

# Studies on polyoxo and polyperoxo-metalates part 5<sup>1</sup>: Peroxide-catalysed oxidations with heteropolyperoxo-tungstates and -molybdates

N. Melanie Gresley, William P. Griffith\*, Anne C. Laemmel, Helena I.S. Nogueira,  
Bernardeta C. Parkin

*Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK*

Received 19 April 1996; accepted 7 June 1996

## Abstract

The new complexes  $[(LO_4)\{MO(O_2)_2\}_2\{MO(O_2)_2(H_2O)\}]^{3-}$  (L = P, As; M = W, Mo) are reported and their use as catalysts in the presence of hydrogen peroxide for epoxidation of alkenes and oxidations of alcohols, tertiary amines and sulfides discussed. Similar oxidations are reported for salts of  $[(LO_3(OH))\{MO(O_2)_2\}_2]^{2-}$  (L = P, As; M = W, Mo),  $[(PhPO_3)\{MO(O_2)_2\}_2\{MO(O_2)_2(H_2O)\}]^{3-}$  (M = W, Mo) and  $[(R_2LO_2)\{MO(O_2)_2\}_2]^-$  (R = Ph, Me; L = P, As; M = W, Mo). Alkene epoxidations and alcohol oxidations are also reported for  $[PW_{11}O_{39}]^{7-}$ ,  $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$  (Ln = Y, La, Ce, Pr, Sm, Tb, Yb) and  $[M^{IV}\{PW_{11}O_{39}\}_2]^{10-}$  (M = Ce, Th).

**Keywords:** Homogeneous oxidation catalysis; Peroxotungstates; Peroxomolybdates; Lanthanides; Epoxidation catalysis; Hydrogen peroxide

## 1. Introduction

There is currently considerable interest [1–13] in the structures and chemical reactivities of heteropolyperoxometalates containing the unusual  $\eta^2$ ,  $\eta^1$ -peroxo linkages; in these one of the oxygen atoms of a peroxo ligand side-bonded to a metal atom forms a weak bond to an adjacent metal atom. This interest was stimulated by the characterisation [1] of ‘Venturello’s complex’,  $[N^nC_6H_{13})_4]_3[(PO_4)\{WO(O_2)_2\}_4]$  **1**. Complexes such as **1** will, with  $H_2O_2$  as co-oxi-

dant, catalyse the oxidations of a wide variety of organic substrates, normally in biphasic solvent systems with phase-transfer agents. Such oxidations with **1** include the epoxidation of alkenes [1–3,8,11], the conversion of tertiary amines to N-oxides [5], internal alkynes to the corresponding  $\alpha$ ,  $\beta$ -epoxy ketones [14], allenes to  $\alpha$ -alkoxy or  $\alpha$ -hydroxy ketones [10], alkenes to carboxylic acids [15], amines to oximes and nitrones [16], anilines to azoxy–nitroso- and nitrobenzenes [17] and sulfides to sulfoxides and sulfones [18].

In this series of papers [2,4,5,11] we have explored the use of molybdenum and, in particular, tungsten isopoly- and heteropolyperoxo complexes containing  $\eta^2$ ,  $\eta^1$ -peroxo moieties

\* Corresponding author. Tel.: +44-171-5945759; fax: +44-171-5945804; e-mail: wpgriffith@ic.ac.uk.

<sup>1</sup> Part 4: Ref. [4].

as catalysts for organic oxidations with hydrogen peroxide as co-oxidant, and discovered a number of new complexes containing such moieties. We have reported the X-ray crystal structures and explored the reactivities of a number of new complexes, including  $[\text{NH}_4]_3[(\text{OH})\{\text{VO}(\text{O}_2)_2\}_2] \cdot \text{H}_2\text{O}$  [19];  $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  [2];  $[\text{NMe}_4][(\text{Me}_2\text{AsO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$ ,  $[\text{NMe}_4][(\text{Ph}_2\text{PO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$ ,  $[\text{NBu}_4][(\text{Ph}_2\text{PO}_2)\{\text{WO}(\text{O}_2)_2\}_2]$  and the mononuclear complex  $[\text{NH}_4][(\text{Ph}_2\text{PO}_2)\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  [4]. Species containing  $\eta^2$ ,  $\eta^1$ -peroxo moieties such as  $[(\text{LO}_4)\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$  ( $\text{L} = \text{P}$  [1],  $\text{As}$  [11]),  $[(\text{RPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{3-}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Ph}$ ,  $t\text{Bu}$ ) [2] and  $[\text{W}_2\text{O}_3(\text{O}_2)_4]^{2-}$  [5] are active oxidation catalysts with  $\text{H}_2\text{O}_2$ , while species which contain only  $\eta^2$ -peroxo linkages such as  $[\text{W}_4\text{O}_6(\text{O}_2)_6(\text{OH})_2(\text{H}_2\text{O})_6]^{2-}$  are not [2].

This paper explores further the oxidation properties of these and related complexes as catalysts for the oxidation with  $\text{H}_2\text{O}_2$  of alkenes, alcohols, tertiary amines and sulfides. We report also the isolation and characterisation of the new trinuclear complexes  $[(\text{LO}_4)\{\text{MO}(\text{O}_2)_2\}_2\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{3-}$  ( $\text{L} = \text{P}$ ,  $\text{M} = \text{W}$  **3**,  $\text{L} = \text{As}$ ,  $\text{M} = \text{W}$  **4**;  $\text{L} = \text{P}$ ,  $\text{As}$ ,  $\text{M} = \text{Mo}$ ), the dinuclear  $[(\text{LO}_3(\text{OH}))\{\text{MO}(\text{O}_2)_2\}_2]^{2-}$  ( $\text{L} = \text{P}$ ,  $\text{M} = \text{W}$  **5**,  $\text{L} = \text{As}$ ,  $\text{M} = \text{W}$  **6**;  $\text{L} = \text{P}$ ,  $\text{As}$ ,  $\text{M} = \text{Mo}$ ) and the study of their spectroscopic properties and oxidative reactivities. We also compare the oxidative abilities of  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ ,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ,  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\text{Ln} = \text{Y}$ ,  $\text{La}$ ,  $\text{Ce}$ ,  $\text{Pr}$ ,  $\text{Sm}$ ,  $\text{Tb}$ ,  $\text{Yb}$ ) and  $[\text{M}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  ( $\text{M} = \text{Ce}$ ,  $\text{Th}$ ).

## 2. Experimental

### 2.1. Materials

$\text{MoO}_3 \cdot \text{H}_2\text{O}$  was supplied by BDH and  $\text{WO}_3 \cdot \text{H}_2\text{O}$  was obtained from Fluka Chemic AG. Phenylphosphonic, diphenylphosphinic, cacodylic acids and lanthanide salts were obtained from Aldrich and used without further purification. Hydrogen peroxide was obtained from

BDH as a 30% w/v aqueous solution and Solvay Interlox as a 35% w/v aqueous solution and were used as supplied.  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ ,  $\text{Na}_2[\text{WO}_4] \cdot 2\text{H}_2\text{O}$  and  $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$  were obtained from BDH.

### 2.2. Preparation of complexes and analyses

#### 2.2.1. $[\text{N}^n\text{C}_6\text{H}_{13})_4]_3[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_4]$ , **1**

Venturello's compound [1] was made as previously described [11]. Yield of white solid 2.62 g, 1.18 mmol, 88%. Found C, 39.0; H, 7.1; N, 1.9%. Calcd. for  $\text{C}_{72}\text{H}_{156}\text{N}_3\text{O}_{24}\text{PW}_4$ : C, 39.1; H, 7.1; N, 1.9%.

#### 2.2.2. $[\text{N}^n\text{C}_6\text{H}_{13})_4]_3[(\text{AsO}_4)\{\text{WO}(\text{O}_2)_2\}_4]$ , **2**

This was made as previously described [11]. Yield of white solid 2.95 g, 1.31 mmol, 98%. Found C, 38.4; H, 7.0; N, 1.8%. Calcd. for  $\text{C}_{72}\text{H}_{156}\text{N}_3\text{O}_{24}\text{AsW}_4$ : C, 38.3; H, 7.0; N, 1.9%.

#### 2.2.3. $[\text{NBu}_4]_3[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$ , **3**

$\text{WO}_3 \cdot \text{H}_2\text{O}$  (2.50 g, 10.0 mmol) was suspended in aqueous hydrogen peroxide solution (8 cm<sup>3</sup>, 30% w/v) and the resulting suspension stirred at 50°C until a colourless solution was obtained. The resulting solution was centrifuged to remove any insoluble material.  $\text{NaH}_2\text{PO}_4$  (0.51 g, 3.33 mmol) in water (5 cm<sup>3</sup>) was added followed by dropwise addition of  $[\text{NBu}_4]\text{Cl}$  (2.78 g, 10 mmol) in water (5 cm<sup>3</sup>). The solid was filtered, washed with cold water (2 × 5 cm<sup>3</sup>) and diethyl ether (10 cm<sup>3</sup>) and air dried. Yield of white solid 5.39 g, 3.30 mmol, 98%. Found C, 34.9; H, 6.4; N, 2.5%. Calcd. for  $\text{C}_{48}\text{H}_{110}\text{N}_3\text{O}_{20}\text{PW}_2$ : C, 35.3; H, 6.7; N, 2.5%.

