bond distances, mean values being 1.70 and 2.21 Å, respectively, the mean distances from these apical atoms to the equatorial planes are, however, similar, *viz.* 1.98(3) and 1.90(2) Å, respectively. The slightly longer distances from the double-bonded oxygen atom to the equatorial plane might be a consequence of the larger electron density of the double bond. The opinion put forward by Kepert³⁸ that the displacement of the metal atoms in polymetallates are due to metal-metal repulsions does not seem convincing since, among other things, this type of displacement occurs in a wide variety of mononuclear complexes.

The W–O_{equatorial} and W–O_{peroxo} (also equatorial) bond lengths, 1.94(2)–2.02(2) and 1.89(3)–2.03(2) Å, respectively, are comparable to single bond distances observed in polytungstates (mean values range between 1.92 and 1.96 Å according to Table 5 in Ref. 29) as well as in peroxotungstates; 1.928(6)–1.968(7) Å was observed in $K_2[WO(O_2)_2(C_2O_4)]$,¹⁵ and an average value of 1.93(2) Å in $K_2[O\{WO(O_2)_2(H_2O)\}_2] \cdot 2H_2O$.¹³ Among the W–O_{peroxo} bonds the W–O_{cis} bond lengths, 1.89(3)–1.91(3) Å, seem to be slightly shorter than the W–O_{trans} bond lengths, 1.94(2)–2.03(2) Å.

The mean O–O distance is 1.48(2) Å and compares well with the mean distances 1.50(1) and 1.50(3) Å found in $K_2[WO(O_2)_2(C_2O_4)]$,¹⁵ and $K_2[O\{WO(O_2)_2(H_2O)\}_2] \cdot 2H_2O$,¹³ respectively.

In the carbonato group the mean C–O bond length is 1.28(3) Å, which is close to C–O distances observed in other carbonates.³⁹ The carbonato group is planar within the experimental errors, the r.m.s. deviation of the atoms from the plane which they define being 0.03 Å. The tungsten atoms W(1) and W(3) are situated near the extended plane defined by the carbonato group (less than 0.08 Å).

$K_6[W_4O_8(O_2)_6(CO_3)] \cdot 6H_2O$, like $(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}] \cdot 16H_2O$,⁴⁰ is a rare example of a peroxopolymetallate with both monoperoxo- and diperoxometallate units.

Supplementary Material. Lists of structure factors, anisotropic thermal parameters and water and potassium environment are available from the author.

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