

# The Crystal Structures of $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ and $[\text{NBu}^n_4]_2[\text{W}_4\text{O}_6(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]$ and Their Use as Catalytic Oxidants†

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The new trinuclear heteropolyperoxo complexes  $[\text{NMe}_4]_2[(\text{RPO}_3)\{\text{MO}(\text{O}_2)_2\}_2\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  ( $\text{R} = \text{Ph}$ ,  $\text{M} = \text{Mo}$  **1** or  $\text{W}$  **2**) have been isolated and the crystal structure of the molybdenum complex is reported. A series of analogous molybdenum complexes ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Bu}^n$  or  $\text{Bu}^t$ ;  $\text{M} = \text{Mo}$ ) have also been synthesised and characterised. The use of these compounds as catalysts for the epoxidation of alkenes, oxidation of alcohols and of tertiary amines with hydrogen peroxide as cooxidant has been studied, and complex **2** is shown to be particularly effective for such oxidations. The crystal structure of the new tetranuclear isopolyperoxo species  $[\text{NBu}^n_4]_2[\text{W}_4\text{O}_6(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]$  **3** is also reported and its properties as a catalyst for alkene epoxidation with hydrogen peroxide as cooxidant studied.

The study of the specific oxidation of organic substrates catalysed by polyoxo<sup>2</sup> or polyperoxo complexes<sup>1,3-5</sup> is of current interest, especially because of the widespread use of the environmentally acceptable hydrogen peroxide as cooxidant in such systems. In earlier papers of this series<sup>1,3</sup> we have shown that analogues of 'Venturello's compound',  $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ ,<sup>6</sup> such as the arsenic species  $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{AsO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ , are effective catalysts for alkene epoxidation or alcohol oxidation with  $\text{H}_2\text{O}_2$  as cooxidant in a biphasic benzene-water mixture.<sup>3</sup> Recently we have shown that both of these complexes as well as the dimeric isopolyperoxo species  $[\text{W}_2\text{O}_3(\text{O}_2)_4]^{2-}$  are, with hydrogen peroxide as cooxidant, good catalysts for the oxidation of tertiary amines to the corresponding *N*-oxides.<sup>1</sup>

Here we report the isolation and characterisation of the novel trinuclear species  $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  **1** and show that its tungsten analogue (**2**) is an effective oxidation catalyst for alkenes, alcohols and tertiary amines. In support of our earlier hypothesis that the presence of an asymmetrically bound  $\eta^2, \eta^1$ -peroxo moiety is desirable for effective oxidation catalysis,<sup>3</sup> we report the isolation and structural characterisation of a new and unusual tetranuclear isopolyperoxo species  $[\text{NBu}^n_4]_2[\text{W}_4\text{O}_6(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]$  **3**; this, unlike complex **1** contains only symmetric  $\eta^2$ -peroxo units and seems in consequence to be a less effective oxidation catalyst. The X-ray crystal structures of complexes **1** and **3** are presented and discussed; although **1** is a poor oxidant of alkenes, **2** and **3** act as catalysts for alkene epoxidation and alcohol oxidation.

## Results and Discussion

**Heteropolyperoxo Trinuclear Species.**—(i) *Preparation of*  $[\text{NMe}_4]_2[(\text{RPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$ . These complexes were isolated as yellow crystalline solids by reacting stoichiometric quantities of  $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{RPO}(\text{OH})_2$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Bu}^n$  or  $\text{Bu}^t$ ) and  $\text{NMe}_4\text{Cl}$  in water-ethanol (70:30), followed by cooling at 0 °C for 3 d.

(ii) *Preparation and crystal structure of complex 1.* Yellow crystals of complex **1** suitable for X-ray analysis were obtained

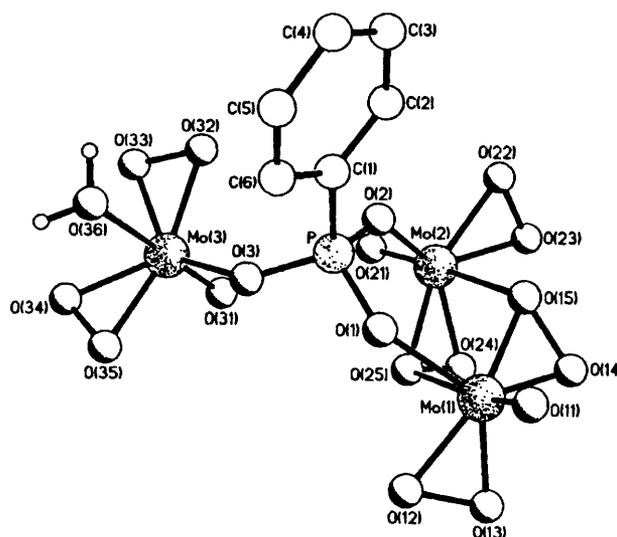


Fig. 1 Crystal structure of  $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  **1**

as described above. The crystal structure, Fig. 1, shows each of the three molybdenum(vi) centres to have distorted pentagonal-bipyramidal geometries. Four of the equatorial sites around each of the metal centres are occupied by two bidentate peroxo groups. The fifth site in each case is filled by a phosphonate oxygen atom [ $\text{Mo}-\text{O}(\text{P})$  2.014(4)–2.035(4) Å]. Selected bond lengths and angles are listed in Table 1, atomic coordinates in Table 2.

Whereas four of the six peroxo groups are of the non-bridging  $\eta^2$  type [ $\text{Mo}-\eta^2(\text{O}_2)$  1.906(4)–1.934(4),  $\eta^2(\text{O}-\text{O})$  1.453(6)–1.477(6) Å;  $\text{O}-\text{Mo}-\text{O}$  44.4(2)–45.2(2)°], two of them are involved in bridging between Mo(1) and Mo(2) in an  $\eta^2, \eta^1$  fashion. The consequence of this 'extra' interaction is not a lengthening of either peroxide bond (which remain at ca. 1.47 Å with an angle subtended at molybdenum of around 44.2°) but an increase in the bond length to the parent molybdenum atoms of the bridging oxygen atoms O(15) and O(25) [ $\text{Mo}(1)-\text{O}(15)$  1.920(4),  $\text{Mo}(1)-\text{O}(15)$  1.979(3),  $\text{Mo}(2)-\text{O}(24)$  1.916(4) and  $\text{Mo}(2)-\text{O}(25)$  1.985(3) Å]. The bridging bond lengths to the second metal atoms [ $\text{O}(15)-\text{Mo}(2)$  2.478(4) and  $\text{O}(25)-\text{Mo}(1)$

