www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 607 (2000) 146–155

Journal of Organometallic Chemistry

Studies on polyoxo and polyperoxo-metalates☆ Part 7. Lanthano- and thoriopolyoxotungstates as catalytic oxidants with H_2O_2 and the X-ray crystal structure of $Na_8[ThW_{10}O_{36}]\cdot 28H_2O$

William P. Griffith *, Neil Morley-Smith, Helena I.S. Nogueira, Abdel G.F. Shoair, Maria Suriaatmaja, Andrew J.P. White, David J. Williams

Department of Chemistry (Inorganic Chemistry), Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

Received 13 March 2000; received in revised form 5 May 2000; accepted 15 May 2000

Dedicated to Professor Martin Bennett, FRS, a great chemist and a good friend since our joint undergraduate and postgraduate days at Imperial College.

Abstract

The effectiveness of salts of $[Ln^{III}W_{10}O_{36}]^{9-}$ (Ln = Y, La, Ce, Pr, Sm, Eu, Gd, Dy, Er, Lu) and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th) as catalysts with H_2O_2 for alcohol oxidations and alkene epoxidations has been studied. It appears that catalysis arises from the polyperoxotungstates formed from H_2O_2. The X-ray crystal structure of the title complex shows that in the $[ThW_{10}O_{36}]^{8-}$ anion the thorium has square antiprismatic geometry in which eight oxygen atoms from two W_5O_{18} moieties form vertex-sharing bonds; Raman data suggest that the structure of the anion is retained in aqueous solution. New $^{31}P[^1H]$-NMR data for $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Yb, Lu) and $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$ in the solid state, in water and in H_2O_2 solution are presented; these species have also been used for oxidation catalysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxidation catalysis; X-ray crystal structure; Lanthanides; Thorium; Polyoxotungstates

---

1. Introduction

There is currently much interest in the use of polyoxometalates as useful catalysts for specific organic oxidations [2]; this paper concerns the use of lanthanopolyoxotungstates and a thoriopolyoxotungstate as catalysts for alcohol and alkene oxidations with H_2O_2 as co-oxidant.

It has been reported that sodium salts of $[LnW_{10}O_{36}]^{9-}$ (Ln = Nd, Sm) and $[Ce^{IV}W_{10}O_{36}]^{8-}$ will catalyse, with H_2O_2, the oxidation of cyclohexanol to cyclohexanone [3], and that $R_7H_2[LnW_{10}O_{36}]$ salts (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb; R = cetylpyridinium, $(Me(CH_2)_{15}NC_5H_5)^+$) catalyse oxidations of benzyl alcohol to benzaldehyde and 2-octanol to octanone [4–7]. Heavier rather than lighter lanthanides were found to be slightly more effective, the reverse being the case for epoxidation of cyclooctene; the cerium complex is an anomalously poor catalyst [8]. Attempts were made to correlate such effects with the f orbital occupancy of the lanthanides [5,9].

In preliminary work we showed that oxidation catalysis with sodium and mixed sodium–tetramethylammonium salts of $[LnW_{10}O_{36}]^{9-}$ and $[Ce^{IV}W_{10}O_{36}]^{8-}$ in refluxing ^{t}BuOH–H_2O_2, is equally well effected by tungstate in the absence of lanthanide [10]. Here we re-examine claims [2–9] made for the efficacy of $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[Ce^{IV}W_{10}O_{36}]^{8-}$ as catalysts with H_2O_2 for the oxidation of alcohols and alkenes using their sodium, cetylpyridinium and *n*-hexylammonium salts. We have prepared and similarly used salts of

---

☆ For Part 6, see Ref. [1].

* Corresponding author. fax: + 44-20-7594-5804.

E-mail address: wgriffith@ic.ac.uk (W.P. Griffith).

PII: S0022-328X(00)00308-9

$[Th^{IV}W_{10}O_{36}]^{8-}$ and report for the first time the X-ray crystal structure of its sodium salt and its Raman spectra. New spectroscopic data for lanthanophosphopolyoxotungstates $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$, earlier studied as oxidation catalysts with H_2O_2 [11], are also presented.

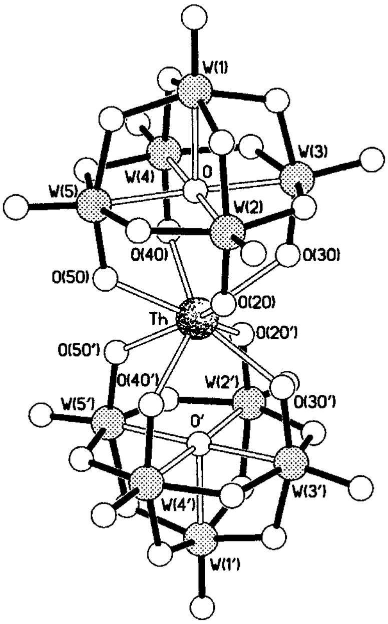

Fig. 1. Ball-and-stick representation of the anionic $[ThW_{10}O_{36}]^{8-}$ thoriopolyoxotungstate unit.

Table 1
Selected bond lengths (Å) for **1** [a]

Th–O(20)	2.444(12)	Th–O(30)	2.455(14)
Th–O(40)	2.454(14)	Th–O(50)	2.447(13)
W(1)–O	2.340(13)	W(1)–O(1)	1.714(12)
W(1)–O(12)	1.92(2)	W(1)–O(13)	1.920(13)
W(1)–O(14)	1.922(13)	W(1)–O(15)	1.91(2)
W(2)–O	2.326(14)	W(2)–O(2)	1.717(12)
W(2)–O(12)	2.013(14)	W(2)–O(20)	1.789(12)
W(2)–O(23)	1.934(14)	W(2)–O(25)	1.954(14)
W(3)–O	2.319(13)	W(3)–O(3)	1.722(14)
W(3)–O(13)	1.988(13)	W(3)–O(23)	1.942(13)
W(3)–O(30)	1.785(14)	W(3)–O(34)	1.944(14)
W(4)–O	2.354(14)	W(4)–O(4)	1.703(14)
W(4)–O(14)	1.99(2)	W(4)–O(34)	1.961(14)
W(4)–O(40)	1.792(14)	W(4)–O(45)	1.937(14)
W(5)–O	2.312(13)	W(5)–O(5)	1.742(14)
W(5)–O(15)	1.99(2)	W(5)–O(25)	1.953(13)
W(5)–O(45)	1.929(13)	W(5)–O(50)	1.792(14)

[a] The oxo ligand oxygen atoms carry the same numbers as their parent tungsten atoms; the bridging oxygen atoms carry the numbers of the two tungsten atoms being bridged, the lower numbered tungsten always coming first, e.g. the oxygen bridging W(1) and W(5) is O(15) and that bridging W(2) and W(3) is O(23), etc.

