A Novel Hexanuclear Heteropolyperoxo Oxidation Catalyst: Preparation, X-Ray Crystal Structure and Reactions of $[NMe_4]_3[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]\cdot 4H_2O$

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The crystal structure of the title compound, **1**, reveals the presence of two distinct types of tungsten atom in which the four bearing peroxo groups have distorted pentagonal-bipyramidal geometries and the remaining two are octahedral; **1** is an effective catalyst for monoalkene epoxidation, and the oxidation of primary and secondary alcohols, with H_2O_2 as co-oxidant.

The chemistry of iso- and hetero-polyperoxo complexes is of considerable current interest, since some of these unusual complexes are alkene epoxidation catalysts with the environmentally acceptable H_2O_2 as co-oxidant.[1–7] During studies on the synthesis of heteropolyperoxotungstates with organophosphonates and organoarsonates we isolated the hexanuclear complex $[NMe_4]_3[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]\cdot 4H_2O$ **1** which has a unique structure. Furthermore, it is an efficient catalyst for the epoxidation of alkenes and the oxidation of alcohols to aldehydes or ketones, each in the presence of H_2O_2 as co-oxidant.

Colourless crystals of **1** were obtained by reacting stoichiometric amounts of $WO_3\cdot H_2O$, H_2O_2 and $MePO(OH)_2$ with a slight excess of $(NMe_4)Cl$ in water–ethanol (70 : 30), followed by storage at 0 °C for 3 days.† The X-ray analysis‡ reveals the complex to contain six independent tungsten centres that can be divided into two types: either six- or seven-coordinate. The two six-coordinate centres, W(3) and W(6) (Fig. 1), have distorted octahedral geometries, with angles at tungsten in the ranges 72–104° and 154–170°. The two metal atoms each coordinate a single terminal oxo donor [1.730(13) and 1.700(12) Å for W(3) and W(6), respectively] and five oxide ligands. The latter fall into three distinct types, (i) three μ(W–O–W) bridging oxygen atoms [1.819(12)–1.921(13) Å], (ii) one μ(W–O–P) bridging atom [W–O 2.067(14) and 2.100(12), O–P 1.553(13) and 1.520(18) Å] and (iii) one μ_3-oxygen atom bridging three tungsten centres [W–O 2.181(12) and 2.254(11) Å]. (In both these latter instances the μ_3-oxide is *trans* to oxo.)

The four seven-coordinate centres, W(1), W(2), W(4) and W(5), all have pentagonal-bipyramidal geometries. Each centre carries an equatorial, symmetric, η^2-peroxo ligand [W–O in the range 1.907(13)–1.960(14), O–O in the range 1.403(18)–1.470(20) and O–W–O angles in the range 42.4(6)–44.8(6)°] with the other equatorial sites being occupied by a μ-oxide [W–O 1.962(17)–1.988(13) Å], a μ-hydroxide [W–O 2.032(11)–2.083(13) Å] and a μ_3-oxide [W–O 1.977(10)–2.032(13) Å]. In all four cases one of the axial positions is filled by an oxo ligand [1.686(11)–1.713(18) Å]; the other axial site, however, is in three instances occupied by a μ(W–O–P) bridging oxygen atom [W–O 2.189(15)–2.264(11), O–P 1.510(12)–1.519(16) Å] whilst in the fourth instance [W(5)] this site is filled by a terminal aqua ligand at a characteristically long distance [W(5)–O(54) 2.299(11) Å]. The W–O bond lengths within the complex are generally as expected. The distances from W(3) and W(6) to the μ_3-oxide atoms [O(14) and O(44), respectively], however, are significantly longer [at 2.181(12) and 2.254(11) Å] than the other two bonds to these μ_3-oxides [1.977(10)–2.032(13) Å] reflecting the *trans* effect of the terminal oxo ligands on W(3) and W(6). The shortest W···W contact within the complex is 3.23 Å between W(1) and W(3).