† Studies on Polyoxo- and Polyperoxo-metalates. Part 3.<sup>1</sup>

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

**Table 1** Selected bond lengths (Å) and angles (°) for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

P–O(1)	1.523(4)	Mo(2)–O(22)	1.934(4)	P–O(2)	1.532(4)	Mo(2)–O(23)	1.913(4)
P–O(3)	1.509(4)	Mo(2)–O(24)	1.916(4)	P–C(1)	1.767(5)	Mo(2)–O(25)	1.985(3)
O(1)–Mo(1)	2.019(4)	O(22)–O(23)	1.477(6)	Mo(1)–O(11)	1.658(4)	O(24)–O(25)	1.471(5)
Mo(1)–O(12)	1.921(4)	O(3)–Mo(3)	2.035(4)	Mo(1)–O(13)	1.906(4)	Mo(3)–O(31)	1.658(5)
Mo(1)–O(14)	1.920(4)	Mo(3)–O(32)	1.924(5)	Mo(1)–O(15)	1.979(3)	Mo(3)–O(33)	1.911(6)
Mo(1)–O(25)	2.469(4)	Mo(3)–O(34)	1.915(4)	O(12)–O(13)	1.468(6)	Mo(3)–O(35)	1.928(4)
O(14)–O(15)	1.463(6)	Mo(3)–O(36)	2.349(6)	O(15)–Mo(2)	2.478(4)	O(32)–O(33)	1.471(8)
O(2)–Mo(2)	2.014(4)	O(34)–O(35)	1.453(6)	Mo(2)–O(21)	1.671(4)		
O(1)–P–O(2)	111.3(2)	O(22)–Mo(2)–O(23)	45.2(2)	O(1)–P–O(3)	107.9(2)	O(15)–Mo(2)–O(24)	80.8(1)
O(2)–P–O(3)	113.2(2)	O(2)–Mo(2)–O(24)	131.3(2)	O(1)–P–C(1)	108.5(2)	O(21)–Mo(2)–O(24)	101.5(2)
O(2)–P–C(1)	106.5(2)	O(22)–Mo(2)–O(24)	129.9(2)	O(3)–P–C(1)	109.4(2)	O(23)–Mo(2)–O(24)	87.4(2)
P–O(1)–Mo(1)	138.6(2)	O(15)–Mo(2)–O(25)	71.2(1)	O(1)–Mo(1)–O(11)	95.8(2)	O(2)–Mo(2)–O(25)	87.6(2)
O(1)–Mo(1)–O(12)	86.2(2)	O(21)–Mo(2)–O(25)	104.7(2)	O(11)–Mo(1)–O(12)	105.4(2)	O(22)–Mo(2)–O(25)	150.8(2)
O(1)–Mo(1)–O(13)	130.5(2)	O(23)–Mo(2)–O(25)	127.5(2)	O(11)–Mo(1)–O(13)	104.4(2)	O(24)–Mo(2)–O(25)	44.3(2)
O(12)–Mo(1)–O(13)	45.1(2)	Mo(2)–O(22)–O(23)	66.7(2)	O(1)–Mo(1)–O(14)	131.3(2)	Mo(2)–O(23)–O(22)	68.2(2)
O(11)–Mo(1)–O(14)	101.5(2)	Mo(2)–O(24)–O(25)	70.4(2)	O(12)–Mo(1)–O(14)	130.6(2)	Mo(1)–O(25)–Mo(2)	108.0(1)
O(13)–Mo(1)–O(14)	88.5(2)	Mo(1)–O(25)–O(24)	110.5(2)	O(1)–Mo(1)–O(15)	87.6(2)	Mo(2)–O(25)–O(24)	65.4(2)
O(11)–Mo(1)–O(15)	104.4(2)	P–O(3)–Mo(3)	138.8(2)	O(12)–Mo(1)–O(15)	150.0(2)	O(3)–Mo(3)–O(31)	94.3(2)
O(13)–Mo(1)–O(15)	128.3(2)	O(3)–Mo(3)–O(32)	88.1(2)	O(14)–Mo(1)–O(15)	44.0(2)	O(31)–Mo(3)–O(32)	102.9(3)
O(1)–Mo(1)–O(25)	75.6(1)	O(3)–Mo(3)–O(33)	132.7(2)	O(11)–Mo(1)–O(25)	170.4(2)	O(31)–Mo(3)–O(33)	101.9(3)
O(12)–Mo(1)–O(25)	78.6(1)	O(32)–Mo(3)–O(33)	45.1(3)	O(13)–Mo(1)–O(25)	84.7(2)	O(3)–Mo(3)–O(34)	131.2(2)
O(14)–Mo(1)–O(25)	81.7(1)	O(31)–Mo(3)–O(34)	102.1(2)	O(15)–Mo(1)–O(25)	71.5(1)	O(32)–Mo(3)–O(34)	130.8(2)
Mo(1)–O(12)–O(13)	66.9(2)	O(33)–Mo(3)–O(34)	88.5(2)	Mo(1)–O(13)–O(12)	68.0(2)	O(3)–Mo(3)–O(35)	87.5(2)
Mo(1)–O(14)–O(15)	70.1(2)	O(31)–Mo(3)–O(35)	101.6(2)	Mo(1)–O(15)–O(14)	65.8(2)	O(32)–Mo(3)–O(35)	155.4(2)
Mo(1)–O(15)–Mo(2)	107.9(1)	O(33)–Mo(3)–O(35)	130.8(2)	O(14)–O(15)–Mo(2)	111.3(3)	O(34)–Mo(3)–O(35)	44.4(2)
P–O(2)–Mo(2)	134.1(2)	O(3)–Mo(3)–O(36)	78.8(2)	O(15)–Mo(2)–O(2)	75.3(1)	O(31)–Mo(3)–O(36)	173.0(2)
O(15)–Mo(2)–O(21)	171.6(2)	O(32)–Mo(3)–O(36)	78.3(2)	O(2)–Mo(2)–O(21)	97.4(2)	O(33)–Mo(3)–O(36)	83.9(2)
O(15)–Mo(2)–O(22)	79.6(1)	O(34)–Mo(3)–O(36)	82.0(2)	O(2)–Mo(2)–O(22)	86.6(2)	O(35)–Mo(3)–O(36)	77.1(2)
O(21)–Mo(2)–O(22)	104.5(2)	Mo(3)–O(32)–O(33)	67.0(3)	O(15)–Mo(2)–O(23)	84.1(1)	Mo(3)–O(33)–O(32)	67.9(3)
O(2)–Mo(2)–O(23)	130.5(2)	Mo(3)–O(34)–O(35)	68.3(2)	O(21)–Mo(2)–O(23)	104.0(2)	Mo(3)–O(35)–O(34)	67.3(2)

**Table 2** Atomic coordinates ( $\times 10^4$ ) for complex **1**

Atom	x	y	z	Atom	x	y	z
P	–1062(1)	5978(1)	3201(1)	O(34)	–3121(5)	4018(2)	1288(3)
O(1)	267(4)	5748(2)	3646(2)	O(35)	–2151(5)	3927(2)	1949(3)
Mo(1)	2262(1)	6071(1)	3716(1)	O(36)	–4239(5)	4624(3)	2632(3)
O(11)	2399(5)	6126(3)	4675(2)	C(1)	–2259(5)	6278(3)	3873(3)
O(12)	2665(4)	5004(2)	3474(2)	C(2)	–2565(7)	7053(3)	3963(4)
O(13)	3865(4)	5518(3)	3448(3)	C(3)	–3492(8)	7278(4)	4511(4)
O(14)	3143(4)	7020(2)	3426(2)	C(4)	–4062(7)	6729(5)	4970(4)
O(15)	1651(4)	7123(2)	3378(2)	C(5)	–3733(7)	5965(4)	4890(4)
O(2)	–842(4)	6677(2)	2671(2)	C(6)	–2851(6)	5725(3)	4356(3)
Mo(2)	703(1)	7023(1)	2023(1)	N(1)	2270(5)	4281(2)	934(2)
O(21)	–74(5)	6848(2)	1155(2)	C(10)	3610(8)	3952(4)	729(6)
O(22)	178(4)	8079(2)	2265(3)	C(11)	2182(10)	4227(5)	1783(4)
O(23)	1520(4)	8028(2)	1910(2)	C(12)	1138(9)	3821(4)	555(5)
O(24)	2488(4)	6588(2)	1896(2)	C(13)	2166(8)	5105(3)	688(4)
O(25)	1647(4)	6031(2)	2312(2)	N(2)	–4567(5)	7954(2)	1337(3)
O(3)	–1606(4)	5268(2)	2770(2)	C(20)	–3051(7)	7860(4)	1318(4)
Mo(3)	–2620(1)	5002(1)	1745(1)	C(21)	–4962(7)	7719(4)	2125(4)
O(31)	–1344(5)	5282(3)	1212(3)	C(22)	–4953(9)	8784(4)	1198(5)
O(32)	–3664(6)	5945(3)	1845(4)	C(23)	–5290(8)	7452(4)	749(4)
O(33)	–4176(6)	5454(3)	1195(4)				

2.469(4) Å] are comparable with those found in  $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]_6$  and in  $[\text{NBu}^n_4]_2[\{\text{PO}_3(\text{OH})\}\{\text{WO}(\text{O}_2)_2\}_2]_7$ .