#### 2.2.4. $[\text{NBu}_4]_3[(\text{AsO}_4)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$ , **4**

The same procedure as for **3** was followed,  $\text{Na}_2\text{HAsO}_4$  (0.62 g, 3.33 mmol) replacing  $\text{NaH}_2\text{PO}_4$ . Yield of white solid 5.24 g, 3.12 mmol, 93%. Found C, 34.5; H, 6.4; N, 2.2%. Calcd. for  $\text{C}_{48}\text{H}_{110}\text{N}_3\text{O}_{20}\text{AsW}_3$ : C, 34.4; H, 6.6; N, 2.5%.

2.2.5.  $[NBu_4^+ ]_3[(AsO_4)(MoO(O_2)_2)_2(MoO(O_2)_2(H_2O))]$

The same procedure as for **4** was followed,  $MoO_3 \cdot H_2O$  (1.44 g, 10.0 mmol) replacing  $WO_3 \cdot H_2O$ . Yield of yellow solid 4.62 g, 3.27 mmol, 98%. Found C, 40.9; H, 7.8; N, 2.8%. Calcd. for  $C_{48}H_{110}N_3O_{20}AsMo_3$ : C, 40.8; H, 7.9; N, 3.0%.

2.2.6.  $[NBu_4^+ ]_2[(PO_3(OH))(WO(O_2)_2)_2]$ , **5**

This new procedure is somewhat simpler than that of Salles et al. [8].  $WO_3 \cdot H_2O$  (2.50 g, 10.0 mmol) was suspended in aqueous hydrogen peroxide solution (8 cm<sup>3</sup>, 30% w/v) and the resulting suspension stirred at 50°C until a colourless solution was obtained. The resulting solution was centrifuged to remove any insoluble material.  $Na_2HPO_4$  (0.71 g, 5.0 mmol) in water (5 cm<sup>3</sup>) was added followed by dropwise addition of  $[NBu_4^+ ]Cl$  (2.78 g, 10 mmol) in water (5 cm<sup>3</sup>). The solid was filtered, washed with cold water (2 × 5 cm<sup>3</sup>) and diethyl ether (10 cm<sup>3</sup>) and air dried. Yield of white solid 5.27 g, 4.75 mmol, 95%. Found C, 34.8; H, 6.6; N, 2.4%. Calcd. for  $C_{32}H_{73}N_2O_{14}PW_2$ : C, 34.6; H, 6.6; N, 2.5%.

2.2.7.  $[NBu_4^+ ]_2[(AsO_3(OH))(WO(O_2)_2)_2]$ , **6**

The same procedure as for **5** was followed,  $Na_2HAsO_4$  (0.93 g, 5.0 mmol) replacing  $Na_2HPO_4$ . Yield of white solid 5.34 g, 4.63 mmol, 93%. Found C, 33.2; H, 6.5; N, 2.3%. Calcd. for  $C_{32}H_{73}N_2O_{14}AsW_2$ : C, 33.4; H, 6.4; N, 2.4%.

2.2.8.  $[NBu_4^+ ]_2[(PO_3(OH))(MoO(O_2)_2)_2]$

The same procedure as for **5** was followed,  $MoO_3 \cdot H_2O$  (1.50 g, 10.0 mmol) replacing  $WO_3 \cdot H_2O$ . Yield of yellow solid 4.15 g, 4.45 mmol, 89%. Found C, 40.9; H, 7.7; N, 2.8%. Calcd. for  $C_{32}H_{73}N_2O_{14}PMo_2$ : C, 41.2; H, 7.9; N, 3.0%.

2.2.9.  $[NBu_4^+ ]_2[(AsO_3(OH))(MoO(O_2)_2)_2]$

The same procedure as for  $[Bu_4^+ N]_2[P(OH)O_3\{MoO(O_2)_2\}_2]$  was followed,

$Na_2HAsO_4$  (0.93 g, 5.0 mmol) replacing  $Na_2HPO_4$ . Yield of white solid 4.44 g, 4.51 mmol, 91%. Found C, 39.6; H, 7.4; N, 2.8%. Calcd. for  $C_{32}H_{73}N_2O_{14}AsMo_2$ : C, 39.4; H, 7.5; N, 2.9%.

2.2.10.  $[NMe_4]^+[(PhPO_3)(WO(O_2)_2)_2(WO(O_2)_2(H_2O))]$ EtOH, **7**

This was made as previously described [2]. Yield of white crystalline solid 2.9 g, 2.51 mmol, 76%. Found C, 16.7; H, 2.9; N, 2.4%. Calcd. For  $C_{16}H_{37}N_2O_{20}PW_3$ : C, 16.6; H, 3.2; N, 2.4%.

2.2.11.  $[NMe_4]^+[(PhPO_3)(MoO(O_2)_2)_2(MoO(O_2)_2(H_2O))]$ , **8**

This was made as previously described [2]. Yield of yellow crystalline solid 2.4 g, 2.82 mmol, 84%. Found C, 19.8; H, 3.5; N, 3.2%. Calcd. For  $C_{14}H_{31}N_2O_{19}PMo_3$ : C, 19.8; H, 3.7; 3.3%.

2.2.12.  $[NBu_4^+ ][(Ph_2PO_2)(WO(O_2)_2)_2]$ , **9**

This was made as previously described [4]. Yield of white crystalline solid 1.9 g, 2.32 mmol, 93%. Found C, 34.4; H, 4.5; N, 1.4%. Calcd. For  $C_{26}H_{54}NO_{12}PW_2$ : C, 34.1; H, 4.7; N, 1.4%.

2.2.13.  $[NMe_4]^+[(Ph_2PO_2)(MoO(O_2)_2)_2]$ , **10**

This was made as previously described [4]. Yield of yellow crystalline solid 1.1 g, 1.63 mmol, 65%. Found C, 29.8; H, 3.1; N, 2.2%. Calcd. For  $C_{16}H_{22}NO_{12}PMo_2$ : C, 29.9; H, 3.4; N, 2.2%.

2.2.14.  $K_7[PW_{11}O_{39}].10H_2O$ , **11**

The preparation was based on the method of Haraguchi et al. [20]. Phosphotungstic acid hydrate (2.9 g, 1.0 mmol) was dissolved in hot water (5 cm<sup>3</sup>) and a concentrated potassium acetate solution (3.2 g, 33 mmol, 5 cm<sup>3</sup> of water; pH adjusted at 7 with acetic acid) was added dropwise under vigorous stirring. The reaction mixture was filtered and the filtrate refrigerated. The precipitate obtained was fil-

tered and dried in a desiccator over silica gel. Yield of white solid 2.8 g, 0.89 mmol, 89%. Found: K, 8.5; P, 0.9%. Calcd. for  $H_{20}O_{49}PK_7W_{11}$ : K, 8.7; P, 1.0%.

2.2.15.  $K_{11}[Ln\{PW_{11}O_{39}\}_2] \cdot nH_2O$  and  $K_{10}[M\{PW_{11}O_{39}\}_2] \cdot nH_2O$

Lanthanophosphopolytungstates of general formula  $[Ln^{III}\{PW_{11}O_{39}\}_2]^{11-}$  ( $Ln = Y, La, Ce, Pr, Sm, Tb, Yb$ ) and  $[M^{IV}\{PW_{11}O_{39}\}_2]^{10-}$  ( $M = Ce, Th$ ) were synthesised using the method of Haraguchi et al. [20]. Phosphotungstic acid hydrate (4.3 g, 1.5 mmol) was dissolved in hot water (5 cm<sup>3</sup>) and an aqueous solution of the appropriate lanthanide salt ( $YCl_3 \cdot 6H_2O, LaCl_3 \cdot 7H_2O, Ce(NO_3)_3 \cdot 6H_2O, (NH_4)_2[Ce(NO_3)_6], Pr(NO_3)_3 \cdot 6H_2O, Sm(NO_3)_3 \cdot 6H_2O, Tb(NO_3)_3 \cdot 5H_2O, Yb(NO_3)_3 \cdot 5H_2O$  or  $Th(NO_3)_4 \cdot 12H_2O$ ; 0.75 mmol in 2 cm<sup>3</sup> of water) added to the hot solution in a molar proportion ( $H_3PW_{12}O_{40}:Ln$ ) of 2:1. A concentrated solution of potassium acetate (5.0 g, 50 mmol in 5 cm<sup>3</sup> of water; pH adjusted at 7 with acetic acid) was then added dropwise with vigorous stirring. The reaction mixture was filtered and the filtrate refrigerated. The precipitate was filtered, recrystallized from water and dried in a desiccator over silica gel. We have recently described characterisation of a number of these [21].

For  $K_{11}[Y\{PW_{11}O_{39}\}_2] \cdot 16H_2O$ , yield of white solid 3.9 g, 0.63 mmol, 84%. Found P, 0.9; K, 7.7; Y, 1.4; W, 56.7%. Calcd. for  $H_{32}O_{94}P_2K_{11}YW_{22}$ : P, 1.0; K, 7.0; Y, 1.4; W, 65.6%.

$K_{11}[La\{PW_{11}O_{39}\}_2] \cdot 35H_2O$ , yield of white solid 4.3 g, 0.66 mmol, 88%. Found P, 0.9; K, 6.5; La, 1.8; W, 56.7%. Calcd. for  $H_{70}O_{113}P_2K_{11}LaW_{22}$ : P, 1.0; K, 6.6; La, 2.1; W, 61.7%.