2. Results and discussion

2.1. Sodium salts of $[Ln^{III}W_{10}O_{36}]^{9-}$ and of $[M^{IV}W_{10}O_{36}]^{8-}$ ($M = Ce$, Th)

These are made by reaction of $Na_2[WO_4]$ and the lanthanide nitrate at pH 7.0–7.5 [12]; the first to be crystallographically characterised was $Na_6H_2[Ce^{IV}W_{10}O_{36}]\cdot 30H_2O$ [13]. The stoicheiometries of $Na_6H_3[SmW_{10}O_{36}]\cdot 28H_2O$ [14] and $Na_8H[GdW_{10}O_{36}]\cdot 30H_2O$ [15] have been established by single-crystal X-ray studies. Thus it is clear that the sodium and water contents can be variable; analyses of our products are most consistent with $Na_9[W_{10}O_{36}]\cdot nH_2O$, with n varying between 20–38.

The less effective catalytic properties of salts of $[Ce^{IV}W_{10}O_{36}]^{8-}$ noted by Kera et al. [8] and by us for cetylpyridinium salts (see below) could arise from tighter bonding between the tetravalent cerium centre and the eight donor oxygen atoms of the two W_5O_{18} moieties to which it is coordinated. To explore this possibility we made another complex with a tetravalent centre, the thoriopolyoxotungstate $N_8[ThW_{10}O_{36}]\cdot 28H_2O$.

2.2. $Na_8[ThW_{10}O_{36}]\cdot 28H_2O$; formulation, X-ray crystal structure and Raman spectra

Reaction of thorium nitrate with hot aqueous sodium tungstate at pH 7.3, a method similar to those used for making $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[Ce^{IV}W_{10}O_{36}]^{8-}$, was reported in 1971 to give $Na_4[ThW_8O_{28}]\cdot 25H_2O$ [16], subsequently reformulated as $Na_6[W_{10}O_{35}]\cdot 27H_2O$ [17]. Although it has been suggested [18] that a better formulation would be $N_8[ThW_{10}O_{36}]\cdot 30H_2O$, no X-ray data have been reported. We have repeated the literature preparations [16,17] and obtained crystals which, after X-ray analysis, proved the formulation to be $Na_8[ThW_{10}O_{36}]\cdot 28H_2O$.

This X-ray analysis shows the thorium complex to be isomorphous with the $Na_6H_2[Ce^{IV}W_{10}O_{36}]\cdot 30H_2O$ [13] and $Na_8[U^{IV}W_{10}O_{36}]\cdot 30H_2O$ [19] analogues, the only disparities being in the assessment of the numbers of sodium ions and water molecules present. The thorium structure matches most closely that of the uranium complex, having ten tungsten atoms and eight distinct sodium cations per thorium centre; only 28 water molecules, however, were identified. The structure (Fig. 1) has crystallographic C_2 symmetry about an axis passing through the thorium atom and normal to the W(1)–Th–W(1′) vector. The geometry at thorium is almost perfect square antiprismatic, the degree of stagger between the upper and lower faces being less than 1° from ideal.

The Th–O distances (Table 1) are typical and lie in the range 2.444(12)–2.455(14) Å, cf. between 2.29 and

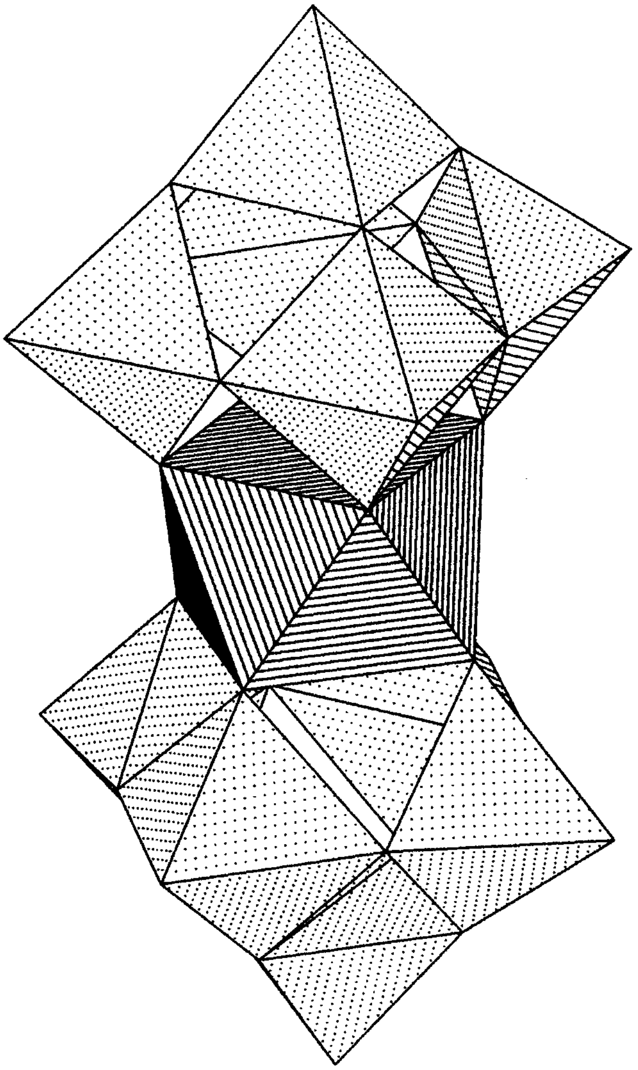

Fig. 2. Polyhedral representation of the octa-anionic $[ThW_{10}O_{36}]^{8-}$ moiety showing the vertex sharing of the square pyramidal WO_5 and square antiprismatic ThO_8 units.

2.32 Å in $Na_8[U^{IV}W_{10}O_{36}]\cdot 30H_2O$ [19]. The W–O distances fall, as expected, into four distinct groups with those to the terminal oxo ligands in the range 1.703(14)–1.742(14) Å, those bridging between two tungsten atoms 1.91(2)–2.013(14) Å, those between tungsten and thorium 1.785(14)–1.792(14) Å whilst those to the 'core' oxygen atom are between 2.312(13) and 2.354(14) Å. It is interesting to note that the 'core' oxygen atom (O) lies only 0.04 Å out of the plane of its equatorially bonded tungsten atoms W(2), W(3), W(4) and W(5) in the direction of W(1); the non-bonded O–Th distance is 3.07 Å. The geometries at each tungsten centre exhibit the normal distortion with the metal atom being displaced in the direction of its oxo ligand. We have observed this effect in other oxotungstates and polyperoxotungstates [20].

In the context of the 'polyhedral' structure (Fig. 2), the five WO_5 square pyramids (discounting the long contacts to the 'core' oxygen atom) and the ThO_8 square antiprism are all vertex linked. The sodium cations are all octahedrally coordinated (though significantly distorted) and edge-sharing. Only two of these NaO_6 octahedra contact the polyoxo anion, in each case sharing an oxo ligand apex [O(3) and O(4), bonded to W(3) and W(4), respectively], approach to the other oxo ligands being by water molecules.

The Raman spectrum of solid $Na_8[ThW_{10}O_{36}]\cdot 28H_2O$ is shown in Fig. 3(a) and that of its saturated aqueous solution in Fig. 3(b). Although there is substantial solid-state splitting in the ν(W=O) region near 1000 cm^{-1} the general similarity of the two profiles suggests retention of the structure of the anion in aqueous solution.