All three metal centres possess an axial oxo group  $[\text{Mo}-\text{O}_{\text{oxo}} 1.658(5)\text{--}1.671(4) \text{ Å}]$ . For Mo(1) and Mo(2) the *trans* axial position is occupied by a bridging oxygen atom from an  $\eta^2, \eta^1$  interaction  $[\text{O}(25)$  and  $\text{O}(15)$  respectively, see above]. The Mo(3) centre has a particularly weakly bound water molecule in this site  $[\text{Mo}(3)-\text{O}(36) 2.349(6) \text{ Å}]$ , cf. an average of 2.20 Å for terminal  $\text{Mo}-\text{OH}_2$  groups<sup>8</sup>, although distances more comparable with that seen here have been observed in the isopolyperoxo species  $\text{K}_2[\text{Mo}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]$  (2.45 Å)<sup>9</sup> and  $[\text{C}_5\text{H}_5\text{NH}]_2[\text{Mo}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]$  [2.455(7) Å].<sup>10</sup>

The angles between the peroxo groups are in the range 128–130° whilst those between the bridging phosphonate donor

atoms and peroxo groups are in the range 108–113° (considering each peroxo group as a unidentate ligand associated with a trigonal-bipyramidal geometry around each metal centre). In all three cases, the molybdenum centre is displaced towards the oxo group relative to the plane of the five oxygen atoms normal to this direction; the deviations are 0.41, 0.41 and 0.34 Å for Mo(1), Mo(2) and Mo(3) respectively. [The five equatorial co-ordinated oxygen atoms are coplanar to within 0.12, 0.10 and 0.07 Å for Mo(1), Mo(2) and Mo(3) respectively.] The angles between the oxo groups and the *trans* ligands are in the range 170–173°.

The geometry around the phosphorus atom is tetrahedral, with angles from 107 to 113°. The phosphorus–oxygen bond lengths do not differ significantly  $[\text{P}-\text{O} 1.509(4)\text{--}1.532(4) \text{ Å}]$ . Symmetry related and lattice translated molecules are linked *via*

O–H...O hydrogen bonds (2.81 and 2.84 Å) between the aqua ligand in one molecule and peroxy oxygen atoms in adjacent molecules producing sheets that extend in the crystallographic *a* and *b* directions (Fig. 2).

(ii) *Vibrational and  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectroscopy.* The infrared and Raman spectra (Table 3) of  $[\text{NMe}_4]_2[(\text{RPO}_3)\{\text{MO}(\text{O}_2)_2\}_2\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{R} = \text{Ph}$ ,  $\text{Me}$ ,  $\text{Et}$ ,  $\text{Bu}^n$  or  $\text{Bu}^l$ ) show features comparable with those observed for  $[\text{XO}_4\{\text{MO}(\text{O}_2)_2\}_4]^{3-}$  and  $[\text{XO}_4\{\text{MO}(\text{O}_2)_2\}_2\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{3-}$  [ $\text{M} = \text{Mo}$  or  $\text{W}$ ,  $\text{X} = \text{P}$  or  $\text{As}$ ].<sup>3</sup> Bands near 970  $\text{cm}^{-1}$  were assigned as  $\nu(\text{M}=\text{O})$ , those near 870  $\text{cm}^{-1}$  as  $\nu(\text{O}-\text{O})$  of the  $\eta^2$ -peroxy ligands and those around 580 and 520  $\text{cm}^{-1}$  as asymmetric and symmetric  $\text{M}(\text{O}_2)$  stretches respectively. In addition to bands due to  $\text{NMe}_4^+$  and the phosphonic acid  $\text{R}$  group,  $\text{P}=\text{O}$  stretches appear near 1080  $\text{cm}^{-1}$ .

The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectra of  $[\text{NMe}_4]_2[(\text{RPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  in non-aqueous solvents show a single resonance [ $\delta$  25.30 ( $\text{CD}_3\text{OD}$ ),  $\text{R} = \text{Ph}$ ;  $\delta$  38.14 ( $\text{CD}_3\text{OD}$ ),  $\text{R} = \text{Me}$ ;  $\delta$  38.56 ( $\text{CD}_3\text{OD}$ ),  $\text{R} = \text{Et}$ ;  $\delta$  39.99 ( $\text{CD}_3\text{OD}$ ),  $\text{R} = \text{Bu}^n$ ;  $\delta$  39.42 ( $\text{CD}_3\text{OD}$ ),  $\text{R} = \text{Bu}^l$ ], suggesting that a single species is present in solution. Similarly, a solution of  $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  gives a 1:6:1 'triplet' at  $\delta = 15.81$  ( $\text{CD}_3\text{CN}$ ) with poorly resolved tungsten satellites ( $^2J_{\text{P-W}} = 18$  Hz). As with  $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ , aqueous solutions of each of these trinuclear complexes give rise to several signals, most probably due to di- and mono-nuclear species,  $[\{\text{RP}(\text{OH})\text{O}_2\}\{\text{MO}(\text{O}_2)_2\}_2]^-$  and  $[\{\text{RP}(\text{OH})\text{O}_2\}\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  respectively.

(iii) *Oxidations.* In the presence of the phase-transfer cation  $\text{N}(\text{C}_6\text{H}_{13})_4\text{Cl}$  in a 2:1 (cation:complex) ratio, complex 2 cleanly catalyses the epoxidation of a number of cyclic and linear alkenes in biphasic 15%  $\text{H}_2\text{O}_2$ -benzene (Table 4). The epoxidation of small ring cycloalkenes are found to be more efficient than those catalysed by  $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$ , but the latter is the better epoxidant for larger rings.<sup>3</sup> Similarly (under identical reaction conditions) 2 also catalyses the oxidation of primary and secondary alcohols, although less efficiently than  $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]$  (Table 5).<sup>3</sup> Tertiary amines (*e.g.* nicotinic acid) are oxidised to the corresponding *N*-oxides in yields of 60–80%.

The molybdenum analogue, 1, in the presence of a stoichiometric amount of  $\text{N}(\text{C}_6\text{H}_{13})_4\text{Cl}$ , will also catalyse alkene epoxidation, though far less efficiently than 2. This often appears to be the case with oxidations with molybdenum and tungsten complexes in which  $\text{H}_2\text{O}_2$  is the cooxidant.<sup>11</sup>

*Isopolyperoxy Tetranuclear Species.*—(i) *Preparation and crystal structure of complex 3.* Colourless crystals of complex 3 were obtained by reacting stoichiometric amounts of  $\text{WO}_3\cdot\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{NBU}_4\text{Cl}$  in water-ethanol (70:30) acidified to pH 1.5 with  $\text{H}_2\text{SO}_4$ , followed by cooling at 0 °C for 3 d. The structural analysis of 3 reveals a complex structure containing four tungsten centres arranged around a crystallographic centre of symmetry (Fig. 3). Selected bond lengths and angles are listed in Table 6, atomic coordinates in Table 7.