For  $K_{11}[Ce\{PW_{11}O_{39}\}_2] \cdot 20H_2O$ , yield of orange solid 3.7 g, 0.59 mmol, 78%. Found P, 0.8; K, 7.0; Ce, 1.9; W, 54.9%. Calcd. for  $H_{40}O_{98}P_2K_{11}CeW_{22}$ : P, 1.0; K, 6.8; Ce, 2.2; W, 64.4%.

$K_{10}[Ce\{PW_{11}O_{39}\}_2] \cdot 20H_2O$ , yield of yellow solid 2.4 g, 0.38 mmol, 51%. Found P, 0.8;

K, 6.4; Ce, 2.1; W, 58.1%. Calcd. for  $H_{40}O_{98}P_2K_{10}CeW_{22}$ : P, 1.0; K, 6.2; Ce, 2.2; W, 64.8%.

$K_{11}[Pr\{PW_{11}O_{39}\}_2] \cdot 20H_2O$ , yield of green solid 3.3 g, 0.52 mmol, 69%. Found P, 0.9; K, 6.9; Pr, 2.0; W, 64.2%. Calcd. for  $H_{40}O_{98}P_2K_{11}PrW_{22}$ : P, 1.0; K, 6.8; Pr, 2.2; W, 64.4%.

$K_{11}[Sm\{PW_{11}O_{39}\}_2] \cdot 20H_2O$ , yield of white solid 3.3 g, 0.52 mmol, 69%. Found P, 0.9; K, 6.8; Sm, 2.5; W, 64.1%. Calcd. for  $H_{40}O_{98}P_2K_{11}SmW_{22}$ : P, 1.0; K, 6.8; Sm, 2.4; W, 64.3%.

$K_{11}[Tb\{PW_{11}O_{39}\}_2] \cdot 12H_2O$ , yield of white solid 4.0 g, 0.65 mmol, 87%. Found P, 0.9; K, 6.9; Tb, 2.5; W, 66.4%. Calcd. for  $H_{24}O_{90}P_2K_{11}TbW_{22}$ : P, 1.0; K, 7.0; Tb, 2.6; W, 65.7%.

$K_{11}[Yb\{PW_{11}O_{39}\}_2] \cdot 17H_2O$ , yield of white solid 4.2 g, 0.67 mmol, 89%. Found P, 0.9; K, 6.8; Yb, 2.8; W, 64.6%. Calcd. for  $H_{34}O_{95}P_2K_{11}YbW_{22}$ : P, 1.0; K, 6.9; Yb, 2.8; W, 64.6%.

$K_{10}[Th\{PW_{11}O_{39}\}_2] \cdot 36H_2O$ , the procedure above for the lanthanides was used rather than the literature preparation [22]. Yield of white solid 1.1 g, 0.17 mmol, 23%. Found P, 0.8; K, 6.0; W, 55.3%. Calcd. for  $H_{72}O_{114}P_2K_{10}ThW_{22}$ : P, 0.9; K, 5.9; W, 60.1%.

### 2.3. Oxidation procedures.

#### 2.3.1. Catalytic oxidation of alkenes and alcohols by 1 and 2

Our previous procedure [11] was followed. Substrate (20 mmol) and catalyst (0.07 mmol) were dissolved in benzene (5 cm<sup>3</sup>) and the solution mixed with  $H_2O_2$  (15%, 7 cm<sup>3</sup>). The two-phase mixture was stirred vigorously for 3 h at 75°C under reflux conditions. After cooling, the organic layer was analyzed by <sup>1</sup>H NMR spectroscopy and/or GC.

#### 2.3.2. Catalytic oxidation of alkenes and alcohols by 3–6

For 3 and 4 the catalyst (0.1 mmol) and  $[N(^{13}C_6H_{13})_4]Cl$  (0.3 mmol) were dissolved in

benzene (8 cm<sup>3</sup>) and the substrate (15 mmol) added. H<sub>2</sub>O<sub>2</sub> (15% w/v, 10 cm<sup>3</sup>) was added to the benzene solution and the biphasic mixture refluxed at 75°C for 3 h. The resulting organic layer was analyzed by GC. For **5** and **6** the same procedure was followed, but 0.2 mmol of [N(<sup>n</sup>C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>]Cl used.

### 2.3.3. Catalytic oxidation of tertiary amines by **1** and **2**

Our previous procedure [5] was followed. The catalyst (0.045 mmol) was dissolved in toluene (10 cm<sup>3</sup>) and the substrate (10 mmol) added. H<sub>2</sub>O<sub>2</sub> (15% w/v, 15 cm<sup>3</sup>) was added and the resulting suspension refluxed at 90°C for 6 h. Upon cooling the solid was filtered off, washed with water (10 cm<sup>3</sup>), diethyl ether (2 × 10 cm<sup>3</sup>) and air dried. The yield, IR spectrum and melting point of the products were recorded.

### 2.3.4. Catalytic oxidation of tertiary amines by **3** and **4**

The catalyst (0.1 mmol) and [N(<sup>n</sup>C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>]Cl (0.3 mmol) were dissolved in toluene (10 cm<sup>3</sup>) and the substrate (15 mmol) added. H<sub>2</sub>O<sub>2</sub> (15% w/v, 10 cm<sup>3</sup>) was added and the resulting suspension refluxed at 90°C for 6 h. Upon cooling the solid was filtered off, washed with water (10 cm<sup>3</sup>), diethyl ether (2 × 10 cm<sup>3</sup>) and air dried. The yield, IR spectra and melting point of the products were recorded.

### 2.3.5. Catalytic oxidation of tertiary amines by **5–10**

The same procedure as for compounds **3** and **4** was followed, but 0.2 mmol of [N(<sup>n</sup>C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>]Cl was used for **5–8** and 0.1 mmol for **9** and **10**.

### 2.3.6. General procedure for catalytic oxidations of sulfides by **5**, **7–10**

The substrate (2 mmol) catalyst (0.01 mmol) and cetylpyridinium chloride (0.02 mmol) were dissolved in chloroform (30 cm<sup>3</sup>). H<sub>2</sub>O<sub>2</sub> (35% w/v, 0.39 cm<sup>3</sup>) was added to the chloroform solution and the biphasic mixture stirred vigorously at ambient temperature for 2 h. The organic layer was analyzed by <sup>1</sup>H NMR spec-

troscopy. For **9** and **10** 0.1 mmol of cetylpyridinium chloride was used.

### 2.3.7. Catalytic oxidation of alkenes and alcohols by **11**, **12**, K<sub>11</sub>[Ln{PW<sub>11</sub>O<sub>39</sub>}<sub>2</sub>] · nH<sub>2</sub>O (Ln = Y, La, Ce, Pr, Sm, Tb, Yb) and K<sub>10</sub>[M{PW<sub>11</sub>O<sub>39</sub>}<sub>2</sub>] · nH<sub>2</sub>O (M = Ce, Th)

[N(<sup>n</sup>C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>]Cl (0.07 mmol for **11**; 0.03 for **12**; 0.11 for Ln = Y, La, Ce<sup>III</sup>, Pr, Sm, Tb and Yb; 0.1 mmol for M = Ce<sup>IV</sup> and Th) was dissolved in benzene (10 cm<sup>3</sup>) and the substrate (10 mmol) added. An aqueous solution of the catalyst (0.01 mmol, 2 cm<sup>3</sup> of water) and hydrogen peroxide (30% w/v, 2.5 cm<sup>3</sup>) was added to the benzene solution and the biphasic mixture refluxed at 71°C for 3 h. The resulting organic layer was analyzed by <sup>1</sup>H NMR for alkenes and gas chromatography for alcohols.

## 2.4. Physical measurements

Infrared spectra of the solids were measured over the range 4000–400 cm<sup>-1</sup> using KBr disks on a Perkin-Elmer 1720 Fourier-transform spectrometer. Raman spectra of the complexes (as powders and as solutions in acetonitrile or water in melting-point tubes) were measured on a Perkin-Elmer 1760X FT-IR instrument fitted with a 1700X NIR FT-Raman accessory using a Nd:YAG laser (1064 nm excitation) or on a Spex Ramalog 5 instrument, with a Datamate data acquisition unit, using excitation at 514.5 nm from a Coherent Radiation Innova 70 argon-ion laser. The NMR spectra were obtained on a JEOL ESX 270 spectrometer (<sup>31</sup>P, 109.25 MHz; <sup>1</sup>H, 270.05 MHz) as CD<sub>3</sub>CN or D<sub>2</sub>O solutions, using external H<sub>3</sub>PO<sub>4</sub> as reference. The GC 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. IC-PAES analysis were recorded on a ARL instrument by Mr. B. Coles of the Geology department, Imperial College. Solid state <sup>31</sup>P NMR

spectra were recorded as powders in zirconia rotors on a Bruker MSL300 using a standard Bruker magic angle spinning (MAS) probe with double-bearing rotation mechanism by Dr. A. Aliev and Mr. D. Butler of the Chemistry Department, University College.