2.3. Oxidations with H_2O_2 catalysed by $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th)

2.3.1. With sodium salts

Our earlier work on catalysis of oxidations by sodium salts of $[LnW_{10}O_{36}]^{n-}$ was incomplete since a variety of sodium and mixed sodium-tetra-alkylammonium salts were used [10]. In Table 2 we report oxidations of benzyl alcohol to benzaldehyde and cyclohexanol to cyclohexanone, catalysed by sodium salts of $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th) in $CHCl_3$–H_2O_2 in the absence of a phase-transfer reagent. Oxidations of 2-octanol by H_2O_2 in the presence of these species gave only small yields of 2-octanone (< 5%) as did oxidations of cyclo-octene to cyclo-octene oxide (< 10%). These species do catalyse oxidations with H_2O_2 but not very efficiently, presumably due to the monophasic nature of the solvent in which they are soluble (aqueous H_2O_2). Oxidations of benzyl alcohol give only benzaldehyde; no attack on the benzene ring is observed, although others have reported that in some cases of oxidation of this alcohol, ring attack may be observed [21].

The $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ salts are made from $Na_2[WO_4]$ and the lanthanide or thorium nitrate at pH 7.3; use of a $Na_2[WO_4]$ solution at pH 7.3 in the absence of lanthanide or thorium gives the 'blank' species referred to in Table 2, and clearly this is as effective a catalyst as $[Ln^{III}W_{10}O_{36}]^{9-}$ or $[M^{IV}W_{10}O_{36}]^{8-}$. From published ^{183}W and ^{17}O-NMR data it is known that in aqueous tungstate at pH 7.0–7.5 the predominant species are the interchanging paratungstates $[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$ [22,23]. The Raman spectra of such paratungstates in solution (made by adjusting aqueous $[WO_4]^{2-}$ to pH 7) are very different from that of aqueous tungstate, but we find that paratungstate solutions in excess H_2O_2 give Raman spectra which am very similar in profile to that [24] of $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. The latter species is known to catalyse the oxidation in H_2O_2 of alcohols [24–26] and of alkenes [25]. Further, we show in Fig. 3(c) the Raman spectrum of a solution of $Na_8[ThW_{10}O_{36}]\cdot28H_2O$ in excess H_2O_2; this is essentially identical in profile with that of paratungstate in H_2O_2 (the band at 880 cm^{-1} is due to free H_2O_2), while this in turn is very similar to that of $[SmW_{10}O_{36}]^{9-}$ in H_2O_2 [10]. We conclude that the spectrum in Fig. 3(c) arises from $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. Of the strongest Raman bands in Fig. 3(c), that at 968 cm^{-1} arises from ν(W=O) and those at 858, 622 and 566 cm^{-1} are likely to be due to ν(O–O), $\nu^s(W(O_2))$ and $\nu^{as}(W(O_2))$, respectively of the coordinated peroxo ligands, using our previous assignments for normal and ^{18}O substituted $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ [24].

From these Raman data and the fact that paratungstate in H_2O_2 is as effective as $[LnW_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th) as oxidation catalysts (as is also the case for their salts with quaternary ammonium cations, see Section 2.3.2) it is clear that $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ is the effective catalyst for all these systems.

2.3.2. With quaternary phase-transfer amine cations

Kera et al. have made a number of salts $R_7H_2[LnW_{10}O_{36}]$ and $R_8[Ce^{IV}W_{10}O_{36}]$ (R = cetylypyridinium, $(Me(CH_2)_{15}NC_5H_5)^+$) [4–8], finding their elemental analyses to be $R_7H_2[Ln^{III}W_{10}O_{36}]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb) [6,8] and the cerium(IV) complex as $R_8[CeW_{10}O_{36}]$ [5]. They have used them as catalysts with $CHCl_3$–aqueous H_2O_2 for oxidations of alcohols and alkenes [4–8]. We have made such salts of $[Ln^{III}W_{10}O_{36}]^{9-}$ (Ln = La, Ce, Pr, Sm, Eu, Gd, Dy, Ho, Er, Lu) and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th). Our analyses agree in general with those of Kera et al. although the samarium and holmium complexes analyse as $R_8H[LnW_{10}O_{36}]$, and the cerium and thorium complexes as $R_8[MW_{10}O_{36}]$.

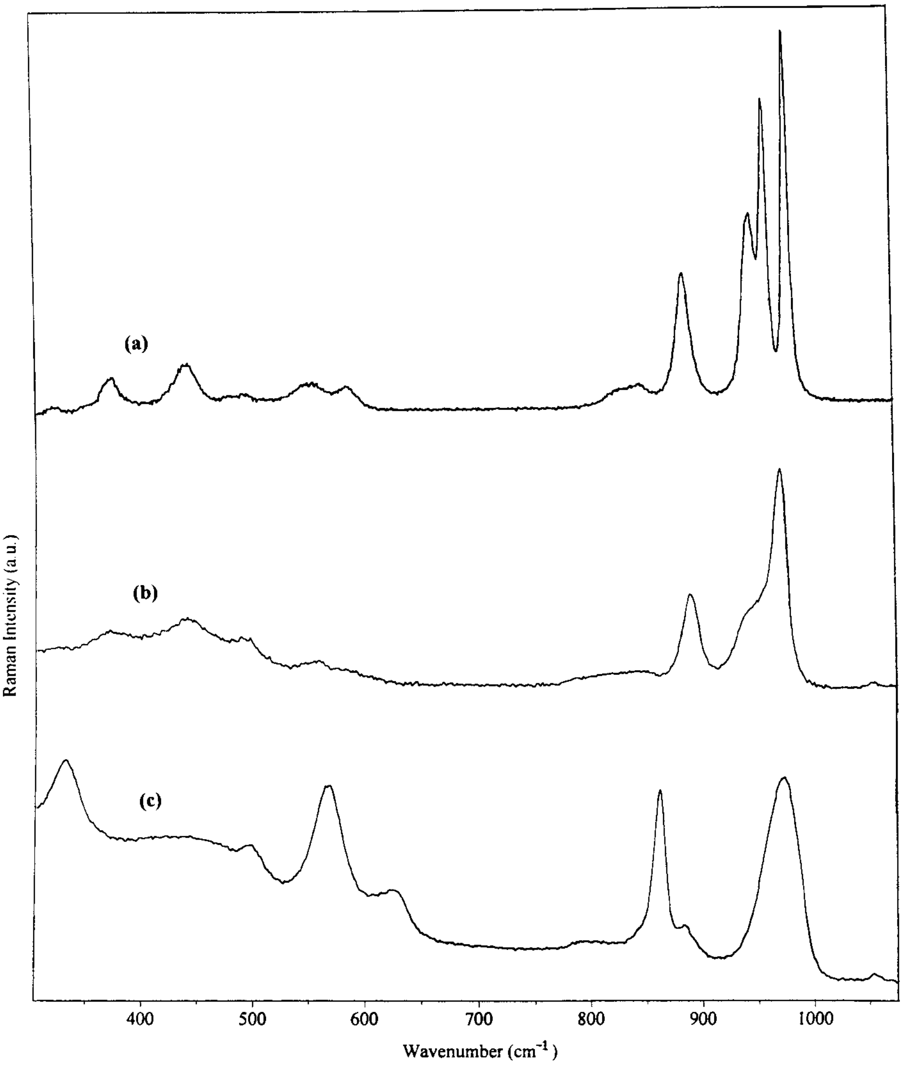

Fig. 3. (a) Raman spectrum of solid $Na_8[ThW_{10}O_{36}]\cdot28H_2O$, (b) Raman spectrum of a saturated aqueous solution of $Na_8[ThW_{10}O_{36}]\cdot28H_2O$, (c) Raman spectrum of a solution of an aqueous solution of $Na_8[ThW_{10}O_{36}]\cdot28H_2O$ (0.2 g in 5 cm^3) and 0.2 cm^3 aqueous 30% H_2O_2. All spectra run with a frequency-doubled Nd-YAG laser at 15 mW power.