Each crystallographically independent tungsten(vi) atom has a distorted pentagonal-bipyramidal geometry. One tungsten,  $\text{W}(1)$ , is bound to two equatorial  $\eta^2$ -peroxy ligands [ $\text{W}(1)-\eta^2(\text{O}_2)$  1.878(12)–1.958(12),  $\eta^2(\text{O}-\text{O})$  1.439(18) and 1.497(15) Å,  $\text{O}-\text{W}-\text{O}$  43.8(6) and 45.9(5)°] with the fifth equatorial position being occupied by a bridging [to  $\text{W}(2')$ ] hydroxide,  $\text{O}(6)$  [ $\text{W}(1)-\text{O}(6)$  2.075(8) Å]. The angles between the equatorial bridging hydroxide oxygen  $\text{O}(6)$  and the two peroxy ligands are 108 and 112° with an angle of 131° between the two peroxy ligands. One of the axial sites of this metal centre is filled by an oxo ligand,  $\text{O}(1)$  [ $\text{W}(1)-\text{O}(1)$  1.697(14) Å], whilst the other contains a triply bridging [to  $\text{W}(2)$  and  $\text{W}(2')$ ] oxide atom,  $\text{O}(7)$  [ $\text{W}(1)-\text{O}(7)$  2.155(7) Å,  $\text{O}(1)-\text{W}(1)-\text{O}(7)$  160.7(5)°]. The non-linearity of the axial substituents is probably due to the constraints imposed upon  $\text{O}(7)$  to permit it to be triply bridging.

The second tungsten centre,  $\text{W}(2)$ , is linked equatorially to its

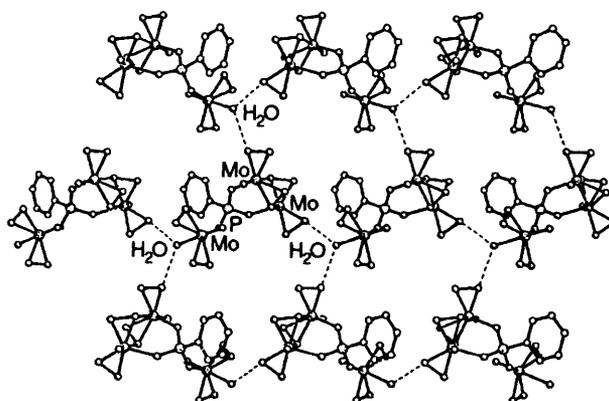


Fig. 2 Structure of complex 1 showing the intermolecular hydrogen bonding

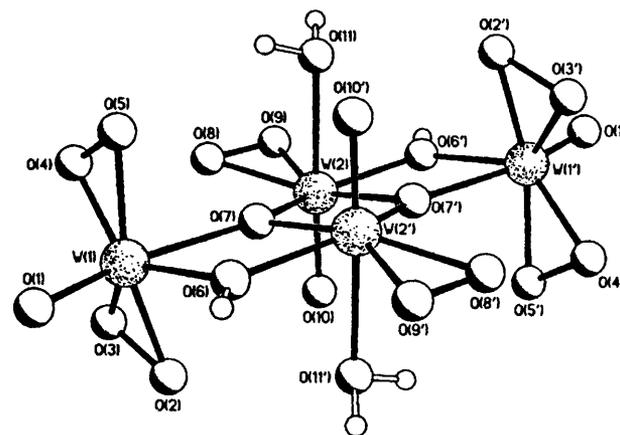


Fig. 3 Crystal structure of  $[\text{NBU}_4]_2[\text{W}_4\text{O}_6(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]_3$

centrosymmetric counterpart,  $\text{W}(2')$ , by a pair of  $\mu_3$ -oxide atoms,  $\text{O}(7)$  and  $\text{O}(7')$  [ $\text{W}(2)-\text{O}(7)$  1.973(7) and  $\text{W}(2)-\text{O}(7')$  2.024(8) Å]. Two of the other equatorial sites are filled by an  $\eta^2$ -peroxy ligand [ $\text{W}(2)-\text{O}(8)$  1.930(10),  $\text{W}(2)-\text{O}(9)$  1.923(9),  $\eta^2(\text{O}-\text{O})$  1.522(13) Å,  $\text{O}-\text{W}-\text{O}$  46.5(4)°] with the final position occupied by the bridging [to  $\text{W}(1')$ ] hydroxide  $\text{O}(6)$  [ $\text{W}(2)-\text{O}(6')$  2.038(8) Å]. Oxo,  $\text{O}(10)$ , and aqua,  $\text{O}(11)$ , ligands fill the axial positions [ $\text{W}(2)-\text{O}(10)$  1.744(9),  $\text{W}(2)-\text{O}(11)$  2.349(10) Å,  $\text{O}(10)-\text{W}(2)-\text{O}(11)$  176.6(4)°].

The transannular  $\text{W}(2)\cdots\text{W}(2')$  and  $\text{O}(7)\cdots\text{O}(7')$  distances are 3.20 and 2.39 Å respectively, whilst those between  $\text{W}(1)$  and  $\text{W}(2')$  and between  $\text{O}(6)$  and  $\text{O}(7)$  are 3.38 and 2.39 Å respectively. The tungsten atoms [ $\text{W}(1)$  and  $\text{W}(2)$ ], the bridging oxygen ligands between them [ $\text{O}(6)$  and  $\text{O}(7)$ ] and their centrosymmetrically related counterparts are coplanar to within 0.09 Å. In each case, the tungsten(vi) atoms are displaced towards their associated oxo groups relative to the plane of the five oxygen atoms normal to these directions; the deviations are 0.32 and 0.30 Å for  $\text{W}(1)$  and  $\text{W}(2)$  respectively. [The five equatorial co-ordinated oxygen atoms are coplanar to within 0.01 and 0.08 Å for  $\text{W}(1)$  and  $\text{W}(2)$  respectively.]

Although the positions of the hydroxy and aqua hydrogen atoms could not be definitively assigned from  $\Delta F$  maps, their presence has been inferred on the basis of the tungsten–oxygen bond lengths, and their positions from their potential intermolecular hydrogen-bonding interactions. The shortness of the  $\text{W}(1)-\text{O}(1)$  and  $\text{W}(2)-\text{O}(10)$  distances (see above) clearly identifies  $\text{O}(1)$  and  $\text{O}(10)$  as oxo ligands. Similarly, the observed long  $\text{W}(2)-\text{O}(11)$  distance is diagnostic of a terminal tungsten–aqua bond. The value observed here, 2.349(10) Å, is significantly longer than the average, 2.12 Å, reported for terminal  $\text{W}-\text{OH}_2$  ligands *trans* to oxo,<sup>8</sup> though very similar to that observed in

Table 3 Vibrational spectroscopic characteristics ( $\text{cm}^{-1}$ ) \* of  $[\text{NMe}_4]_2[(\text{RPO}_3)_2(\text{MO}(\text{O}_2)_2)_2(\text{MO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$  and  $[\text{NBu}^n_4]_2[\text{W}_4\text{O}_{16}(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]$ 