The identification of the O(15) and O(45) centres as hydroxy groups has been arrived at on the basis of the noticeably longer bonds to these two atoms (all >2.0 Å whereas those to the W–O–W μ-oxide atoms are all <2.0 Å). This assignment is also consistent with the charge requirement of the complex anion.

As in other heteropolyperoxotungstates,[5] all four pentagonal-bipyramidal centres have their tungsten atoms displaced out of the plane of the equatorial substituents towards their oxo ligand (deviations in the range 0.25–0.29 Å).

The two tetrahedral methylphosphonate ligands are chemically inequivalent, consistent with the $^{31}P\{^1H\}$ NMR data (see below). The P(1) phosphonate forms three P–O–W bridges [P–O 1.510(12)–1.553(13) Å] whilst the P(2) phosphonate forms only two such linkages [P–O 1.514(15) and 1.520(18) Å]. The third oxygen atom on this latter centre, O(5), remains protonated [P(2)–O(5) 1.561(13) Å] and is involved in strong intercomplex O–H···O hydrogen bonding to form dimer pairs [O(5)···O(4A) 2.67 Å]. These pairs are in turn linked *via* further strong O–H···O hydrogen bonds to one of the included solvent water molecules [O(1)···O(71) 2.73, O(71)···O(15A) 2.57 Å] to form chains that extend in the crystallographic $1\bar{1}\bar{1}$ direction.

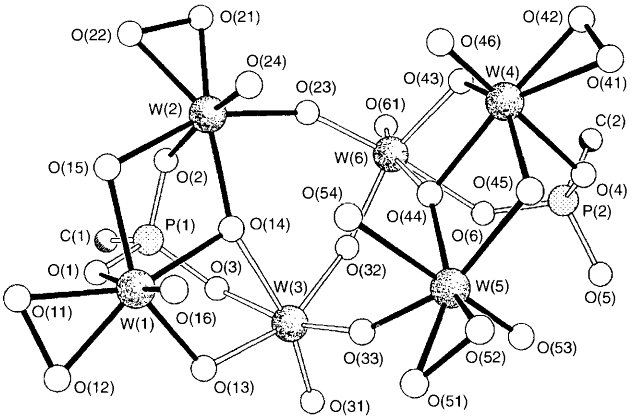

Fig. 1 X-Ray crystal structure of the hexatungstate trianion of **1**. Selected bond lengths (Å) and angles (°): W(1)–O(1) 2.193(14), W(1)–O(11) 1.933(15), W(1)–O(12) 1.922(18), W(1)–O(13) 1.965(12), W(1)–O(14) 2.032(13), W(1)–O(15) 2.055(12), W(1)–O(16) 1.713(18), W(2)–O(2) 2.189(15), W(2)–O(14) 2.003(12), W(2)–O(15) 2.083(13), W(2)–O(21) 1.907(13), W(2)–O(22) 1.923(13), W(2)–O(23) 1.988(13), W(2)–O(24) 1.713(17), W(3)–O(3) 2.067(14), W(3)–O(13) 1.900(12), W(3)–O(14) 2.181(12), W(3)–O(31) 1.730(13), W(3)–O(32) 1.921(13), W(3)–O(33) 1.850(15), W(4)–O(4) 2.264(11), W(4)–O(41) 1.927(19), W(4)–O(42) 1.953(18), W(4)–O(43) 1.965(13), W(4)–O(44) 2.027(15), W(4)–O(45) 2.032(11), W(4)–O(46) 1.698(11), W(5)–O(33) 1.962(17), W(5)–O(44) 1.977(10), W(5)–O(45) 2.073(17), W(5)–O(51) 1.960(14), W(5)–O(52) 1.948(13), W(5)–O(53) 1.686(11), W(5)–O(54) 2.299(11), W(6)–O(6) 2.100(12), W(6)–O(23) 1.819(12), W(6)–O(32) 1.879(15), W(6)–O(43) 1.917(17), W(6)–O(44) 2.254(11), W(6)–O(61) 1.700(12), P(1)–C(1) 1.773(23), P(1)–O(1) 1.510(12), P(1)–O(2) 1.519(16), P(1)–O(3) 1.553(13), P(2)–C(2) 1.692(21), P(2)–O(4) 1.514(15), P(2)–O(5) 1.561(13), P(2)–O(6) 1.520(18), O(11)–O(12) 1.470(20), O(21)–O(22) 1.414(21), O(41)–O(42) 1.403(18), O(51)–O(52) 1.450(27), W(1)–O(1)–P(1) 119.9(10), W(2)–O(2)–P(1) 124.7(6), W(3)–O(3)–P(1) 126.9(8), W(4)–O(4)–P(2) 126.1(8), W(6)–O(6)–P(2) 129.2(9), W(1)–O(14)–W(2) 109.5(5), W(1)–O(14)–W(3) 100.0(6), W(2)–O(14)–W(3) 145.6(5), W(2)–O(23)–W(6) 152.9(7), W(3)–O(32)–W(6) 143.9(7), W(3)–O(33)–W(5) 153.3(7), W(4)–O(44)–W(5) 110.0(6), W(4)–O(44)–W(6) 98.4(4), W(5)–O(44)–W(6) 148.3(7).