Data on these salts as catalysts for oxidations of benzyl alcohol, cyclohexanol, 2-octanol and cyclo-octene are given in Table 2. At first we used the literature conditions (a 6 h treatment with 1:1 $CHCl_3$–H_2O_2) [6] but found that oxidations for 3 h gave very similar yields of products. In general the trends in our yields of oxidation products are similar to those reported [4–8] but, unlike the previous work, we report catalytic turnover numbers, calculated using the molecular weights of the lanthanopolyoxotungstates. The previous workers did not carry out 'blank' runs in which a polyoxotungstate was used in place of a lanthanopolyoxotungstate, apart from showing in one instance that $(^nBu_4N)_4[W_{10}O_{32}]$ was less effective than $R_7H_2[LnW_{10}O_{36}]$ [8]. We carried out 'blank' oxidations in the absence of lanthanide by adding cetylpyridinium chloride to $[WO_4]^{2-}$ at pH 7.3, conditions analogous to those used for preparation of $R_7H_2[LnW_{10}O_{36}]$, after which H_2O_2 was added. The product (likely to be a mixture of cetylpyridinium salts of the paratungstates $[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$), gives yields and turnovers comparable — and in some cases superior to — those found for $R_7H_2[LnW_{10}O_{36}]$ and $R_8[Ce^{IV}W_{10}O_{36}]$. This suggests, as foreshadowed in our earlier work [10] and with the oxidations above for sodium salts that the lanthanide has no catalytic influence — in fact in some cases it may be inhibitory.

Table 2 indicates that cerium and heavier lanthanide complexes are generally somewhat less effective as catalysts than other $[Ln^{III}W_{10}O_{36}]^{9-}$ species for oxidation of benzyl alcohol, cyclohexanol and 2-octanol. On the grounds of its known redox potential [12], $[Ce^{III}W_{10}O_{36}]^{9-}$ is probably oxidised by H_2O_2 to $[Ce^{IV}W_{10}O_{36}]^{8-}$. The heavier lanthanides have smaller sizes due to the lanthanide contraction, while the radius of cerium(IV) is 0.15 Å smaller than that of cerium(III). Differences in catalytic effectiveness may arise from stronger Ln–O bonding via a greater partial ionic character between the smaller central atom to the two W_5O_{18} moieties, thus rendering degradation by H_2O_2 to polyperoxotungstates more difficult; such an effect is likely to be even more pronounced for cerium(IV) since a greater central atom charge is also involved. The complex $[Th^{IV}W_{10}O_{36}]^{8-}$ is comparable in catalytic efficiency with $[Ln^{III}W_{10}O_{36}]^{9-}$ so this latter factor is clearly less important, perhaps because thorium(IV) is slightly larger (ca. 0.05 Å) than cerium(IV).

Oxidations of benzyl alcohol, cyclohexanol, 2-octanol and cyclo-octene with $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th) in the presence of the phase transfer catalyst $((^nC_6H_{13})_4N)Cl$ in $CHCl_3$–aqueous H_2O_2 are listed in Table 2. Yields and turnovers are considerably superior to those observed for cetylypyridinium salts, but again 'blank' oxidations carried out using $[WO_4]^{2-}$ initially at pH 7.3 (before addition of H_2O_2) in the absence of lanthanide give equally good results, once more suggesting that lanthanides are not necessary for these oxidations. We were unable to isolate pure samples of the *n*-hexylammonium salts although the lanthanum salt gave analyses close to the formula $((^nC_6H_{13})_4N)_5H_4[LaW_{10}O_{36}]$.

Again, $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ is likely to be the effective catalyst in all these reactions rather than $[Ln^{III}W_{10}O_{36}]^{9-}$ or $[M^{IV}W_{10}O_{36}]^{8-}$.

2.4. Salts of $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$

Studies on the oxidation of cyclohexanol to cyclohexanone in the presence of $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ (Ln = La, Pr, Nd, Sm, Gd) with H_2O_2 in various solvents have recently been reported and it was suggested that these are effective catalysts [27]. We have, however, shown previously from ^{31}P-NMR and Raman data, that catalysis of the oxidation of primary alcohols to aldehydes, secondary alcohols to ketones and alkenes to epoxides by $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ (Ln = Y, La, Ce, Pr, Sm, Tb, Yb) and $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$ in $CHCl_3$–H_2O_2 in the presence of $((^nC_6H_{13})_4N)Cl$ is effected by $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$. These latter three species are formed by degradation of $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ and $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$ by H_2O_2 rather than by the lanthanophosphopolyoxotungstates themselves [11].

In Table 3 we report for the first time $^{31}P[^1H]$ MAS NMR data for solid $K_{11}[Ln^{III}\{PW_{11}O_{39})_2]\cdot nH_2O$ salts (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Yb, Lu), for $K_{10}[Ce^{IV}\{PW_{11}O_{39}\}_2]\cdot nH_2O$ and $^{31}P[^1H]$ spectra for their solutions in aqueous H_2O_2. Our $^{31}P[^1H]$ data for their aqueous solutions agree well with literature values [28,29]. The ^{31}P resonances are shifted little from solid to solution, suggesting that the structures of the anions of the solids are retained by their solutes; likewise, the Raman spectrum of $K_{11}[Sm^{III}\{PW_{11}O_{39}\}_2]$ is very similar to that of its aqueous solution [11], also suggesting minimal change of structure in aqueous solution. Only one ^{31}P peak is observed for the aqueous solutions, suggesting equivalence of the positions of the two phosphorus atoms, with chemical shifts varying from + 69 (Er) to − 201 ppm (Tb). For some solid samples two peaks were observed in the MAS ^{31}P-NMR, probably due to slight asymmetry in the structure with respect to the two $\{PW_{11}O_{39}\}$ moieties. Although we and others have been unable to obtain single crystals of any of these salts suitable for X-ray analysis, in the related complex $Cs_{12}[U^{IV}\{GeW_{11}O_{39}\}_2]\cdot 13H_2O$ the crystal structure [30] shows that the $\{GeW_{11}O_{39}\}$ units form a distorted square antiprismatic arrangement of their donor oxygen atoms around the central uranium atom such that there are slight inequivalences of the two Ge atoms.