Complex	$\nu(\text{M}=\text{O})$	$\nu(\text{O}-\text{O})$	$\nu_{\text{asym}}[\text{M}_2\text{O}]$	$\nu_{\text{sym}}[\text{M}(\text{O})_2]$	$\nu_{\text{asym}}[\text{M}(\text{O})_2]$	$\nu_{\text{sym}}[\text{M}(\text{O})_2]$	$\nu[\text{M}(\text{OH})_2]$	Other bands
<b>1</b> $[\text{NMe}_4]_2[(\text{PhPO}_3)_2(\text{MoO}(\text{O}_2)_2)_2(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$	964vs 983 (10) 956vs	869vs 889 (9) 847vs	768s 767 (2)	657s	584s 539 (5)	319m 322 (4)	3381vs	$\delta(\text{HOH})$ 1657s
<b>2</b> $[\text{NMe}_4]_2[(\text{PhPO}_3)_2(\text{WO}(\text{O}_2)_2)_2(\text{WO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$	953 (10) 962vs 983 (10)	862 (3) 865vs 883 (8), 878 (7)	761 (2) 764s 752 (2)	623s 628 (1) 657 (1)	549s 561 (4) 566s	316m 322 (5) 321m	3424vs	1637s 1648s
$[\text{NMe}_4]_2[(\text{MePO}_3)_2(\text{MoO}(\text{O}_2)_2)_2(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$	961vs 979 (10)	868vs 875 (8)	765s 754 (3)	651s 655 (1)	579s 562 (4)	322m 324 (5)	3372vs	1652s
$[\text{NMe}_4]_2[(\text{EtPO}_3)_2(\text{MoO}(\text{O}_2)_2)_2(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$	963vs 980 (10)	864vs 877 (7)	767s 755 (3)	653s 655 (1)	580s 564 (5)	321m 323 (5)	3374vs	1655s
$[\text{NMe}_4]_2[(\text{Bu}^n\text{PO}_3)_2(\text{MoO}(\text{O}_2)_2)_2(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]$	963vs 982 (10)	863vs 875 (8)	764s 754 (2)	652s 656 (1)	581s 561 (4)	320m 323 (5)	3376vs	1653s
<b>3</b> $[\text{NBu}^n_4]_2[\text{W}_4\text{O}_{16}(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_2]$	969vs, 943vs 967 (10), 959 (9)	874vs, 854vs 858 (4)	748s	657s 638 (1)	583vs, 570vs 567 (8)	— 312 (6)	3338vs	1637s

\* Raman data in italics (relative intensities in parentheses).

$K_2[W_2O_3(O_2)_4(H_2O)_2] \cdot 2H_2O$ ,<sup>12</sup> emphasising the weak nature of the binding of the aqua ligand in these species. The proximity in the crystal of O(6) and of O(1) of a lattice-translated complex [2.57(2) Å] is too short for a non-hydrogen-bonded O...O approach, thus O(6) must be protonated. Consideration of charges and formal oxidation states rules out the possibility of a bridging aqua ligand.

The role of the aforementioned hydrogen-bonding interaction is significant in determining the packing of the complexes in the crystal. Lattice-translated molecules are linked by pairs of O-H...O hydrogen bonds between O(1) and O(6') and between O(1') and O(6) across a crystallographic symmetry centre producing a hydrogen-bonded chain of molecules that extends in the crystallographic *a* direction (Fig. 4). The partial-occupancy hydrate molecule is positioned such as to be able to form intra-complex hydrogen bonds *via* one long and two short interactions [O(50)...O(5) 2.35(3), O(50)...O(11) 2.45(4) and O(50)...O(10') 2.90(4) Å]. Due to the symmetry within the complex, there are two of these 50%-occupancy water molecules per tetratungsten anion.

The structure of complex 3 reported here has gross features very similar to those observed in the analogous molybdenum complex  $[NBu^n_4]_2[Mo_4O_6(O_2)_6(HOME)_2(OMe)_2]$ .<sup>13</sup> In this latter species two of the axial and two of the Mo...X...Mo bridging positions have been replaced by OMe and MeOH

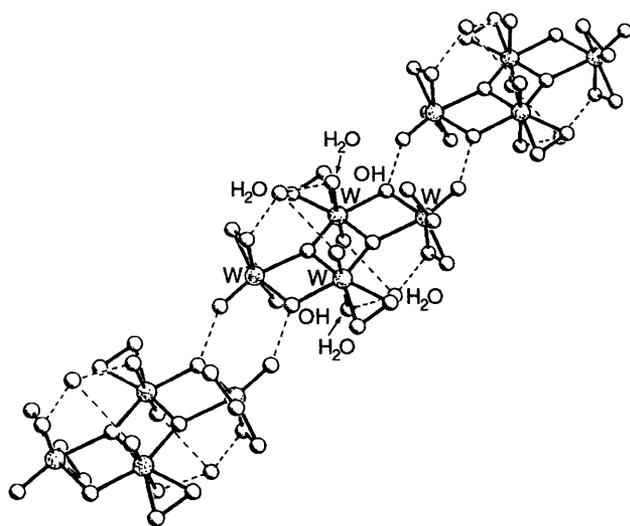


Fig. 4 Structure of complex 3 showing the intermolecular hydrogen bonding

groups respectively. The authors did not, however, indicate how a differentiation between the identities of these two substituents was achieved.

(ii) *Oxidations.* Epoxidation of cyclic and linear alkenes by  $[N(C_6H_{13})_4]_2[W_4O_6(O_2)_6(OH)_2(H_2O)_2]$  [generated by addition of two equivalents of  $N(C_6H_{13})_4Cl$  to complex 3] in biphasic 15%  $H_2O_2$ -benzene gave epoxides in much poorer yields than those observed for  $[N(C_6H_{13})_4]_3[XO_4\{WO(O_2)_2\}_4]$  (X = P or As)<sup>3</sup> or  $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$ <sup>1</sup> (Table 4). Although the reasons for the poor catalytic activity of 3 are not immediately apparent, we believe that the absence of  $\eta^2, \eta^1$ -peroxide linkages are a determining factor.

## Conclusion

It is clear that complex 3, which contains six conventional symmetric  $\eta^2$ -peroxy groups and none of the asymmetric  $\eta^2, \eta^1$ -counterparts is a far less effective alkene epoxidant than complex 2 (under similar reaction conditions). Although we were unable to obtain crystals of 2 to allow a direct comparison of its structure with that of 1, it is thought likely that they have similar structures.

In general, it seems that tungsten complexes containing asymmetric  $\eta^2, \eta^1$ -peroxy ligands are efficient epoxidation catalysts with  $H_2O_2$  as cooxidant, *cf.*  $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ <sup>6</sup> and  $[NBu^n_4]_2[PO_3(OH)\{WO(O_2)_2\}_2]$ .<sup>7</sup> The compounds  $Q_2[W_2O_3(O_2)_4]$  [Q = PPh<sub>4</sub>, AsPh<sub>4</sub>, Ph<sub>3</sub>PCH<sub>2</sub>-Ph or  $N(C_6H_{13})_4$ ] are also believed to contain asymmetric peroxy units,<sup>1</sup> and have been shown to be active epoxidation

Table 4 Oxidation of linear and cyclo alkenes by  $[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$  and  $[W_4O_6(O_2)_6(OH)_2(H_2O)_2]^{2-}$

Substrate	Product	Yield (%) [Turnover]	
		2	3
Cyclopentene	1,2-Epoxy cyclopentane	87 [168]	4 [8]
Cyclohexene	1,2-Epoxy cyclohexane	22 [43]	2 [4]
Cycloheptene	1,2-Epoxy cycloheptane	73 [141]	—
Cyclooctene	1,2-Epoxy cyclooctane	95 [183]	21 [41]
Cyclododecene	1,2-Epoxy cyclododecane	67 [129]	6 [12]
<i>cis</i> -Stilbene	<i>cis</i> -2,3-Diphenyloxirane	59 [114]	—
<i>trans</i> -Stilbene	<i>trans</i> -2,3-Diphenyloxirane	78 [151]	—
Hex-1-ene	1,2-Epoxyhexane	34 [66]	1 [2]
Hept-1-ene	1,2-Epoxyheptane	57 [110]	—
Oct-1-ene	1,2-Epoxyoctane	53 [103]	5 [10]
Non-1-ene	1,2-Epoxy nonane	48 [93]	—
Dec-1-ene	1,2-Epoxydecane	55 [106]	6 [12]
Undec-1-ene	1,2-Epoxyundecane	51 [99]	—
Dodec-1-ene	1,2-Epoxydodecane	48 [93]	4 [8]