Though the other full- and partial-occupancy water molecules are extensively hydrogen bonded, they do not form any additional interanion linkages.

In the presence of the phase transfer cation, $[N(n\text{-}C_6H_{13})_4]Cl$ in a 1 : 4 (complex : cation) ratio, **1** cleanly catalyses the epoxidation of a number of cyclic and linear alkenes (Table 1) in a biphasic benzene—15% aqueous H_2O_2 mixture at 70 °C; conditions similar to those used for epoxidation by $[N(n\text{-}C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$.[2] Typically, 0.03 mmol of **1**, 0.12 mmol of $[N(n\text{-}C_6H_{13})_4]Cl$ and 10 mmol of substrate were dissolved in benzene (10 cm^3) and 7.0 cm^3 of 15% *m*/*v* H_2O_2 added. The mixture was stirred at 70 °C for 3 h, after which time the products were characterised by GC and their purity checked by ^{1}H NMR spectroscopy. Complex **1** is thus as effective a catalyst as $[N(n\text{-}C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ in respect of both yields and turnovers.[2] The oxidations are stereospecific (thus *cis*- and *trans*-stilbene gave *cis*- and *trans*-stilbene oxide, respectively) and the ^{1}H NMR of the epoxides, in all cases, show no evidence of contamination by side products. As with $[N(n\text{-}C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$,[2] **1** oxidises primary alcohols to aldehydes and secondary alcohols to ketones (Table 2).

Table 1 Oxidation of linear and cycloalkenes by $[NMe_4]_3[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]^a$

Substrate	Product	Yield (%)	Turnover^b
Cyclopentene	Epoxycyclopentane	90	307
Cyclohexene	Epoxycyclohexane	36	122
Cycloheptene	Epoxycycloheptane	74	248
Cyclooctene	Epoxycyclooctane	97	323
Cyclododecene	Epoxycyclododecane	63	211
cis-Stilbene	*cis*-Stilbeneoxide	24	80
trans-Stilbene	*trans*-Stilbeneoxide	77	257
2,3-Dimethylbut-2-ene	2,3-Dimethyl-2,3-epoxybutane	96	320
2,4,4-Trimethylpent-2-ene	2,3-Epoxy-2,4,4-trimethylpentane	32	107
Dec-1-ene^c	1,2-Epoxydecane	65	218
Undec-1-ene^c	1,2-Epoxyundecane	57	189
Dodec-1-ene^c	1,2-Epoxydodecane	42	140

^{a} Oxidations carried out at 70 °C for 3 h with H_2O_2 as co-oxidant. ^{b} Turnover = mol product (mol catalyst)$^{-1}$. ^{c} As for *a* but for 20 h.