Table 2
Oxidations by H_2O_2 catalysed by polyoxotungstates $[Ln^{III}W_{10}O_{36}]^{9-}$, $[Ce^{IV}W_{10}O_{36}]^{8-}$ and $[Th^{IV}W_{10}O_{36}]^{8-}$

Substrate	Cation	Ln:	Blank [a]	Y	La	Ce^{III}	Ce^{IV}	Pr	Sm	Eu	Gd	Dy	Ho	Er	Lu	Th
			Yields (%) [Turnover] [b]													
Benzyl	Na		11	11 [6]		10 [6]	10 [6]			13 [8]	8 [5]	12 [8]		10 [6]	14 [9]	10 [6]
	Cetylpy		93		75 [70]	66 [61]	73 [73]	88 [83]		83 [78]	77 [72]	78 [73]	49 [49]	42 [40]	51 [48]	79 [80]
	n-Hexyl		91	87 [54]	95 [59]	58 [36]	51 [32]	88 [55]	91 [57]	92 [58]	96 [60]	95 [59]	93 [58]	96 [60]	97 [61]	99 [62]
Cyclohexanol [a]	Na		20		18 [11]	6 [4]	5 [3]	6 [4]	4 [3]	3 [2]	4 [3]	6 [4]	7 [4]	11 [7]		9 [6]
	Cetylpy		43		70 [66]	33 [30]	47 [47]	74 [70]		59 [55]	35 [33]		44 [44]	29 [27]	33 [31]	57 [58]
	n-Hexyl		79	57 [36]	57 [36]	51 [32]	37 [23]	63 [39]	62 [39]	61 [38]	65 [41]	52 [33]	52 [33]	55 [34]	50 [31]	68 [43]
2-Octanol	*n*-Hexyl		68	48 [30]	60 [38]	61 [38]	51 [32]	70 [44]	80 [50]	77 [48]	75 [47]	62 [39]	63 [39]	70 [44]	60 [38]	70 [44]
Cyclooctene	*n*-Hexyl		94	91 [57]	84 [53]	60 [38]		92 [58]	89 [56]	85 [53]	95 [59]	88 [55]	85 [53]	91 [57]	95 [59]	96 [60]

[a] 'Blank' made from $[WO_4]^{2-}$ at pH 7.3 (see experimental section).

[b] Conditions, 0.08 mmol of lanthanopolyoxotungstate or thoriopolyoxotungstate in 20 cm³ of $CHCl_3$ with 20 cm³ of 30% H_2O_2 heated to 60°C for 3 h.

In Table 3 the $^{31}P[^1H]$-NMR spectra of a number of other $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ (Ln = Y, La, Ce, Tb, Lu) and $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$ complexes in H_2O_2 are given. On measuring the NMR spectra as soon as possible after addition of H_2O_2, in each case a single peak is seen significantly shifted from that of the parent lanthanophosphopolyoxotungstate. These peaks may arise from mononuclear complexes, $[Ln\{PW_{11}O_{39}\}]^{4-}$ and $[Ce^{IV}\{PW_{11}O_{39}\}]^{3-}$, formed as intermediates during degradation of their binuclear parents by H_2O_2: such ^{31}P shifts are also observed for a 1:1 mixture of the lanthanide nitrate and $[PW_{11}O_{39}]^{7-}$. Although we have been unable to isolate any solids, formation of related mononuclear species has been proposed by Peacock and Weakley [12]; Maksimov et al have isolated a complex formulated as $H_5[PW_{11}CeO_{40}]$ [31], though this was not characterised.

After 24 h these peaks disappear and are replaced by others, listed as A, B, C and D in Table 3. Peak A probably arises from $(PO_4)^{3-}$. Peaks B, C and D are most clearly seen for the samarium complex, and their ^{183}W satellites allowed their identification as being due to the phosphopolyperoxotungstates $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$, respectively [11]. Similar assignments for B, C and D have been made for $[PW_{11}O_{39}]^{7-}$ [32] and for $[PW_{12}O_{40}]^{3-}$ [33] in H_2O_2. Raman spectra of $[Sm\{PW_{11}O_{39}\}_2]^{11-}$ also showed that this anion is degraded in aqueous H_2O_2 to give a spectrum very similar to that of the above phosphopolyperoxotungstates [11].

It is noteworthy that, for $[Ce^{III}\{PW_{11}O_{39}\}_2]^{11-}$ and $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$ the ^{31}P resonances change much more slowly than do those of $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ after addition of H_2O_2, consistent with our observation that the cerium species are less effective oxidation catalysts [11] than the other $[Ln^{III}W_{10}O_{36}]^{9-}$ complexes. As is the case for the $[Ce^{III}W_{10}O_{36}]^{9-}$–$[Ce^{IV}W_{10}O_{36}]^{8-}$ couple, redox potential data suggest that H_2O_2 oxidises $[Ce^{III}\{PW_{11}O_{39}\}_2]^{11-}$ to $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$ [12]. These species catalyse oxidations of alcohols and alkenes with H_2O_2 much more slowly than do other $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$ species, as seen above for $[Ce^{III}W_{10}O_{36}]^{9-}$ and $[Ce^{IV}W_{10}O_{36}]^{8-}$ compared with other $[LnW_{10}O_{36}]^{9-}$ complexes. Presumably, again, the breakup by H_2O_2 of these binuelear species is retarded by the smaller, more highly charged cerium(IV) centre, and this is reflected in the ^{31}P-NMR data.

3. Conclusions

The sodium, cetylpyridinium and *n*-hexylammonium salts $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ (M = Ce, Th) have been evaluated as catalysts for the oxidation of

Table 3
^{31}P-NMR data for $K_{11}[Ln^{III}\{PW_{11}O_{39}\}_2]\cdot nH_2O$ salts

Ln:	$K_{11}[Ln\{PW_{11}O_{39}\}_2]$ (solid)	$[Ln\{PW_{11}O_{39}\}_2]^{11-}$ (aqueous solution)	$[Ln\{PW_{11}O_{39}\}]^{4-}$ (aqueous solution)	$[Ln\{PW_{11}O_{39}\}_2]^{11-}$ in H_2O_2[a]				
				A[e]	B[f]	C[g]	D[h]	E[i]
Y	−13.3	−12.2	−14.7	−0.2	−0.65s[b]	−1.46s	−2.84s	
La	−11.8, −12.1	−11.4	−11.7	0.16	−0.41s	−1.16s	−2.43s	
Ce^{III}	−16.1, −20.8	−18.2			0.82s	2.00sh[c]		1.36
Ce^{IV}	−13.3, −13.4	−12.8	−13.5		0.85s	2.20sh		1.34
Pr	−14.4, −17.4	−13.4	−19.5					
Nd		−23.3	−25.9					
Sm	−14.9	−15.3	−15.7	−0.09	−0.63s	−1.14	−2.62s	
Eu		−0.3	4.6					
Tb	−174.9	−201.6	−237.6		−16.56b[d]	−40.28b		
Ho		−96.8	−96.9					
Er		69.0	87.1					
Yb	29.9	35.7	30.0		−3.18b	−6.06b	− 13.94b	
Lu		−12.72	−12.65	0.03	−0.49s	−1.21s	−2.39s	
$[PW_{11}O_{39}]^{7-}$–H_2O_2				0.24	−0.32s			

[a] In excess of 30% H_2O_2 (H_2O_2–W 12:1).
[b] s = band with two ^{183}W satellites.
[c] sh = band with two shoulders from ^{183}W satellites.
[d] b = broad band, probably due to ^{183}W satellites.
[e] A: $(PO_4)^{3-}$.
[f] B: $[(PO_3(OH))\{WO(O_2)_2\}]^{2-}$.
[g] C: $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$.
[h] D: $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$.
[i] E: Other species.

alcohols and the epoxidation of cyclo-octene in $CHCl_3$–H_2O_2. It appears that the lanthanide or thorium hetero-atom plays no effective role in such catalysis (and indeed in some cases has an inhibitory effect); degradation to $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ occurs and it is this species that is almost certainly responsible for all the oxidations.