Table 5 Oxidation of primary and secondary alcohols by  $[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{2-}$

Substrate	Product	Yield (%)	Turnover*
Benzyl alcohol	Benzaldehyde	35	71
2-Methylbenzyl alcohol	2-Methylbenzaldehyde	42	84
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	28	56
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	14	29
Piperonyl alcohol	Piperonaldehyde	34	68
(±)-Menthol	(±)-Menthone	16	33
1,2,3,4-Tetrahydronaphthol	3,4-Dihydro-2 <i>H</i> -naphthalen-1-one	9	19
(±)-1-Phenylethanol	Acetophenone	91	182
2-Phenylethanol	2-Phenylethanal	31	62
Cyclopentanol	Cyclopentanone	32	64
Cyclohexanol	Cyclohexanone	33	67
2-Methylcyclohexanol	2-Methylcyclohexanone	69	137
3-Methylcyclohexanol	3-Methylcyclohexanone	90	179
4-Methylcyclohexanol	4-Methylcyclohexanone	91	183
Cycloheptanol	Cycloheptanone	52	105
Cyclooctanol	Cyclooctanone	48	96

\* Turnover = mol product/mol catalyst.

**Table 6** Selected bond lengths (Å) and angles (°) for complex 3 with e.s.d.s in parentheses

W(1)–O(1)	1.697(14)	W(1)–O(2)	1.958(12)
W(1)–O(3)	1.878(12)	W(1)–O(4)	1.907(12)
W(1)–O(5)	1.954(13)	W(1)–O(6)	2.075(8)
W(1)–O(7)	2.155(7)	O(2)–O(3)	1.497(15)
O(4)–O(5)	1.439(18)	O(7)–W(2)	1.973(7)
W(2)–O(8)	1.930(10)	W(2)–O(9)	1.923(9)
W(2)–O(10)	1.744(9)	W(2)–O(11)	2.349(10)
W(2)–O(6')	2.038(8)	W(2)–O(7')	2.024(8)
O(8)–O(9)	1.522(13)		
O(1)–W(1)–O(2)	97.8(8)	O(1)–W(1)–O(3)	103.6(7)
O(2)–W(1)–O(3)	45.9(5)	O(1)–W(1)–O(4)	105.3(7)
O(2)–W(1)–O(4)	131.9(6)	O(3)–W(1)–O(4)	87.4(5)
O(1)–W(1)–O(5)	101.5(9)	O(2)–W(1)–O(5)	160.6(7)
O(3)–W(1)–O(5)	129.6(5)	O(4)–W(1)–O(5)	43.8(6)
O(1)–W(1)–O(6)	91.9(5)	O(2)–W(1)–O(6)	86.3(4)
O(3)–W(1)–O(6)	130.8(4)	O(4)–W(1)–O(6)	133.3(4)
O(5)–W(1)–O(6)	90.8(5)	O(1)–W(1)–O(7)	160.7(5)
O(2)–W(1)–O(7)	80.9(4)	O(3)–W(1)–O(7)	89.3(4)
O(4)–W(1)–O(7)	89.2(5)	O(5)–W(1)–O(7)	80.2(6)
O(6)–W(1)–O(7)	68.9(3)	W(1)–O(2)–O(3)	64.2(6)
W(1)–O(3)–O(2)	69.9(6)	W(1)–O(4)–O(5)	69.8(7)
W(1)–O(5)–O(4)	66.4(7)	W(1)–O(6)–W(2')	110.7(4)
W(1)–O(7)–W(2)	144.9(4)	W(1)–O(7)–W(2')	108.1(3)
W(2)–O(7)–W(2')	106.5(3)	O(7)–W(2)–O(8)	83.2(4)
O(7)–W(2)–O(9)	129.4(4)	O(8)–W(2)–O(9)	46.5(4)
O(7)–W(2)–O(10)	95.6(4)	O(8)–W(2)–O(10)	102.7(5)
O(9)–W(2)–O(10)	99.9(4)	O(7)–W(2)–O(11)	82.9(4)
O(8)–W(2)–O(11)	80.2(4)	O(9)–W(2)–O(11)	83.4(4)
O(10)–W(2)–O(11)	176.6(4)	O(7)–W(2)–O(6')	144.7(3)
O(8)–W(2)–O(6')	125.2(3)	O(9)–W(2)–O(6')	80.2(3)
O(10)–W(2)–O(6')	97.3(4)	O(11)–W(2)–O(6')	82.3(4)
O(7)–W(2)–O(7')	73.5(3)	O(8)–W(2)–O(7')	149.7(4)
O(9)–W(2)–O(7')	148.3(3)	O(10)–W(2)–O(7')	98.6(4)
O(11)–W(2)–O(7')	78.0(3)	O(6')–W(2)–O(7')	72.2(3)
W(2)–O(8)–O(9)	66.5(5)	W(2)–O(9)–O(8)	67.0(5)

**Table 7** Atomic coordinates ( $\times 10^4$ ) for complex 3

Atom	x	y	z
W(1)	6 999(1)	868(1)	4 880(1)
O(1)	5 242(13)	914(7)	4 838(15)
O(2)	6 840(12)	673(6)	3 553(8)
O(3)	7 192(10)	1 433(6)	3 861(8)
O(4)	7 837(15)	1 644(6)	5 669(10)
O(5)	7 827(19)	1 002(7)	6 214(9)
O(6)	7 016(8)	–240(4)	5 052(7)
O(7)	9 082(7)	433(4)	4 974(5)
W(2)	10 991(1)	639(1)	4 798(1)
O(8)	10 542(9)	1 610(5)	5 092(8)
O(9)	12 057(9)	1 520(5)	4 999(7)
O(10)	10 497(10)	630(5)	3 579(6)
O(11)	11 617(11)	579(5)	6 437(7)
N	4 823(12)	2 098(7)	7 710(8)
C(10)	3 888(16)	2 399(8)	6 842(11)
C(11)	3 492(17)	3 199(9)	6 896(11)
C(12)	2 479(20)	3 437(10)	5 979(12)
C(13)	2 053(24)	4 225(11)	6 087(14)
C(20)	4 113(16)	2 101(9)	8 538(10)
C(21)	2 750(17)	1 671(10)	8 410(13)
C(22)	2 226(26)	1 706(12)	9 287(15)
C(23)	866(27)	1 387(16)	9 269(20)
C(30)	5 171(15)	1 327(8)	7 485(11)
C(31)	6 161(22)	902(9)	8 220(13)
C(32)	6 471(21)	175(9)	7 927(14)
C(33)	7 593(25)	–197(12)	8 551(18)
C(40)	6 168(14)	2 533(8)	8 039(10)
C(41)	7 092(16)	2 596(9)	7 359(12)
C(42)	8 434(16)	3 011(9)	7 780(13)
C(43)	9 409(18)	3 059(11)	7 134(13)
O(50)	9 881(35)	742(18)	7 383(26)

and were considered to be observed. The data were corrected for Lorentz and polarisation factors.