### 3. Results and discussion

**3.1. Trinuclear complexes**  $[NBu_4]_3[(PO_4)\{MO-(O_2)_2\}_2\{MO-(O_2)_2(H_2O)\}]$ , ( $M = W$ ,  $L = P$ , **3**;  $As$ , **4**;  $M = Mo$ ,  $L = As$ )

The existence of heteropolyperoxotungstates of this type has been postulated from studies on the  $^{31}P$  NMR spectra of mixtures of tungstate and phosphate in  $H_2O_2$  near pH 1.6 [11] or from solutions formed by reaction of  $H_3[PW_{12}O_{40}]$  in  $H_2O_2$  [2,3,8] but such species have hitherto not been isolated. We have however earlier reported and structurally characterised an analogous organophosphonate complex,  $[NMe_4]_2[(PhPO_3)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]$ , and shown that its tungsten analogue is a reasonably effective catalyst for the epoxidation of alkenes and the oxidation of alcohols with  $H_2O_2$  as a co-oxidant with  $[N(C_6H_{13})_4]Cl$  as phase transfer agent [2]. We now find that reaction of  $MO_3 \cdot H_2O$  ( $M = Mo$ ,

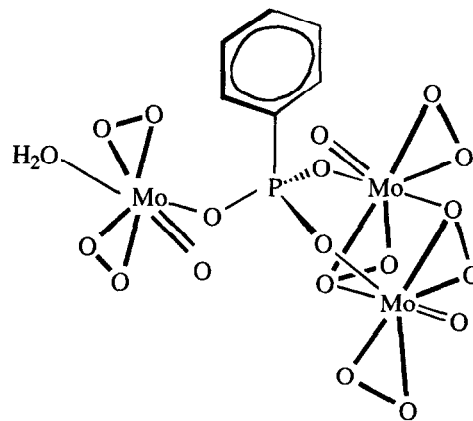


Fig. 1. Schematic representation of the structure [2] of  $[(PhPO_3)_3\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]^{2-}$ .

$W$ ) and  $NaH_2PO_4$  or  $Na_2HAsO_4$  in excess  $H_2O_2$  in the presence of tetra-*n*-butylammonium chloride in the appropriate mole ratios leads to formation of  $[NBu_4]_3(LO_4)\{MO-(O_2)_2\}_2\{MO(O_2)_2(H_2O)\}$  ( $L = P$  (**3**),  $As$  (**4**)).

Although we have as yet been unable to obtain crystals suitable for single crystal X-ray structural determination, microanalyses, vibrational and  $^{31}P$  NMR data suggest that this is the correct formulation of the tungsten and molybdenum complexes. Raman and infrared spectra of **3** and **4** (Table 1) are similar to those obtained for  $[NMe_4]_2-[(PhPO_3)\{MoO(O_2)_2\}_2-\{MoO(O_2)_2(H_2O)\}]$  with the exception of bands due to the phenyl group and to cation bands.

Table 1  
Vibrational spectroscopic data ( $cm^{-1}$ ) for complexes **3–6** and the molybdenum analogues of **5** and **6**<sup>a</sup>

Complex	$\nu(M=O)$	$\nu(O-O)$	$\nu_{sym}[M(O)_2]$	$\nu_{asym}[M(O)_2]$
$[(PO_4)(WO(O_2)_2)_2\{WO(O_2)_2(H_2O)\}]^{3-}$ <b>3</b>	964vs	846vs	575s	521s
$[(AsO_4)(WO(O_2)_2)_2\{WO(O_2)_2(H_2O)\}]^{3-}$ <b>4</b>	972 [974]vs	858 [858]s	577 [576]m	538 [537]m
$[(PO_3(OH))(WO(O_2)_2)_2]^{2-}$ <b>5</b>	970vs	847vs	572s	512s
$[(AsO_3(OH))(WO(O_2)_2)_2]^{2-}$ <b>6</b>	978 [978]vs	860 [861]s	574 [574]m	536 [536]m
$[(PO_3(OH))(MoO(O_2)_2)_2]^{2-}$	960vs	842vs	570s	518s
$[(AsO_3(OH))(MoO(O_2)_2)_2]^{2-}$	969 [972]vs	853 [855]m	576 [575]m	534 [533]w
$[(PO_3(OH))(MoO(O_2)_2)_2]^{2-}$	968vs	843vs	588s	511s
$[(AsO_3(OH))(MoO(O_2)_2)_2]^{2-}$	976 [977]vs	853 [855]m	575 [575]m	526 [525]w
$[(PO_3(OH))(MoO(O_2)_2)_2]^{2-}$	962vs	869vs	591m	520m
$[(AsO_3(OH))(MoO(O_2)_2)_2]^{2-}$	977 [978]vs	888 [887]s	592 [592]m	527 [528]w
$[(AsO_3(OH))(MoO(O_2)_2)_2]^{2-}$	961vs	870s	589m	519m
$[(AsO_3(OH))(MoO(O_2)_2)_2]^{2-}$	972 [971]vs	880 [881]s	588 [589]m	523 [523]s

vs = very strong; s = strong; m = medium; w = weak band intensity.

<sup>a</sup> Raman data in italics (solution Raman data in  $CH_3CN$  in parentheses); bands due to the ligand and counter-ion not listed.

The  $^{31}\text{P}$  NMR spectrum of **3** in  $\text{CD}_3\text{CN}$  has a single shift at  $\delta$  3.34 ppm (versus  $\text{H}_3\text{PO}_4$ ) and the shift observed for the solid state MAS  $^{31}\text{P}$  NMR spectra of this complex is relatively close to this at 1.21 ppm. The Raman spectra of the solids are similar in profile to those of their solutions, so the structure is likely to be similar to that found by us for  $[(\text{PhPO}_3)(\text{MoO}(\text{O}_2)_2)_2\text{-}\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{2-}$  [2], a  $\text{PO}_4$  unit replacing  $(\text{PhPO}_3)$  (Fig. 1).

With  $[\text{N}^n\text{C}_6\text{H}_{13}]_4\text{Cl}$  as phase transfer catalyst **3** and **4** are effective catalysts in benzene–aqueous 15%  $\text{H}_2\text{O}_2$  at  $75^\circ\text{C}$  for alkene epoxida-

tion, oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones (Table 2). Here we compare their efficacies as catalysts with those of  $[\text{N}^n\text{C}_6\text{H}_{13}]_4[\text{L}(\text{LO}_4)(\text{WO}(\text{O}_2)_2)_4]$  ( $\text{L} = \text{P}$ , **1**;  $\text{As}$ , **2**) and the dimers (see below;  $[\text{NBu}_4]_2[\text{L}(\text{LO}_3(\text{OH}))(\text{WO}(\text{O}_2)_2)_2]$ ,  $\text{L} = \text{P}$ , **5** and  $\text{As}$ , **6**). From Table 2 it appears that the trinuclear species **3** and **4** are significantly more effective than **1**, **2**, **5**, and **6** for epoxidation of smaller cyclic alkenes but less effective for linear alkene epoxidations. For alcohol oxidations all six complexes have comparable catalytic abilities, while for tertiary amine oxida-

Table 2  
Oxidation of alkenes, alcohols and tertiary amines by **1–6**<sup>a</sup>

Substrate	Product	$[(\text{XO}_4)(\text{WO}(\text{O}_2)_2)_4]^{3-}$ <sup>b</sup>		$[(\text{XO}_4)(\text{WO}(\text{O}_2)_2)_2\text{-}\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{3-}$ <sup>c</sup>		$[(\text{XO}_3(\text{OH}))(\text{WO}(\text{O}_2)_2)_2]^{2-}$ <sup>c</sup>	
		<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Cyclopentene	epoxide	48 (137) <sup>d</sup>	69 (197) <sup>d</sup>	80 (120)	89 (134)	74 (111)	64 (96)
Cyclohexene	epoxide	18 (51) <sup>d</sup>	36 (103) <sup>d</sup>	41 (62)	34 (51)	67 (100)	23 (36)
Cycloheptene	epoxide	62 (177) <sup>d</sup>	83 (237) <sup>d</sup>	98 (147)	95 (143)	89 (133)	92 (138)
Cyclooctene	epoxide	99 (283) <sup>d</sup>	99 (283) <sup>d</sup>	93 (140)	92 (138)	91 (136)	91 (136)
Cyclododecene	epoxide	99 (283) <sup>d</sup>	99 (283) <sup>d</sup>	88 (134)	89 (134)	97 (145)	96 (144)
Oct-1-ene	epoxide	62 (177) <sup>d</sup>	48 (137) <sup>d</sup>	35 (53)	32 (48)	35 (52)	36(53)
Non-1-ene	epoxide	93 (266) <sup>d</sup>	94 (269) <sup>d</sup>	59 (89)	62 (93)	75 (112)	34 (51)
Dec-1-ene	epoxide	89 (254) <sup>d</sup>	97 (277) <sup>d</sup>	67 (101)	70 (105)	62 (93)	55 (82)
Undec-1-ene	epoxide	85 (243) <sup>d</sup>	99 (283) <sup>d</sup>	61 (92)	65 (98)	52 (78)	53 (79)
Dodec-1-ene	epoxide	96 (274) <sup>d</sup>	99 (283) <sup>d</sup>	60 (90)	67 (101)	63 (94)	47 (70)
Benzylalcohol	aldehyde	99 (283) <sup>d</sup>	99 (283) <sup>d</sup>	96 (144)	97 (146)	99 (149)	99 (149)
2-Methylbenzylalcohol	aldehyde	99 (283) <sup>d</sup>	99 (283) <sup>d</sup>	99 (149)	99 (149)	98 (147)	96 (144)
Cyclopentanol	ketone	84 (240) <sup>d</sup>	85 (243) <sup>d</sup>	82 (123)	84 (126)	55 (82)	64 (96)
Cyclohexanol	ketone	95 (271) <sup>d</sup>	96 (274) <sup>d</sup>	97 (146)	97 (146)	68 (102)	94 (141)
Cycloheptanol	ketone	99 (283) <sup>d</sup>	99 (283) <sup>d</sup>	98 (147)	99 (149)	98 (147)	99 (149)
Cyclooctanol	ketone	99 (283) <sup>d</sup>	99 (283) <sup>d</sup>	99 (149)	99 (149)	99 (149)	99 (149)
Isonicotinic acid	N-oxide	83 (184) <sup>e</sup>	65 (147) <sup>e</sup>	75 (112)	76 (114)	63 (94)	63 (94)
Nicotinic acid	N-oxide	73 (161) <sup>e</sup>	77 (174) <sup>e</sup>	66 (99)	72 (108)	41 (62)	58 (87)
Picolinic acid	N-oxide	62 (137) <sup>e</sup>	86 (195) <sup>e</sup>	23 (35)	32 (48)	11 (17)	17 (26)
2,3-pyridine-dicarboxylic acid	N-oxide	68 (151) <sup>e</sup>	75 (169) <sup>e</sup>	66 (99)	71 (107)	53 (80)	54 (81)
2,5-pyridine-dicarboxylic acid	N-oxide	94 (208) <sup>e</sup>	96 (215) <sup>e</sup>	91 (137)	96 (144)	87 (131)	86 (129)
2,6-pyridine-dicarboxylic acid	N-oxide	76 (168) <sup>e</sup>	79 (178) <sup>e</sup>	79 (119)	81 (122)	69 (104)	77 (116)
3,4-pyridine-dicarboxylic acid	N-oxide	79 (175) <sup>e</sup>	82 (182) <sup>e</sup>	83 (125)	85 (128)	54 (81)	69 (104)