^{31}P[H]-NMR spectra have been measured of solid $K_{11}[Ln^{III}\{PW_{11}O_{39}\}_2]\cdot nH_2O$ salts, $K_{10}[Ce^{IV}\{PW_{11}O_{39}\}_2]\cdot nH_2O$ and of their solutions in water and aqueous H_2O_2. For the latter, the data suggest that they are degraded to phosphopolyperoxotungstates which, rather than the lanthanophosphopolyoxotungstates, are responsible for the oxidation catalysis.

4. Experimental

4.1. General procedures

Lanthanide salts, sodium tungstate, benzyl alcohol, 2-octanol, cyclohexanone and cyclo-octene were purchased from Aldrich and hydrogen peroxide (AnalaR 30%) from BDH; all were used without further purification.

The solution ^{31}P[^{1}H] data were measured on a JEOL ESX 270 spectrometer (^{31}P, 109.25 MHz, ^{1}H, 270.05 MHz) as ^2H_2O solution. Solid-state MAS ^{31}P-NMR spectra were recorded at 121.4 MHz (7.05 T) on a Bruker MSL300 spectrometer using a standard Bruker magic angle sample spinning (MAS) probe with double-bearing rotation mechanism. The samples were studied as polycrystalline powders in zirconia rotors (4 mm external diameter) and MAS frequencies at 8–13 kHz (with stability better than ± 10 Hz) were used. ^{31}P transverse magnetisation was prepared using a single pulse excitation and ^{1}H high-power decoupling was applied during acquisition. Spectra were recorded at ambient probe temperature. All ^{31}P chemical shifts are given relative to aqueous 85% H_3PO_4 solution.

Raman spectra were measured on a Perkin–Elmer 1760X Fourier Transform Raman instrument with 1064 nm. Nd–YAG excitation with a power of 2 W, and on a Dilors LabRam Infinity instrument with a 532 nm. frequency-doubled Nd–YAG excitation at 15 mW. The GC data were obtained on a Perkin–Elmer Autosystem instrument using a Perkin–Elmer stainless-steel column packed with 5% Carbowax 20M on Chromosorb WHO AW (DCMS treated). Microanalyses were obtained from North London University (C, H, N) or from ICPAES measurements on an ARL instrument (Na, Ln, W) by Mr. B. Coles of the Geology Department, Imperial College.

4.2. Preparation of sodium salts of $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{9-}$ (M = Ce, Th)

For the lanthanide complexes an adaptation of the method of Peacock and Weakley [12] was used. To 5.0 g (15 mmol) of $Na_2[WO_4]·2H_2O$ in 5 cm^3 of water, adjusted to pH 7.0 with glacial acetic acid, was added the lanthanide nitrate (1.5 mmol) in 2 cm^3 of water and the solution heated to 90°C with stirring until dissolution was complete (ca. 15 min). The solution was filtered hot and left to cool; crystals of the product were filtered off and dried.

The 'blank' material (i.e. a mixture of sodium paratungstates ($[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$ [22,23]) was made by following the above procedure but omitting addition of the lanthanide salt.

The thorium salt was made by an adaptation of the literature method [16,17] by using exactly the procedure as above, thorium. nitrate $Th(NO_3)_4·6H_2O$ replacing the lanthanide nitrate. The product was recrystallised from water.

4.2.1. Analytical data

$Na_9[YW_{10}O_{36}]·20H_2O$. Yield 10%. (Anal. Found: Na, 7.1; Y, 2.5. Calc.: Na, 6.7; Y, 2.9%).

$Na_9[LaW_{10}O_{36}]·28H_2O$. Yield 51%. (Anal. Found: La 4.3; Na, 6.3; W, 56.9. Calc.: La, 4.3; Na, 7.1; W, 56.3%).

$Na_9[CeW_{10}O_{36}]·38H_2O$. Yield 26%. (Anal. Found: Ce, 3.8; Na, 5.8; W, 51.1. Calc.: Ce, 4.7; Na, 6.0; W, 53.3%).

$Na_9[PrW_{10}O_{36}]·28H_2O$. Yield 55%. (Anal. Found: Na, 7.8; Pr, 3.4; W, 55.9. Calc.: Na, 6.2; Pr, 4.3; W, 56.3%).

$Na_9[SmW_{10}O_{36}]·30H_2O$. Yield 25%. (Anal. Found: Na, 7.0; Sm, 4.8; W, 54.0. Calc.: Na, 6.3; Sm, 4.5; W, 55.5%).

$Na_9[EuW_{10}O_{36}]·20H_2O$. Yield 36%. (Anal. Found: Eu, 4.4; Na, 6.5; W, 51.4. Calc. Na, 6.3; Sm, 4.65; W, 56.3%).

$Na_9[GdW_{10}O_3]·30H_2O$. Yield 20%. (Anal. Found: Gd, 4.5; Na, 6.7; W, 50.5. Calc.: Gd, 4.7; Na, 6.2; W, 55.4%).

$Na_9[HoW_{10}O_{36}]·30H_2O$. Yield 20%. (Anal. Found: Ho, 4.2; Na, 7.4; W, 48.4. Calc.: Ho, 4.9; Na, 6.2; W, 55.3%).

4.3. Preparation of $K_2[W_2O_3(O_2)_4(H_2O)_2]·2H_2O$

The method is adapted from that of Stomberg [34]. To potassium hydroxide (1.0 g, 17 mmol) in the minimum amount of water was added $WO_3·H_2O$ (2 g. 7 mmol) and the mixture stirred until all of the solid had dissolved. The solution was filtered and hydrogen peroxide (7 cm^3 of a 30% aqueous solution) was added dropwise and sufficient dilute HCl added to render the yellow solution colourless. The mixture was then cooled to 5°C for a day, after which white crystals of the product were collected.

Anal. Found: H, 1.0; K, 11.0; O_2^{2-}, 18.6. Calc.: H, 1.2; K, 11.3; O_2^{2-}, 18.4%.

4.4. Preparation of cetylpyridinum salts of $[Le^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{9-}$ (M = Ce, Th)

Cetylpyridinium chloride (1.0 g, 2.8 mmol) in 10 cm^3 of water was added to a solution of 1.0 g (0.32 mmol) of $Na_9[LnW_{10}O_{36}]·nH_2O$ in 5 cm^3 of water. The precipitate was filtered, washed with water and dried. The solution was left to cool and the product filtered off and dried. The 'blank' material (i.e. a mixture of the cetylpyridinium salts of the paratungstates $[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$ [22,23]) was made by following the above procedure but omitting addition of the lanthanide salt.