**Structure analysis and refinement.** The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the aqua ligand were located from a  $\Delta F$  map and refined isotropically subject to distance and angle constraints. The positions of the remaining hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and allowed to ride on their parent carbon atoms. Refinement, based on  $F$ , was by full-matrix least squares to give  $R = 0.043$ ,  $R' = 0.048$  [ $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ ,  $R' = \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$ ,  $w^{-1} = \sigma^2(F) + 0.0007F^2$ ]. The maximum and minimum residual electron densities in the final  $\Delta F$  map were 0.83 and –0.90  $\text{e} \text{Å}^{-3}$  respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.005 and 0.021 respectively.

**Crystal data for complex 3.**  $\text{C}_{32}\text{H}_{78}\text{N}_2\text{O}_{22}\text{W}_4 \cdot \text{H}_2\text{O}$ ,  $M = 1596.4$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.725(4)$ ,  $b = 18.580(11)$ ,  $c = 14.738(7)$  Å,  $\beta = 103.87(2)^\circ$ ,  $U = 2586(2)$  Å<sup>3</sup>,  $Z = 2$  (the molecule has crystallographic  $C_2$  symmetry),  $D_c = 2.05$   $\text{g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 89$   $\text{cm}^{-1}$ ,  $F(000) = 1532$ . A clear block of dimensions 0.27  $\times$  0.27  $\times$  0.30 mm was used, coated in epoxy resin to inhibit desolvation.

**Data collection and processing.** Data were measured on a Siemens P4/PC diffractometer with Mo-K $\alpha$  radiation (graphite monochromator) using  $\omega$  scans. 4560 Independent reflections were measured ( $2\theta \leq 50^\circ$ ) of which 3308 had  $|F_o| > 4\sigma(|F_o|)$  and were considered to be observed. The data were corrected for Lorentz and polarisation factors and an empirical absorption correction was applied; the maximum and minimum transmission factors were 0.53 and 0.07 respectively.

**Structure analysis and refinement.** The structure was solved by direct methods. The full-occupancy non-hydrogen atoms were refined anisotropically. The structure was found to contain a partial-occupancy water molecule which was refined isotropically with a fixed occupancy of 0.50. The positions of the hydrogen atoms of the counter ion were idealised (C–H 0.96

catalysts. Very recently a vanadium complex containing such ligands,  $[\text{NH}_4]_5[\text{PO}_4\{\text{VO}(\text{O}_2)_2\}_2] \cdot \text{H}_2\text{O}$ , has been reported.<sup>14</sup>

Various suggestions have been made in an effort to explain the apparent correlation between asymmetric  $\eta^2, \eta^1$ -peroxo ligation and catalytic activity in tungsten complexes.<sup>1,3</sup> These include ion-pairing effects,<sup>15</sup> facile generation of a vacant metal co-ordination site<sup>6</sup> and O–O bond lengthening.<sup>16,17</sup> We believe, as proposed by Venturello *et al.*,<sup>6</sup> that the most feasible explanation for the reactivity of species containing asymmetric  $\eta^2, \eta^1$ -peroxo units is that the asymmetry leads to one oxygen atom being more electrophilic than the other. This would facilitate nucleophilic attack by the alkene on the peroxide, as suggested by Sharpless *et al.*<sup>18</sup>

Clearly, further research into these catalysts is required before more confident hypotheses on the mechanism of the epoxidation process can be made. Of particular importance will be detailed structural information pertaining to the nature of symmetric and asymmetric peroxo ligation.

## Experimental

**Crystal Structure Determinations.**—*Crystal data for complex 1.*  $\text{C}_{14}\text{H}_{31}\text{Mo}_3\text{N}_2\text{O}_{19}\text{P}$ ,  $M = 850.2$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.749(3)$ ,  $b = 17.154(5)$ ,  $c = 17.282(5)$  Å,  $\beta = 93.06(2)^\circ$ ,  $U = 2886(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.96$   $\text{g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 14$   $\text{cm}^{-1}$ ,  $F(000) = 1688$ . A yellow block of dimensions 0.73  $\times$  0.50  $\times$  0.40 mm was used.

**Data collection and processing.** Data were measured on a Siemens P4/PC diffractometer with Mo-K $\alpha$  radiation (graphite monochromator) using  $\omega$  scans. 5096 Independent reflections were measured ( $2\theta \leq 50^\circ$ ) of which 4364 had  $|F_o| > 4\sigma(|F_o|)$

Å), assigned isotropic thermal parameters,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and allowed to ride on their parent carbon atoms. Refinement, based on  $F$ , was by full-matrix least squares to give  $R = 0.051$ ,  $R' = 0.050$  [ $w^{-1} = \sigma^2(F) + 0.0007F^2$ ]. The maximum and minimum residual electron densities in the final  $\Delta F$  map were 2.60 and  $-2.36 \text{ e } \text{Å}^{-3}$  respectively. This high residual electron density is due to two remaining peaks of over 2.5 e less than 0.85 Å away from the two tungsten atoms (probably due to residual absorption effects). With the exception of these peaks, the residual electron density drops to 1.7 e. Many different absorption corrections including face-indexed numerical and semi-empirical based on azimuthal scans were tried, but an empirical correction using SHELXA-90<sup>19</sup> gave the lowest residual electron density (and  $R$  factor). The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively.

For both structures, computations were carried out on a 50 MHz 486DX PC computer using the SHELXTL PC program system.<sup>20</sup>

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

**General.**—Infrared spectra of the solids were measured over the range 4000–200  $\text{cm}^{-1}$  using KBr discs on a Perkin-Elmer 1720 Fourier-transform spectrometer, Raman spectra of the solids (as powders in melting-point tubes) on a Perkin-Elmer 1760X FT-IR instrument fitted with a 1700X NIR FT-Raman accessory using a Nd:YAG laser (1064 nm excitation). The NMR spectra were obtained on a JEOL ESX 270 spectrometer (<sup>31</sup>P, 109.25 MHz) as CD<sub>3</sub>OD or CD<sub>3</sub>CN solutions, using external H<sub>3</sub>PO<sub>4</sub> as reference. The gas chromatography data were obtained on a Perkin-Elmer Autosystem instrument using a Perkin-Elmer stainless-steel column (2 m) packed with 5% Carbowax 20M on Chromasorb WHP AW (DCMS treated). Microanalyses were carried out by the Microanalytical Laboratories at Imperial College.

The trioxides MoO<sub>3</sub>·H<sub>2</sub>O and WO<sub>3</sub>·H<sub>2</sub>O were obtained from BDH and Fluka Chemie AG, respectively, and PhPO(OH)<sub>2</sub>, MePO(OH)<sub>2</sub>, EtPO(OH)<sub>2</sub>, Bu<sup>n</sup>PO(OH)<sub>2</sub>, Bu<sup>t</sup>PO(OH)<sub>2</sub>, NMe<sub>4</sub>Cl and NBu<sup>n</sup>Cl were purchased from Aldrich; each of these materials was used without further purification. Hydrogen peroxide was obtained from BDH as a 30% w/v aqueous solution and was used as supplied.