<sup>a</sup> Yields in % with turnovers in parentheses.

<sup>b</sup>  $[\text{N}(\text{C}_6\text{H}_{13})_4]$  salt.

<sup>c</sup>  $[\text{N}(\text{C}_4\text{H}_9)_4]$  salt.

<sup>d</sup> Under conditions previously described [11].

<sup>e</sup> Under conditions previously described [5].

tions the dinuclear complexes **5** and **6** are less effective. Although **1** and **2** will oxidise alcohols at room temperature in a benzene/peroxide mixture [11] they are much more efficient in respect of yields and turnovers of products if such oxidations are carried out at 75°C. The molybdenum analogue of **4**,  $[\text{NBu}_4^+ ]_3 [(\text{AsO}_4) \{ \text{MoO}(\text{O}_2)_2 \}_2 \{ \text{MoO}(\text{O}_2)_2 (\text{H}_2\text{O}) \}]$ , is far less useful as a catalyst; the lower efficiency of molybdenum complexes with  $\text{H}_2\text{O}_2$  has been noted by us [4,11] and by Salles et al. [12] for catalysts containing  $\eta^2$ ,  $\eta^1$ -peroxo linkages, and for stoichiometric oxidations effected by molybdenum as compared with tungsten complexes  $\eta^2$ -peroxocomplexes by Amato et al. [23]. Similarly, as we also previously noted [2,5,6,11], polyperoxotungstates are far more effective as catalysts for epoxidation of cyclic rather than linear alkenes.

The effect of changing the nature of the phase transfer agent, and also changing the ratio of phase transfer agent to metal peroxo catalyst for oxidations involving complexes **3–6** is considered in Section 3.2 below.

### 3.2. Dinuclear complexes $[\text{NBu}_4^+ ]_2 [(\text{LO}_3(\text{OH})) \{ \text{MO}(\text{O}_2)_2 \}_2]$ , ( $M = \text{W}, \text{L} = \text{P}, \text{As}$ , **5**, **6**; $M = \text{Mo}, \text{L} = \text{P}, \text{As}$ )

The tungsten complexes **5** and **6** were isolated by Salles et al. and the single crystal X-ray structures reported [8]. The structures of the anions are similar to those reported by us for  $[\text{NMe}_4^+ ]_3 [(\text{Me}_2\text{AsO}_2) \{ \text{MoO}(\text{O}_2)_2 \}_2]$ ,  $(\text{NBu}_4^+ )_2 [(\text{Ph}_2\text{PO}_2) \{ \text{MoO}(\text{O}_2)_2 \}_2]$  and for  $(\text{NBu}_4^+ )_2 [(\text{Ph}_2\text{PO}_2) \{ \text{WO}(\text{O}_2)_2 \}_2]$  [4] (see Fig. 2), though there is no interanionic hydrogen bonding in these species. We have prepared **5** and report here its  $^{31}\text{P}$  NMR and Raman spectra, and also complex **6** and the two analogous molybdenum complexes  $(\text{NBu}_4^+ )_2 [(\text{LO}_3(\text{OH})) \{ \text{MO}(\text{O}_2)_2 \}_2]$  ( $\text{L} = \text{P}, \text{As}$ ).

The  $^{31}\text{P}$  NMR shifts of **5** show relatively large solvent effects, in agreement with literature observations [3,8]. Thus in  $\text{CD}_3\text{CN}$  **5** gives a single peak at  $\delta$  2.29 with two satellites from

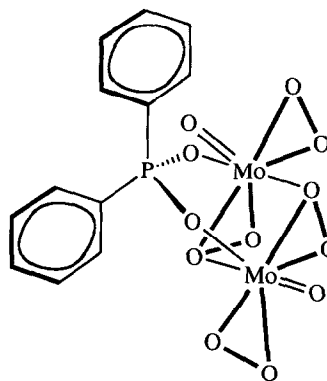


Fig. 2. Schematic representation of the structure [2] of  $[(\text{Ph}_2\text{PO}_2) \{ \text{MoO}(\text{O}_2)_2 \}_2]^-$ .

$^{183}\text{W}$  ( $J_{\text{PW}}$  15 Hz), and a single peak at  $\delta$  2.05 in  $\text{MeCN}/\text{CDCl}_3$  (4:1); in  $\text{D}_2\text{O}$  it lies at  $\delta$  1.0 at pH 3.5, while the  $^{31}\text{P}$  MAS NMR spectrum of **5** as a solid shows a single resonance at  $\delta$  0.94. In the case of the organophosphinate complex  $[\text{NBu}_4^+ ] [(\text{Ph}_2\text{PO}_2) \{ \text{WO}(\text{O}_2)_2 \}_2]$  **9**, the  $^{31}\text{P}$  NMR of the solution in  $\text{CD}_3\text{CN}$  ( $\delta$  51.9) is close to that of the solid ( $\delta$  52.7 and 53.9; this splitting is attributable to the observed [4] crystal disorder).

Infrared [8] and Raman [24] spectra of **5** in the solid and in its solution in acetonitrile indicate no change of structure from solid to solution. We find that this is also likely to be the case for **6** and the analogous molybdenum complexes  $[(\text{LO}_3(\text{OH})) \{ \text{MO}(\text{O}_2)_2 \}_2]^{2-}$  ( $\text{L} = \text{P}, \text{As}$ ; Table 1).

The efficacy of **5** as an epoxidation catalyst for limonene to give the mono- and di-epoxides at room temperatures has been reported [8]. We find that it is an effective catalyst with  $\text{H}_2\text{O}_2$  as cooxidant for alkene epoxidation and for oxidation of primary alcohols to aldehydes, secondary alcohols to ketones and tertiary amines to N-oxides (Table 2). The selective oxidation of dialkyl and diaryl sulfides  $\text{R}_2\text{S}$  by **5** to the corresponding sulfones  $\text{R}_2\text{SO}_2$  is essentially quantitative in the presence of cetylpyridinium chloride as phase transfer agent. Ishii et al. have reported similar though more limited data for **1** [17]; Ballistreri et al. have studied mechanistic



aspects of the oxidation by  $[\text{PO}_4\{\text{MoO}(\text{O}_2)_2\}_4]^{3-}$  of sulfides [25].

The presence of an ionisable proton in **5** led us to try to determine its  $\text{p}K_a$  from shifts in the  $^{31}\text{P}$  NMR peak assigned [11] to this species in aqueous  $\text{H}_2\text{O}_2$  with pH. Although the  $\delta$  value did change from  $\delta$  1.0 at pH 3.5 to  $\delta$   $-0.25$  at pH 1.7 no point of inflection was seen. There was little change in the yield and turnovers for epoxidation of cyclooctene using **5** as a catalyst in benzene–aqueous 15%  $\text{H}_2\text{O}_2$  at  $75^\circ\text{C}$  with  $[\text{N}^n\text{C}_6\text{H}_{13}]_4\text{Cl}$  as phase transfer agent over a three hour period at pH 4.0 or pH 0.5, suggesting that if  $[(\text{PO}_3(\text{OH}))\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$  were the major species at the lower pH and the deprotonated  $[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_2]^{3-}$  at the higher pH this change had little effect on the oxidation catalysis by these species.