4.4.1. Analytical data

In the analyses below R = cetylpyridinium, $(Me(CH_2)_{15}(NC_5H_5))^+$, $C_{21}H_{38}N^+$.

$R_7H_{21}[YW_{10}O_{31}]$. Yield 63%. Anal. Found: C, 38.3; H, 6.0; N, 2.1. Calc.: C, 38.1; H, 5.9; N, 2.1%.

$R_7H_2[LaW_{10}O_{36}]$. Yield 62%. Anal. Found: C, 39.6; H, 6.4; N, 1.6. Calc.: C, 37.7; H, 5.8; N, 2.0%.

$R_7H_2[CeW_{10}O_{36}]$. Yield 60%. Anal. Found: C, 35.0; H, 6.0; N, 2.0. Calc.: C, 37.6; H, 5.8; N, 2.1%.

$R_8[Ce^{IV}W_{10}O_{36}]$. Yield 62%. Anal. Found: C, 40.7; H, 6.2; N, 2.2. Calc.: C, 40.4; H, 6.1; N, 2.2%.

$R_8H[SmW_{10}O_{16}]$. Yield 63%. Anal. Found: C, 39.3; H, 6.0; N, 2.0. Calc.: C, 40.3; H, 6.1; N, 2.2%.

$R_7H_2[EuW_{10}O_{36}]$. Yield 62%. Anal. Found: C, 37.8; H, 5.6; N, 1.8. Calc.: C, 37.6; H, 5.8; N, 2.1%.

$R_7H_2[GdW_{10}O_{36}]$. Yield 60%. Anal. Found: C, 37.8; H, 5.7; N, 2.0. Calc.: C, 37.3; H, 5.8; N, 2.1%.

$R_7H_2[DyW_{10}O_{36}]$. Yield 63%. Anal. Found: C, 37.3; H, 6.0; N, 2.2. Calc.: C, 37.3; H, 3.8; N, 2.1%.

$R_8H[HoW_{10}O_{36}]$. Yield 62%. Anal. Found: C, 39.7; H, 6.6; N, 2.1. Calc.: C, 40.2; H, 6.1; N, 2.2.

$R_7H_2[ErW_{10}O_{36}]$. Yield 64%. Anal. Found: C, 37.6; H, 5.7; N, 2.0. Calc.: C, 37.4; H, 5.8; N, 2.1%.

$R_7H_2[LuW_{10}O_{36}]$. Yield 62%. Anal. Found: C, 37.6; H, 5.8; N, 2.1. Calc.: C, 37.4; H, 5.7; N, 2.1%.

$R_8[ThW_{10}O_{36}]$. Yield 62%. Anal. Found: C, 39.4; H, 6.3; N, 1.7. Calc.: C, 39.3; H, 6.1; N, 2.2%.

4.5. Preparation of potassium salts of $[Le^{III}\{PW_{11}O_{39}\}_2]^{11-}$ and $[Ce^{IV}\{PW_{11}O_{39}\}_2]^{10-}$

The method of Haraguchi et al. [35] was used. Hydrated $H_3[PW_{12}O_{40}]·nH_2O$ (4.3 g, 1.5 mmol) was dissolved in hot water (5 cm^3) and a solution (0.75 mmol in 2 cm^3 of water) of the lanthanide salt was added ($LaCl_3·7H_2O$, $Ce(NO_3)_3·6H_2O$, $(NH_4)_2[Ce(NO_3)_6]$, $Ln(NO_3)_3·6H_2O$ (Ln = Y, Pr, Sm, Tb, Yb). A solution of potassium acetate (5.0 g, 50 mmol) in water (5 cm^3) was added, and the pH adjusted to 7 by addition of acetic acid dropwise with vigorous stirring. After filtration the solution was left in the refrigerator and crystals of the complexes recovered.

4.5.1. Analytical data

$K_{11}[Y\{PW_{11}O_{39}\}_2]\cdot 16H_2O$. Yield 84%. Anal. Found: K, 7.7; P, 0.9; Y, 1.4. Calc.: K, 7.0; P, 1.0; Y, 1.4%.

$K_{11}[La\{PW_{11}O_{39}\}_2]\cdot 35H_2O$. Yield 88%. Anal. Found: K, 6.3; La, 1.8; P, 0.9. Calc.: K, 6.6; La, 2.1; P, 1.0%.

$K_{11}[Ce^{III}\{PW_{11}O_{39}\}_2]\cdot 20H_2O$. Yield 78%. Anal. Found.: Ce, 1.9; K, 7.0; P, 0.8. Calc.: Ce, 1.9; K, 6.8; P, 1.0%.

$K_{10}[Ce^{IV}\{PW_{11}O_{39}\}_2]\cdot 20H_2O$. Yield 51%. Anal. Found: Ce, 2.1; K, 6.4; P, 0.8. Calc.: Ce, 2.2; K, 6.2; P, 1.0%.

$K_{11}[Pr\{PW_{11}O_{39}\}_2]\cdot 20H_2O$. Yield 69%. Anal. Found: K, 6.9; P, 0.9; Pr, 1.8; W, 64.2. Calc.: K, 6.8; P, 1.0; Pr, 2.2; W, 64.4%.$K_{11}[Sm\{PW_{11}O_{39}\}_2]\cdot 20H_2O$. Yield 69%. Anal. Found: K, 6.8; Sm, 2.3; P, 0.9; W, 64.1. Calc.: K, 6.8; Sm, 2.4; P, 1.0; W, 64.3%.$K_{11}[Tb\{PW_{11}O_{39}\}_2]\cdot 12H_2O$. Yield 87%. Anal. Found: K, 6.9; P, 0.9; Tb, 2.3; W, 66.4. Calc.: K, 7.0; P, 1.0; Tb, 2.6; W, 65.7%.$K_{11}[Yb\{PW_{11}O_{39}\}_2]\cdot 17H_2O$. Yield 89%. Anal. Found: K, 6.8; P, 0.9; W, 64.6; Yb, 2.3. Calc.: K, 6.9; P, 1.0; W, 64.6%; Yb, 2.8%.

4.6. Oxidations with $Na_9[Ln^{III}W_{10}O_{36}]\cdot nH_2O$ and $N_8[ThW_{10}O_{36}]\cdot 28H_2O$

In a 100 cm^3 flask was placed the catalyst (0.08 mmol), $CHCl_3$ (20 cm^3) the substrate (benzyl alcohol, 2-octanol, cyclohexanone or cyclo-octene; 5 mmol) and the mixture was heated to 60°C. Then 30% aqueous H_2O_2 (20 cm^3) was added slowly over a period of 10 min. Refluxing was continued, with stirring, for 3 h. The mixture was then cooled and the organic layer separated. The aqueous layer was washed with chloroform (3 × 25 cm^3) and the combined chloroform solutions dried over $MgSO_4$ and filtered. The filtrate was then analysed by GC.

4.7. Oxidations with $R_7H_2[Ln^{III}W_{10}O_{36}]$ and $R_8[M^{IV}W_{10}O_{36}]$ ($R =$ cetylpyridinium, $M =$ Ce, Th)

The procedure was similar to that above, the cetylpyridinium salt (0.25 g, 0.6 mmol) replacing $Na_9[Ln^{III}W_{11}O_{36}]\cdot nH_2O$.