**Syntheses.**—[NMe<sub>4</sub>]<sub>2</sub>[(PhPO<sub>3</sub>)<sub>2</sub>{MoO(O<sub>2</sub>)<sub>2</sub>}<sub>2</sub>{MoO(O<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)}] **1**. Hydrated molybdenum trioxide, MoO<sub>3</sub>·H<sub>2</sub>O (1.44 g, 10.0 mmol), was suspended in aqueous hydrogen peroxide solution (7 cm<sup>3</sup>, 30% w/v) and the resulting suspension stirred at 30 °C until a yellow solution was obtained. Upon cooling to ambient temperature, PhPO(OH)<sub>2</sub> (0.53 g, 3.33 mmol) in water (5 cm<sup>3</sup>) was added followed by dropwise addition of NMe<sub>4</sub>Cl (0.73 g, 6.67 mmol) in water (10 cm<sup>3</sup>). Ethanol (5 cm<sup>3</sup>) was added and the mixture was cooled to  $-15$  °C. The bright yellow crystalline solid was filtered off, washed with cold ethanol (2 × 5 cm<sup>3</sup>) and diethyl ether (10 cm<sup>3</sup>) and air dried. Yield 2.1 g, 2.47 mmol (74%) (Found: C, 19.7; H, 3.6; N, 3.1; O<sub>2</sub><sup>2-</sup>, 22.4. Calc. for C<sub>14</sub>H<sub>31</sub>Mo<sub>3</sub>N<sub>2</sub>O<sub>19</sub>P: C, 19.8; H, 3.7; N, 3.3; O<sub>2</sub><sup>2-</sup>, 22.6%). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  25.30.

[NMe<sub>4</sub>]<sub>2</sub>[(PhPO<sub>3</sub>)<sub>2</sub>{WO(O<sub>2</sub>)<sub>2</sub>}<sub>2</sub>{WO(O<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)}]·EtOH **2**. Hydrated tungsten trioxide, WO<sub>3</sub>·H<sub>2</sub>O (2.50 g, 10.0 mmol), was suspended in aqueous hydrogen peroxide solution (7 cm<sup>3</sup>, 30% w/v) and the resulting suspension stirred at 50 °C until a colourless solution was obtained. The solution was centrifuged to remove any undissolved residue then PhPO(OH)<sub>2</sub> (0.53 g, 3.33 mmol) in water (5 cm<sup>3</sup>) was added followed by dropwise addition of NMe<sub>4</sub>Cl (0.73 g, 6.67 mmol) in water (10 cm<sup>3</sup>). Ethanol (5 cm<sup>3</sup>) was added and the mixture was cooled to  $-15$  °C. The colourless microcrystalline solid was filtered off, washed with cold ethanol (2 × 5 cm<sup>3</sup>) and diethyl ether (10 cm<sup>3</sup>) and air dried. Yield 2.8 g, 2.42 mmol (73%) (Found: C,

16.7; H, 2.8; N, 2.4; O<sub>2</sub><sup>2-</sup>, 16.4. Calc. for C<sub>16</sub>H<sub>37</sub>N<sub>2</sub>O<sub>20</sub>PW<sub>3</sub>: C, 16.6; H, 3.2; N, 2.4; O<sub>2</sub><sup>2-</sup>, 16.7%). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$  15.81 (<sup>2</sup>J<sub>P-W</sub> = 18 Hz).

[NMe<sub>4</sub>]<sub>2</sub>[(RPO<sub>3</sub>)<sub>2</sub>{MoO(O<sub>2</sub>)<sub>2</sub>}<sub>2</sub>{MoO(O<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)}] (R = Me, Et, Bu<sup>n</sup> or Bu<sup>t</sup>). These complexes were prepared by a similar procedure to that described above giving yellow crystalline solids. R = Me, yield 2.2 g, 2.79 mmol (84%) (Found: C, 13.9; H, 3.4; N, 3.6; O<sub>2</sub><sup>2-</sup>, 24.1. Calc. for C<sub>9</sub>H<sub>29</sub>Mo<sub>3</sub>N<sub>2</sub>O<sub>19</sub>P: C, 13.7; H, 3.7; N, 3.6; O<sub>2</sub><sup>2-</sup>, 24.4%). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  38.14. R = Et, yield 1.8 g, 2.24 mmol (67%) (Found: C, 14.9; H, 3.7; N, 3.6. Calc. for C<sub>10</sub>H<sub>31</sub>Mo<sub>3</sub>N<sub>2</sub>O<sub>19</sub>P: C, 15.0; H, 4.0; N, 3.5%). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  38.56. R = Bu<sup>n</sup>, yield 2.3 g, 2.77 mmol (83%) (Found: C, 17.4; H, 4.0; N, 3.4. Calc. for C<sub>12</sub>H<sub>35</sub>Mo<sub>3</sub>N<sub>2</sub>O<sub>19</sub>P: C, 17.4; H, 4.3; N, 3.4%). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  39.99. R = Bu<sup>t</sup>, yield 2.4 g, 2.89 mmol (87%) (Found: C, 17.5; H, 4.0; N, 3.4. Calc. for C<sub>12</sub>H<sub>35</sub>Mo<sub>3</sub>N<sub>2</sub>O<sub>19</sub>P: C, 17.4; H, 4.3; N, 3.4%). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>3</sub>OD):  $\delta$  39.42.

[NBu<sub>4</sub>]<sub>2</sub>[W<sub>4</sub>O<sub>6</sub>(O<sub>2</sub>)<sub>6</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] **3**. Hydrated tungsten trioxide, WO<sub>3</sub>·H<sub>2</sub>O (1.25 g, 5.0 mmol), was suspended in hydrogen peroxide (4 cm<sup>3</sup>, 30% w/v) and stirred at 50 °C until a colourless solution was obtained. The mixture was centrifuged to remove any insoluble residues and the resulting solution was adjusted to pH 1.5 with H<sub>2</sub>SO<sub>4</sub> (2.0 mol dm<sup>-3</sup>). Tetrabutylammonium chloride (2.78 g, 10.0 mmol) in water (10 cm<sup>3</sup>) was added dropwise. Ethanol (5 cm<sup>3</sup>) was added and the solution cooled to 4 °C. The colourless crystalline solid was filtered off, washed with cold ethanol (2 × 5 cm<sup>3</sup>) and diethyl ether (10 cm<sup>3</sup>) and air dried. Yield 1.25 g, 0.79 mmol (63%) (Found: C, 24.6; H, 4.8; N, 1.8; O<sub>2</sub><sup>2-</sup>, 12.5. Calc. for C<sub>32</sub>H<sub>78</sub>N<sub>2</sub>O<sub>22</sub>W<sub>4</sub>: C, 24.4; H, 5.0; N, 1.8; O<sub>2</sub><sup>2-</sup>, 12.2%).

**General Procedure for Epoxidation of Cycloalkenes.**—The catalyst (**2** or **3**) (0.06 mmol) was dissolved in benzene (5 cm<sup>3</sup>) and the cycloalkene (25 mmol) was added. Hydrogen peroxide (15% w/v, 6 cm<sup>3</sup>) was added to the organic component and the biphasic mixture was refluxed at 70 °C for 3 h. The resulting organic layer was then analysed by gas chromatography.

**General Procedure for Epoxidation of Linear Alkenes.**—The catalyst (**2** or **3**) (0.06 mmol) was dissolved in benzene (5 cm<sup>3</sup>) and the alkene (10 mmol) was added. Hydrogen peroxide (15% w/v, 12 cm<sup>3</sup>) was added to the benzene solution and the biphasic mixture was refluxed at 70 °C for 20 h. The resulting organic layer was then analysed by gas chromatography and/or by <sup>1</sup>H NMR spectroscopy.

**General Procedure for Oxidation of Primary and Secondary Alcohols.**—The catalyst (**2**) (0.06 mmol) was dissolved in benzene (5 cm<sup>3</sup>) and the alcohol (10 mmol) was added. Hydrogen peroxide (15% w/v, 10 cm<sup>3</sup>) was added to the benzene solution and the biphasic mixture was refluxed at 70 °C for 3 h. The resulting organic layer was then analysed by gas chromatography and/or by gas chromatography/mass spectrometry.

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