The effect of changing the amount and nature of the phase transfer agent  $[\text{N}^n\text{C}_6\text{H}_{13}]_4\text{Cl}$  was briefly studied for the trinuclear complex **3** and the dinuclear complex **5** with cyclooctene as substrate. For **3** the expected phase transfer agent:metal catalyst mole ratio of 3:1 gave optimum yields and turnovers, but for **5** the optimum ratio was 1:1. Brégeault et al. came to a similar conclusion for **5** using 1-octene and other phase transfer catalysts [25]. For both **3** and **5** the use of a large excess of  $[\text{N}^n\text{C}_6\text{H}_{13}]_4\text{Cl}$  led to low yields and turnovers.

### 3.3. Phenylphosphonate and diphenylphosphinate complexes $[\text{NMe}_4]_2\text{-}[(\text{PhPO}_3)\{\text{MO}(\text{O}_2)_2\}_2[\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})]]$ ( $M = \text{W}$ , **7**, $\text{Mo}$ , **8**; $[\text{NBu}_4^n]_2[(\text{PhPO}_2)\{\text{WO}(\text{O}_2)_2\}_2]$ , **9** and $[\text{NBu}_4^n]_2[(\text{PhPO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$ , **10** as oxidants

We have reported the X-ray crystal structures of  $[\text{NMe}_4]_2\text{-}[(\text{PhPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  [2] and  $[\text{NBu}_4^n]_2[(\text{Ph}_2\text{PO}_2)\{\text{WO}(\text{O}_2)_2\}_2]$  [4] and their properties as catalysts for alkene epoxidations and alcohol oxidations. The unusual hexanuclear complex  $[\text{NMe}_4]_3[(\text{MePO}_3)\{\text{MePO}_2(\text{OH})\}\text{W}_6\text{O}_{13}(\text{O}_2)_4(\text{OH})_2(\text{H}_2\text{O})_2]$ , which contains only  $\eta^2$  peroxo linkages, in solution is

an effective oxidation catalyst in  $\text{H}_2\text{O}_2$ ; however  $^{31}\text{P}$  NMR data suggest that in such solutions it breaks up to the trinuclear species  $[(\text{MePO}_3)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{2-}$  which does contain  $\eta^2$ ,  $\eta^1$ -peroxo moieties [6].

In Table 3 we give additional data using **7–10** for oxidations of dialkyl or diaryl sulfides to sulfoxides and sulfones, respectively, and tertiary amines to N-oxides. It is surprising that the molybdenum complexes are reasonably effective for these oxidations, although their tungsten analogues are better in this respect and, for sulfide oxidations, give better final yields of sulfones (as noted in Section 3.2 above, **5** gives essentially quantitative yields of sulfone under the same conditions). In general for these oxidations the only dependence on the phase transfer agent:catalyst ratio was a reduced yield of product for large ratios.

### 3.4. Bond distances in $\eta^2$ , $\eta^1$ -peroxo complexes

Unfortunately, X-ray crystal structure data for molybdenum complexes containing these units are much better than those of the catalytically more active tungsten complexes. In the three examples of the latter  $[\text{N}^n\text{C}_6\text{H}_{13}]_3\text{-}[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_4]$  [1],  $[\text{NBu}_4^n]_2[(\text{PO}_3(\text{OH}))\{\text{WO}(\text{O}_2)_2\}_2]$  [8] and  $[\text{NBu}_4^n]_2[(\text{Ph}_2\text{PO}_2)\{\text{WO}(\text{O}_2)_2\}_2]$  [4] there are problems of partial disorder which prevent a clear comparison of W–O and O–O bond lengths between the  $\eta^2$ ,  $\eta^1$ -peroxo and  $\eta^2$ -peroxo moieties. It does however seem, for the first two examples at least [1,8] that the W–O distance to the bridging oxygen atom in the  $\eta^2$ ,  $\eta^1$ -peroxo moiety is slightly longer than that in the  $\eta^2$ -peroxo unit. For the molybdenum complexes  $[\text{NBu}_4^n]_3[(\text{PO}_4)\{\text{MoO}(\text{O}_2)_2\}_4]$  [12],  $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{MoO}(\text{O}_2)_2\}_2\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$  [2],  $[\text{NMe}_4]_2[(\text{Me}_2\text{AsO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$  and  $[\text{NBu}_4^n]_2[(\text{Ph}_2\text{PO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$  [4] however the X-ray data are much less equivocal. For these complexes it is clear that the two Mo–O distances in the  $\eta^2$ ,  $\eta^1$ -peroxo units are essentially identical to each other;

Table 3  
Oxidation of dialkyl and diaryl sulfides and tertiary amines by 7–10<sup>a</sup>

Substrate	Product	[(PhPO <sub>3</sub> )(MO(O <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sup>2-</sup> {MO(O <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)} <sup>2-</sup> <sup>b</sup>		[(Ph <sub>2</sub> PO <sub>2</sub> )(MO(O <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sup>-</sup> <sup>b</sup>	
		7	8	9	10
Methylsulfide	sulfide	0	2 (4)	0	6 (12)
	sulfoxide	8 (16)	17 (34)	3 (6)	16 (32)
	sulfone	92 (184)	81 (162)	97 (194)	78 (156)
Thioanisole	sulfide	0	0	0	0
	sulfoxide	3 (6)	72 (144)	2 (4)	60 (120)
	sulfone	97 (194)	28 (56)	98 (196)	40 (80)
Benzylphenylsulfide	sulfide	5 (10)	21 (42)	2 (4)	12 (24)
	sulfoxide	6 (12)	23 (46)	6 (12)	13 (26)
	sulfone	89 (178)	56 (112)	92 (184)	75 (150)
Methyl- <i>p</i> -tolylsulfide	sulfide	0	0	0	0
	sulfoxide	5 (10)	51 (102)	3 (6)	28 (56)
	sulfone	95 (190)	49 (98)	97 (194)	72 (144)
Ethylphenylsulfide	sulfide	7 (14)	35 (70)	2 (4)	11 (22)
	sulfoxide	8 (16)	36 (72)	9 (18)	12 (24)
	sulfone	85 (170)	29 (58)	89 (178)	77 (154)
4-Bromothioanisole	sulfide	7 (14)	19 (38)	3 (6)	15 (30)
	sulfoxide	24 (48)	30 (60)	25 (50)	26 (52)
	sulfone	69 (138)	51 (102)	72 (144)	59 (118)
Isonicotinic acid	N-oxide	57 (87)	20 (30)	57 (87)	18 (27)
Nicotinic acid	N-oxide	61 (92)	18 (27)	72 (108)	16 (24)
Picolinic acid	N-oxide	52 (78)	13 (20)	58 (86)	11 (17)
2,3-pyridinedicarboxylic acid	N-oxide	68 (102)	21 (32)	71 (107)	22 (63)
2,5-pyridinedicarboxylic acid	N-oxide	24 (36)	9 (14)	27 (41)	8 (12)
2,6-pyridinedicarboxylic acid	N-oxide	75 (113)	27 (41)	86 (129)	28 (42)
3,4-pyridinedicarboxylic acid	N-oxide	73 (110)	29 (44)	85 (128)	24 (36)

<sup>a</sup> Yields in % with turnovers in parentheses.

<sup>b</sup> [Me<sub>4</sub>N] salts.

the same is true for the O–O distances in both the  $\eta^2$ - and in the  $\eta^2$ ,  $\eta^1$ -peroxo units. However, the Mo–O distances in the  $\eta^2$ ,  $\eta^1$ -peroxo units are significantly different from each other by ca. 0.07–0.1 Å.

### 3.5. [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> (11) and lanthanopolyoxotungstates as catalysts

Though there have been a number of studies on H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] · nH<sub>2</sub>O (12) as an oxidation

Table 4  
Oxidation of alkenes and alcohols catalysed by lanthanophosphopolytungstates<sup>a</sup>

Substrate	K <sub>7</sub> [PW <sub>11</sub> O <sub>39</sub> ] (11)	H <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] (12)	K <sub>11</sub> [Ln(PW <sub>11</sub> O <sub>39</sub> ) <sub>2</sub> ]							
			Y	La	Ce <sup>III</sup>	Ce <sup>IV</sup>	Pr	Sm	Tb	Yb
Cyclopentene	72 (720)	—	69 (690)	77 (770)	31 (310)	19 (190)	60 (600)	87 (870)	89 (890)	75 (750)
Cyclooctene	82 (820)	90 (900)	82 (820)	81 (810)	33 (330)	14 (140)	79 (790)	81 (810)	72 (720)	77 (770)
Cyclododecene	57 (570)	95 (950)	56 (560)	57 (570)	17 (170)	14 (140)	69 (690)	65 (650)	58 (580)	52 (520)
1-Octene	14 (140)	29 (290)	17 (170)	15 (150)	6 (60)	4 (40)	18 (180)	22 (220)	16 (160)	16 (160)
1-Nonene	18 (180)	27 (270)	20 (200)	20 (200)	4 (40)	5 (50)	20 (200)	21 (210)	17 (170)	17 (170)
1-Dodecene	13 (130)	29 (290)	18 (180)	18 (180)	5 (50)	3 (30)	20 (200)	13 (130)	17 (170)	18 (180)
Benzylalcohol	87 (870)	72 (720)	97 (970)	93 (930)	64 (640)	75 (750)	95 (950)	98 (980)	99 (990)	95 (950)
Cyclopentanol	50 (500)	41 (410)	71 (710)	60 (600)	36 (360)	36 (360)	69 (690)	—	—	62 (620)
Cyclohexanol	69 (690)	53 (530)	77 (770)	78 (780)	50 (500)	49 (490)	87 (870)	78 (780)	84 (840)	79 (790)