4.8. Oxidations with $[Ln^{III}W_{10}O_{36}]^{9-}$ and $[M^{IV}W_{10}O_{36}]^{8-}$ ($M =$ Ce, Th) with $((^nC_6H_{13})_4N)Cl$

In a 100 cm^3 flask was placed $[Ln^{III}W_{10}O_{36}1^{9-}$ or $[M^{IV}W_{10}O_{36}]^{8-}$ (0.08 mmol), $CHCl_3$ (20 cm^3), the substrate (benzyl alcohol, 2-octanol, cyclohexanone or cyclo-octene; 5 mmol) and $((^nC_6H_{13})_4N)Cl$ (0.045 g, 0.12 mmol) and the mixture heated to 60°C. A similar procedure was used for the 'blank' but no lanthanide nitrate was used. Then 30% aqueous H_2O_2 (20 cm^3) was added slowly over a period of 10 min. Refluxing was continued, with stirring, for 3 h. The mixture was then cooled and the organic layer separated. The aqueous layer was washed with chloroform (3 × 25 cm^3) and the combined chloroform solutions dried over $MgSO_4$ and filtered. The filtrate was then analysed by GC.

5. Crystallography

5.1. Crystal data for $Na_8[ThW_{10}O_{36}]\cdot 28H_2O$

$M = 3334.9$, monoclinic, space group $C2/c$ (no. 15), $a = 18.144(3)$, $b = 18.638(3)$, $c = 18.443(2)$ Å, $\beta = 95.79(1)°$, $V = 6205(1)$ Å^3, $Z = 4$, $D_{calc} = 3.570$ g cm^{-3}, $\mu(Mo{-}K_\alpha) = 21.02$ cm^{-1}, $F(000) = 5944$, $T = 203$ K; clear blocks, 0.40 × 0.23 × 0.23 mm, Siemens P4/PC diffractometer, ω-scans, 5473 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.056$, $wR_2 = 0.$ 136 for 4349 independent observed reflections $[|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°]$ and 386 parameters [36].

6. Supplementary material

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141115. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Calouste Guibenkian Foundation (H.I.S.N.) and the Egyptian Ministry of Education (A.G.F.S.) for grants for postgraduate work. We thank the University of London Intercollegiate Research Service for support of the Raman instruments at Imperial College and the solid state NMR instrument at University College London, and Dr Abil Aliev, University College London, for help with the MAS NMR studies.

References

[1] Part 6: N.M. Gresley, W.P. Griffith, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (1997) 89.
[2] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.

[3] R. Shiozaki, H. Goto, Y. Kera, Bull. Chem. Soc. Jpn. 66 (1993) 2790.
[4] R. Shiozaki, A. Inagaki, A. Nishino, H. Kominami, Y. Kera, Kidorui 26 (1995) 274.
[5] R. Shiozaki, H. Kominami, H. Kera, Synth. Comm. 26 (1996) 1663.
[6] R. Shiozaki, A. Inagaki, A. Ozaki, H. Kominami, S. Yamaguchi, J. Ichihara, Y. Kera, J. Alloy. Compd. 261 (1997) 132.
[7] Y. Kera, Y. Mochizuki, S. Yamaguchi, J. Ichikara, H. Kominami, Kidorui 32 (1998) 308.
[8] R. Shiozaki, A. Inagaki, H. Kominami, S. Yamaguchi, J. Ichitara, Y. Kera, J. Mol. Catal. 124 (1997) 29.
[9] R. Shiozaki, A. Wagaki, A. Nishio, E. Nishio, M. Maekawa, H. Kominami, Y. Kera, J. Alloys Compounds 24 (1996) 193.
[10] W.P. Griffith, R.G.H. Moreea, H.I.S. Nogueira, Polyhedron 15 (1996) 3493.
[11] N.M. Gresley, W.P. Griffith, A.C. Laemmel, H.I.S. Nogueira, B.C. Parkin, J. Mol. Catal. 117 (1997) 185.
[12] R.D. Peacock, T.J.R. Weakley, J. Chem. Soc. Sect. A (1971) 1836.
[13] J. Iball, J.N. Low, T.J.R. Weakley, J. Chem. Soc. Dalton Trans. (1974) 2021.
[14] T. Ozeki, T. Yamase, Acta Crystallogr. Sect. C 50 (1994) 327.
[15] T. Yamase, T. Ozeki, M. Tosaka, Acta Crystallogr. Sect. C 50 (1994) 1849.
[16] G.H. Marcu, I. Todorut, A. Botar, Rev. Roum. Chim. 16 (1971) 1335.
[17] A.V. Botar, T.J.R. Weakley, Rev. Roum. Chim. 18 (1973) 1155.
[18] L.P. Kazanskii, A.M. Golubev, I.I. Baburinaq, E.A. Torchenkova, V.I. Spitsyn, Bull. Acad. Sci. USSR Div. Chem. Sci. (1978) 1956.
[19] A.M. Golubev, L.A. Muradyan, L.P. Kazanskii, E.A. Torchenkova, V.I. Simonov, V.I. Spitsyn, Sov. J. Coord. Chem. 3 (1977) 715.
[20] W.P. Griffith, B.C. Parkin, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (1995) 3131.
[21] K.F. Wedermeyer, Houben-Weyl: Methoden der Organischen Chemie, vol. 6/1c, Thieme, Stuttgart, 1976, p. 30.
[22] J.J. Hastings, O.W. Howarth, J. Chem. Soc. Dalton Trans. (1992) 209.
[23] R.I. Maksimovskaya, K.G. Burtseva, Polyhedron 4 (1985) 1559.
[24] N.J. Campbell, A.C. Dengel, C.J. Edwards, W.P. Griffith, J. Chem. Soc. Dalton Trans. (1989) 1203.
[25] A.J. Bailey, W.P. Griffith, B.C. Parkin, J. Chem. Soc. Dalton Trans. (1995) 1833; 1203.
[26] O. Bortolini, V. Conte, F. di Furia, G. Modena, J. Org. Chem. 51 (1986) 2661.
[27] V. Indira, S. Gopinathan, C. Gopinathan, Indian J. Chem. 37A (1998) 816.
[28] M.A. Fedotov, B.Z. Pertsikov, D.K. Danovich, Polyhedron 9 (1990) 1249.
[29] G.M. Maksimov, G.N. Kustova, K.I. Matveev, T.P. Lazarenko, Sov. J. Coord. Chem. 16 (1990) 117.
[30] C.M. Tourné, G.F. Tourné, M.C. Brianso, Acta Crystallogr. Sect. B 36 (1980) 2012.
[31] G.M. Maksimov, R.I. Maksimovskaya, I.V. Kozhevnikov, Russ. J. Inorg. Chem. 37 (1992) 1180.
[32] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681.
[33] L. Salles, C. Aubry, B. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.M. Brégeault, Inorg. Chem. 33 (1994) 871.
[34] R. Stomberg, Acta Chem. Scand. 22 (1968) 1076.
[35] N. Haraguchi, Y. Okaue, T. Isobe, Y. Matsuda, Inorg. Chem. 33 (1994) 10125.
[36] SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.