Table 2 Oxidation of primary and secondary alcohols by $[NMe_4]_3[(MePO_3)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(OH_2)]^a$

Substrate	Product	Yield (%)	Turnover^b
Benzyl alcohol	Benzaldehyde	84	282
2-Methylbenzyl alcohol	2-Methylbenzaldehyde	98	327
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	99	331
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	39	129
Piperonyl alcohol	Piperonaldehyde	35	117
(±)-Menthol	(±)-Menthone	65	218
(±)-1-Phenylethanol	Acetophenone	99	330
Cyclopentanol	Cyclopentanone	31	103
Cyclohexanol	Cyclohexanone	59	196
2-Methylcyclohexanol	2-Methylcyclohexanone	92	308
3-Methylcyclohexanol	3-Methylcyclohexanone	85	284
4-Methylcyclohexanol	4-Methylcyclohexanone	88	293
Cycloheptanol	Cycloheptanone	>99	332
Cyclooctanol	Cyclooctanone	80	265

^{a} Oxidations carried out at 70 °C for 3 h with H_2O_2 as co-oxidant. ^{b} Turnover = mol product (mol catalyst)$^{-1}$.

The ^{31}P NMR spectrum of **1** in CD_3CN shows chemical shifts at δ 34.51 and 35.67 (relative to H_3PO_4) with poorly resolved tungsten satellites, consistent with the presence of two distinct phosphorus environments. Addition of H_2O_2 to this solution results in the immediate disappearance of these signals and the emergence of a peak at δ 30.96 with a smaller peak at δ 32.24. The most probable explanation of this observation is that in the presence of H_2O_2, the hexanuclear unit breaks up, generating the trinuclear species $[NMe_4]_2[MePO_3\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]$, analogous to the known complex $[NMe_4]_2[PhPO_3\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]$; the latter is an effective catalyst probably by virtue of the asymmetric η^1,η^2-peroxo linkages it contains.[5] The smaller peak further downfield may arise from a dinuclear species, possibly $[NMe_4]_2[MePO_3\{WO(O_2)_2\}_2]$. Similar chemical shift patterns have been observed for aqueous solutions[2] of $[PO_4\{WO(O_2)_2\}_4]^{3-}$. IR and Raman spectra of **1** show, in addition to bands arising from the $MePO_3$ moiety, bands at *ca.* 960, 864, 595 and 535 cm^{-1} assigned to $\nu(W{=}O)$, $\nu(O\text{–}O)$, $\nu_{asym}[W(O_2)]$ and $\nu_{sym}[W(O_2)]$, respectively, similar to those found in $[(NMe_4)_2][PhPO_3\{MO(O_2)_2\}_2\{MO(O_2)_2(H_2O)\}]$ (M = Mo, W).[5]

The results described above demonstrate that polynuclear polyperoxo species, as exemplified by **1**, are clean, stereospecific and efficient catalysts for alkene epoxidations with H_2O_2 as co-oxidant.

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Footnotes

† Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **1**: $C_{14}H_{47}N_3O_{30}P_2W_6{\cdot}4H_2O$, M = 1974.7, triclinic, space group $P\bar{1}$, a = 10.842(2), b = 14.649(2), c = 16.650(2) Å, α = 68.01(2), β = 76.27(2), γ = 70.86(2)°, U = 2297(1) Å^3, Z = 2, D_c = 2.86 g cm^{-3}, μ(Mo-Kα) = 151 cm^{-1}, $F(000)$ = 1812. A clear block of dimensions 0.33 × 0.10 × 0.10 mm was used. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods and the full-occupancy non-hydrogen atoms refined anisotropically using full-matrix least squares to give R = 0.046, R_w = 0.049 [$w^{-1} = \sigma^2(F) + 0.0007F^2$] for 4489 independent, observed, absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 45°$].[8] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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