<sup>a</sup> Yields in % with turnovers in parentheses.

catalyst with  $\text{H}_2\text{O}_2$  as co-oxidant [3,13] there seem to have been few such studies on the lacunary anion  $[\text{PW}_{11}\text{O}_{39}]^{7-}$ . We have reported that it will epoxidise alkenes and oxidise alcohols under these conditions in three cases [21], and Hill et al. have shown that **11** is a slightly less effective catalyst than **12** for epoxidation of 1-octene with  $\text{H}_2\text{O}_2$  [3]. In Table 4 we report oxidations catalysed by **11** and **12** of alkenes and alcohols using  $[\text{N}(\text{C}_6\text{H}_{13})_4]\text{Cl}$  as phase transfer agent in benzene–aqueous 15%  $\text{H}_2\text{O}_2$  at  $71^\circ\text{C}$  over a three hour period. The  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  anion in  $\text{Na}_2[\text{N}(\text{CH}_3)_4]_4\text{H}[\text{PW}_{11}\text{O}_{39}] \cdot 7\text{H}_2\text{O}$  has been shown by X-ray studies [26] to have a more open structure than has  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  in  $(\text{H}_5\text{O}_2)_3[\text{PW}_{12}\text{O}_{40}]$  [27] and so might be expected to be a more effective catalyst in  $\text{H}_2\text{O}_2$  than the latter. However, this is not the case for alkenes as Table 4 shows, although **11** is a slightly better catalyst for alcohol oxidations than **12**. It seems very likely that **11** and **12** are split up in aqueous  $\text{H}_2\text{O}_2$  to a variety of species, probably in the main to the known  $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ ,  $[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ ,  $[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{3-}$  and  $[(\text{PO}_3(\text{OH}))\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$  as has been proposed for **12** [3,8]. This is supported by  $^{31}\text{P}$  NMR studies on  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  in  $\text{H}_2\text{O}_2$ : the same pattern of spectra is observed as that obtained when  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  is treated in a similar way (Fig. 3a).

Earlier work suggested that the lanthanopolyoxotungstates  $[\text{Ln}^{\text{III}}\text{W}_{10}\text{O}_{36}]^{9-}$  ( $\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Sm}, \text{Tb}, \text{Yb}$ ) will catalyse the oxidation of benzyl alcohol to benzaldehyde, cyclohexanol to cyclohexanone and of cyclo-octene to the epoxide in *tert*-butanol with  $\text{H}_2\text{O}_2$  as co-oxidant at  $92^\circ\text{C}$  [28,29] but Raman data suggested that the effective oxidant was  $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$  [21]. A possible catalytic role for lanthanophosphopolyoxotungstates  $[\text{Ln}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Tb}$ ) for the oxidation of benzyl alcohol, cyclohexanol and cyclo-octene under similar conditions was investigated, but though these are good catalysts, there was relatively little differ-

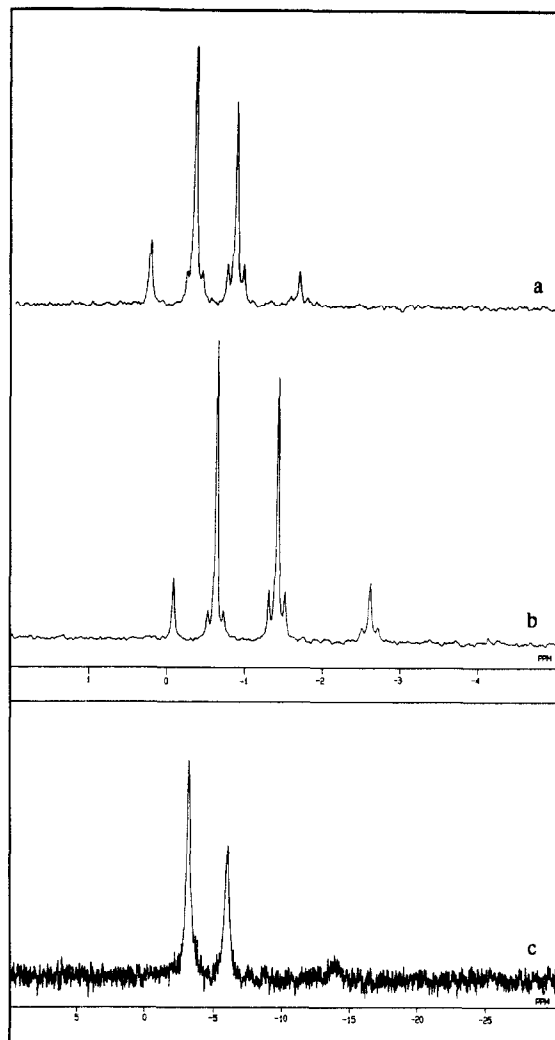


Fig. 3.  $^{31}\text{P}$  NMR spectra in excess 15%  $\text{H}_2\text{O}_2$  in  $\text{D}_2\text{O}$  of (a)  $[\text{PW}_{11}\text{O}_{39}]^{2-}$ ; (b)  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$ ; (c)  $[\text{Yb}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$ .

ence between yields and turnovers effected by **11**, **12** or  $[\text{Ln}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Tb}$ ) [21].

In Table 4 we report oxidations of a variety of cyclic and linear alkenes and alcohols with excess  $\text{H}_2\text{O}_2$  in the presence of  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Sm}, \text{Tb}, \text{and Yb}$ ) and of  $[\text{M}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  ( $\text{M} = \text{Ce}, \text{Th}$ ; the terbium (IV) complex  $[\text{Tb}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  is reduced [21] to  $[\text{Tb}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  under these conditions). It is apparent that **11**, **12** and  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  have comparable effectiveness as oxidation catalysts and that the lanthanide

plays no significant catalytic role. This is supported by  $^{31}\text{P}$  NMR data. The position of the  $^{31}\text{P}$  resonance from an aqueous solution of  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\delta -15.3$ ) is in agreement with the value of  $\delta -15.4$  reported by Fedotov et al. [30]. This is close to the position ( $\delta -14.9$ ) from MAS  $^{31}\text{P}$  NMR for solid  $\text{K}_{11}[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2] \cdot 20\text{H}_2\text{O}$ , suggesting no structural change from solid to solution. The  $\delta -15.3$  solution peak initially shifts to  $\delta -15.7$  when excess  $\text{H}_2\text{O}_2$  at pH 0 is added: this may arise from formation of an intermediate species  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}]^{4-}$ ; formation of such 1:1 complexes has been proposed before [31]. After 24 h peaks at  $\delta -2.62$ ,  $-1.41$  and  $-0.63$  appear (Fig. 3b) which we identify as arising from  $[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ ,  $[(\text{PO}_4)\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^{3-}$ , and  $[(\text{PO}_3(\text{OH}))\{\text{WO}(\text{O}_2)_2\}_2]^{2-}$ , respectively, following our own assignments [2] and those of others [3,8]; the paramagnetic samarium nucleus has shifted these upfield. With other lanthanophosphopolyoxotungstates  $[\text{Ln}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  similar effects have been observed; for example with  $[\text{Yb}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  there is considerable broadening of the peaks and larger upfield shift (Fig. 3c).

The Raman spectra of the products of reaction of  $[\text{Ln}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  in solution with  $\text{H}_2\text{O}_2$  are very similar to those obtained by similar reaction of  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  and  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ . This is illustrated in Fig. 4 for  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$ ; Fig. 4a shows the Raman spectrum of solid  $\text{K}_{11}[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2] \cdot 20\text{H}_2\text{O}$ , and Fig. 4b that of its aqueous solution at pH 5. The two profiles are very similar, suggesting that  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  retains its structural integrity in such solutions in agreement with the  $^{31}\text{P}$  NMR data. When  $\text{H}_2\text{O}_2$  is added, however, the spectrum becomes very different (Fig. 4c) and close to that observed for **12** in  $\text{H}_2\text{O}_2$ , known [8,13] to contain the polyperoxophosphotungstates mentioned above.

Oxidations with  $[\text{Ce}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$ ,  $[\text{Ce}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  and  $[\text{Th}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  in the presence of excess  $\text{H}_2\text{O}_2$  are far less effective than those with  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$ .

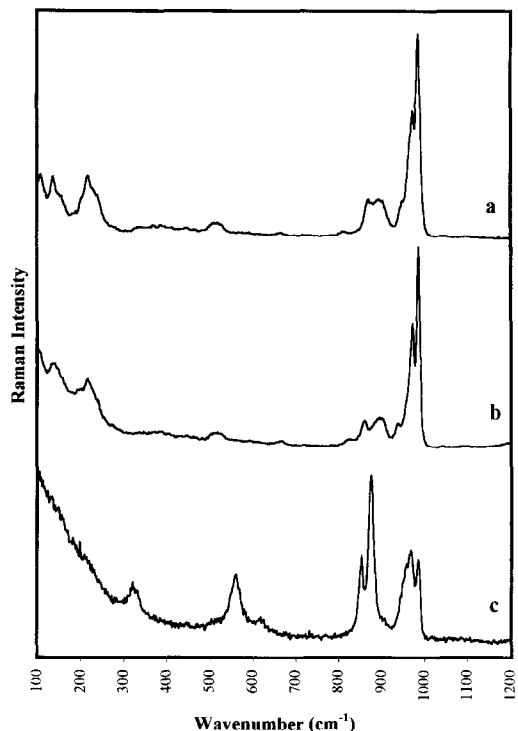


Fig. 4. Raman spectra of (a) Solid  $\text{K}_{11}[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2] \cdot 20\text{H}_2\text{O}$ ; (b) 0.2 M  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  in  $\text{H}_2\text{O}$ ; (c) 0.1 M  $[\text{Sm}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  in excess 15%  $\text{H}_2\text{O}_2$ .

The  $^{31}\text{P}$  NMR spectra of the cerium complexes indicate a markedly slower breakdown to polyperoxophosphotungstates in the presence of excess  $\text{H}_2\text{O}_2$  than do  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\text{Ln} = \text{Y, La, Pr, Sm, Tb, Yb}$ ). It is likely, from known redox potentials [31], that  $[\text{Ce}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  is oxidised to the more inert  $[\text{Ce}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$ , and this is supported by  $^{31}\text{P}$  NMR data. The  $\delta -12.8$  ppm resonance of  $[\text{Ce}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  in water shifts to  $\delta -13.5$  ppm after a day when  $\text{H}_2\text{O}_2$  is added, probably due to formation of a 1:1 species  $[\text{Ce}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}]^{3-}$  (the existence of such a species has been postulated by Peacock and Weakley [31]). Likewise the  $\delta -18.2$  ppm resonance of  $[\text{Ce}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  shifts to  $\delta -13.5$  ppm after addition of  $\text{H}_2\text{O}_2$ . This latter resonance is slower to disappear to be replaced by polyperoxophosphotungstate resonances than is the case with  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  ( $\text{Ln} = \text{Y, La, Pr, Sm, Tb, Yb}$ ). In the case of  $[\text{Th}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  the

position of the single resonance due to this species at  $\delta - 12.2$  ppm is not changed by excess  $\text{H}_2\text{O}_2$  after 5 days and no polyperoxophosphotungstate resonances are observed. It seems that tetravalent centres ( $\text{Ce}^{\text{IV}}$ ,  $\text{Th}^{\text{IV}}$ ) bind more strongly to the lacunary  $\{\text{PW}_{11}\text{O}_{39}\}$  units than do trivalent lanthanide and yttrium centres, inhibiting formation of the catalytically active polyperoxophosphotungstates.

#### 4. Conclusion

In this paper we have shown that a number of complexes containing the  $\eta^2$ ,  $\eta^1$ -peroxo linkage are effective oxidation catalysts when used in conjunction with  $\text{H}_2\text{O}_2$  and a phase transfer agent for the oxidation of alkenes, alcohols, tertiary amines and sulfides. Lanthanopolyoxotungstate complexes  $[\text{Ln}^{\text{III}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{11-}$  are decomposed in  $\text{H}_2\text{O}_2$  to polyperoxophosphotungstates containing  $\eta^2$ ,  $\eta^1$ -peroxo linkages;  $[\text{Ce}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  and  $[\text{Th}^{\text{IV}}\{\text{PW}_{11}\text{O}_{39}\}_2]^{10-}$  are, however, slower to react with  $\text{H}_2\text{O}_2$ .

#### Acknowledgements

We thank the EPSRC and Solvay Interlox for a CASE award to one of us (NMG) and the Calouste Gulbenkian Foundation for an award (HISN). We thank Bill Sanderson and Craig Jones (Solvay Interlox), Abil Aliev and David Butler (University College London) for helpful discussions. The University of London Intercollegiate Research Service is thanked for the Raman spectrometer and for use of the solid state NMR instrument.

#### References

- [1] C. Venturello, R. D'Aloisio, J.C. Bart and M. Ricci, *J. Mol. Catal.* 32 (1985) 107; C. Venturello and M. Gambaro, *Synthesis* 4 (1989) 295; C. Venturello and R. D'Aloisio, *J. Org. Chem.* 53 (1988) 1553.
- [2] W.P. Griffith, B.C. Parkin, A.J.P. White and D.J. Williams, *J. Chem. Soc. Dalton Trans.* (1995) 3131.
- [3] D.C. Duncan, R.C. Chambers, E. Hecht and C.L. Hill, *J. Am. Chem. Soc.* 117 (1995) 681.
- [4] N.M. Gresley, W.P. Griffith, B.C. Parkin, A.J.P. White and D.J. Williams, *J. Chem. Soc. Dalton Trans.* (1996) 2039.
- [5] A.J. Bailey, W.P. Griffith and B.C. Parkin, *J. Chem. Soc. Dalton Trans.* (1995) 1833.
- [6] W.P. Griffith, B.C. Parkin, A.J.P. White and D.J. Williams, *J. Chem. Soc., Chem. Commun.* (1995) 2183.
- [7] R. Neumann and H. Miller, *J. Chem. Soc., Chem. Commun.* (1995) 2277.
- [8] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, V. Jeannin and J.-M. Brégeault, *Inorg. Chem.* 33 (1994) 871; J.-V. Piquemal, L. Salles, C. Bois, F. Robert and J.-M. Brégeault, *C. R. Acad. Sci. (Paris)* 319 (1994) 1481.
- [9] F.P. Ballistreri, G.A. Tomaselli, R.M. Toscano, V. Conte and F. Di Furia, *J. Mol. Catal.* 89 (1994) 295.
- [10] S. Sakaguchi, S. Watase, Y. Katayama, Y. Sakata, Y. Nishiyama and Y. Ishii, *J. Org. Chem.* 59 (1994) 5681.
- [11] A.C. Dengel, W.P. Griffith and B.C. Parkin, *J. Chem. Soc., Dalton Trans.*, (1993) 2683.
- [12] L. Salles, C. Aubry, F. Robert, G. Chottard, R. Thouvenot, H. Ledon and J.-M. Brégeault, *New J. Chem.* 17 (1993) 367.
- [13] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet and H. Ledon, *Inorg. Chem.* 30 (1991) 4409.
- [14] Y. Ishii and Y. Sakata, *J. Org. Chem.* 55 (1990) 5545.
- [15] Y. Ishii, K. Yamawaki, Y. Ura, H. Yamada, T. Yoshida and M. Ogawa, *J. Org. Chem.* 53 (1989) 3587.
- [16] S. Sakaue, T. Sakata, Y. Nishiyama and Y. Ishii, *Chem. Lett.* 289 (1992).
- [17] S. Sakaue, T. Tsubakino, Y. Nishiyama and Y. Ishii, *J. Org. Chem.* 58 (1993) 3633.
- [18] Y. Ishii, H. Tanaka and Y. Nishiyama, *Chem. Lett.* (1994) 1.
- [19] N.C. Campbell, J. Flanagan, W.P. Griffith and A.C. Skapski, *Trans. Met. Chem.* 10 (1985) 353.
- [20] N. Haraguchi, Y. Okaue, T. Isobe and Y. Matsuda, *Inorg. Chem.* 33 (1994) 1015.
- [21] W.P. Griffith, R.G.H. Moreea and H.I.S. Nogueira, *Polyhedron*, 15 (1996) 3493.
- [22] A. Botar and T.J.R. Wheatley, *Rev. Roum. Chim.* 18 (1973) 1155 (ch); G.H. Marcu and A. Botar, *Inorg. Synth.* 23 (1985) 189.
- [23] G. Amato, A. Arcoria, F.P. Ballistreri, G.A. Tomaselli, O. Bortolini, V. Conte, F. Di Furia, G. Modena and G. Valle, *J. Mol. Catal.* 37 (1986) 166.
- [24] J.-M. Brégeault, R. Thouvenot, S. Zoughebi, L. Salles, A. Atlamsani, E. Duprey, C. Aubry, F. Robert and G. Chottard, *New Developments in Selective Oxidations II*, V.C. Corberan and S.V. Bellon (Eds.) (Elsevier, 1994) p. 571.
- [25] F.P. Ballistreri, A. Bazzo, G.A. Tomaselli and R.M. Toscano, *J. Org. Chem.* 57 (1992) 7074.
- [26] J. Fuchs, A. Thiele and R. Palm, *Z. Naturforsch.* 36B (1981) 544.

- [27] G.M. Brown, M.R.N.-Spifiet, W.R. Busing and H.A. Levy, *Acta Cryst. B* 33 (1977) 1038.
- [28] R. Shiozaki, H. Goto and Y. Kera, *Bull. Chem. Soc. Jpn.* 66 (1995) 2790; R. Shiozaki, H. Kominami and Y. Kera, *Synth. Commun.* 26 (1996) 1663.
- [29] R. Shiozaki, H. Kominami and Y. Kera, *Synth. Commun.* 26 (1996) 1663; R. Shiozaki, A. Inagaki, A. Nishino, H. Kominami and Y. Kera, *Kidorui* 26 (1995) 274.
- [30] M.A. Fedotov, B.Z. Pertsikov and D.K. Danovich, *Polyhedron* 9 (1990) 1249.
- [31] R.D. Peacock and T.J.R. Weakley, *J. Chem. Soc. A* (1971) 1837.