

Crystal structures of $[(\text{Me}_2\text{AsO}_2)_2\{\text{Me}_2\text{AsO}(\text{OH})\}\{\text{WO}(\text{O}_2)_2\text{O}\} \cdot \text{H}_2\text{O}$ and $[\text{NMe}_4][(\text{Ph}_2\text{PO}_2)_2\{\text{WO}_2(\text{O}_2)\}_2\{\text{WO}(\text{O}_2)(\text{OH})(\text{OH}_2)\}] \cdot \text{EtOH} \cdot \text{H}_2\text{O} \cdot 0.5\text{MeOH}^\dagger$

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The crystal structures of the complexes $[(\text{Me}_2\text{AsO}_2)_2\{\text{Me}_2\text{AsO}(\text{OH})\}\{\text{WO}(\text{O}_2)_2\text{O}\} \cdot \text{H}_2\text{O}$ **1** and $[\text{NMe}_4][(\text{Ph}_2\text{PO}_2)_2\{\text{WO}_2(\text{O}_2)\}_2\{\text{WO}(\text{O}_2)(\text{OH})(\text{OH}_2)\}] \cdot \text{EtOH} \cdot \text{H}_2\text{O} \cdot 0.5\text{MeOH}$ **2** have been determined and their Raman and infrared spectra recorded. In the binuclear complex **1** two distorted pentagonal-bipyramidal WO_7 units are bridged *via* two tetrahedral Me_2AsO_2 ligands, a μ -oxo and the oxygen atom of a protonated $\text{Me}_2\text{AsO}(\text{OH})$ ligand. The trinuclear complex **2** has two $\{\text{WO}(\text{O}_2)_2\}$ units and one $\{\text{WO}(\text{O}_2)(\text{OH})(\text{H}_2\text{O})\}$ unit linked *via* a μ_3 -oxo, two μ -oxo and two diphenylphosphinate ligands. In both complexes the peroxide ligands are side bonded in a symmetric η^2 fashion.

There is currently much interest in the structures of, and bonding in, isopolyperoxometalates and heteropolyperoxometalates¹⁻⁶ and the function of the latter in particular as catalysts for a wide variety of organic oxidations with hydrogen peroxide as co-oxidant.^{2,7-9} As part of our continuing studies into the synthesis of such materials we have investigated the use of organo-phosphorus and -arsenic ligands in heteropolyperoxo complexes with the aim of facilitating their attachment to solid-state supports. Recently we have reported the crystal structures of four such complexes: $[\text{NMe}_4][(\text{Me}_2\text{AsO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$, $[\text{NMe}_4][(\text{Ph}_2\text{PO}_2)\{\text{MoO}(\text{O}_2)_2\}_2]$, $[\text{NBu}^n_4][(\text{Ph}_2\text{PO}_2)\{\text{WO}(\text{O}_2)_2\}_2]$ and $[\text{NH}_4][(\text{Ph}_2\text{PO}_2)\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$.² The only other organoarsinate complex which has been structurally characterised is $[\text{NBu}^n_4][(\text{MeAsO}_3)\{\text{WO}(\text{O}_2)_2\}_2]$.¹⁰

In the course of this work we isolated two complexes, both of which exhibit unusual structural features not hitherto reported.

Results and Discussion

Preparations and crystallography

$[(\text{Me}_2\text{AsO}_2)_2\{\text{Me}_2\text{AsO}(\text{OH})\}\{\text{WO}(\text{O}_2)_2\text{O}\} \cdot \text{H}_2\text{O}$ **1**. The complex was isolated as a colourless crystalline solid from $\text{WO}_3 \cdot \text{H}_2\text{O}$, H_2O_2 , $\text{Na}[\text{Me}_2\text{AsO}_2]$ and $[\text{NMe}_4]\text{Cl}$ in a water-ethanol mixture followed by storage at 0°C for 3 months. Despite frequent attempts to synthesize the compound in the absence of $[\text{NMe}_4]\text{Cl}$ these efforts proved unsuccessful.

The X-ray analysis of complex **1** reveals a structure containing a $\text{W}_2\text{As}_2\text{O}_6$ 'core' comprising two distorted pentagonal-bipyramidal WO_7 units that are bridged *via* two tetrahedral Me_2AsO_2 ligands, a μ -oxo and the oxygen atom of a protonated $\text{Me}_2\text{AsO}(\text{OH})$ ligand, as shown in Fig. 1. The geometries of the two tungsten co-ordination spheres are, within statistical significance, virtually identical [root mean square (r.m.s.) deviation 0.04 \AA] with in each case the tungsten atom being displaced by *ca.* 0.31 \AA out of the plane of its equatorial substituents in the direction of the oxo ligand, a distortion typical of heteropolyperoxometalates.² Both peroxide ligands are bound in a symmetric η^2 fashion with $\text{W}-\text{O}$ bond lengths in the range $1.929(7)$ – $1.966(7) \text{ \AA}$ [the $\text{O}-\text{O}$ distances are $1.462(10)$ and $1.470(9) \text{ \AA}$ with associated $\text{O}-\text{W}-\text{O}$ angles of $44.4(3)$ and

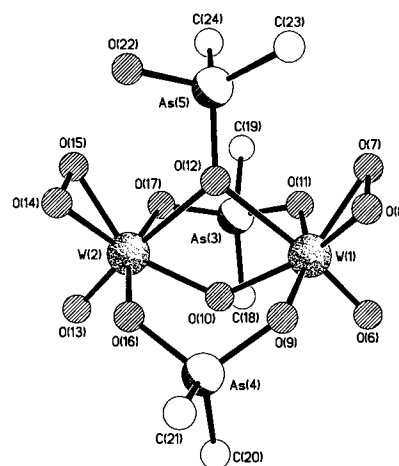


Fig. 1 Molecular structure of complex **1**. The non-bonded transannular $\text{W} \cdots \text{W}$ separation is 3.42 \AA

$44.3(3)^\circ$ respectively] (Table 1). The two $\text{W}-\text{O}-\text{W}$ bridges are asymmetric with $\text{W}-\mu$ -oxo distances of $1.970(6)$ and $1.923(6) \text{ \AA}$ and $\text{W}-\text{O}[\text{Me}_2\text{AsO}(\text{OH})]$ distances of $2.279(6)$ and $2.326(6) \text{ \AA}$ for $\text{W}(1)$ and $\text{W}(2)$ respectively. It is noticeable that the geometry at the bridging oxo atom $\text{O}(10)$ is almost trigonal at $123.0(3)^\circ$, representing a marked contraction from the geometry observed for many related bridged tungsten species.^{5,6}

The distortions from tetrahedral geometry at the bridging arsenic centres are small, with angles in the ranges $105.1(5)$ – $113.1(5)$ and $102.3(4)$ – $115.0(4)^\circ$ at $\text{As}(3)$ and $\text{As}(4)$ respectively. The same is also true for the 'pendant' Me_2AsO_2 ligand [angles in the range $103.9(5)$ – $113.5(6)^\circ$], though the $\text{As}-\text{OH}$ distance is, as expected, significantly longer than the $\text{As}-\text{O}$ distances [$1.750(7) \text{ \AA}$, *cf.* a range of $1.681(7)$ – $1.698(7) \text{ \AA}$ for the three arsenic tetrahedra].

There are no dominant intermolecular packing interactions, though there is evidence for weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonding between the methyl groups in one molecule and peroxo oxygen atoms in another.

$[\text{NMe}_4][(\text{Ph}_2\text{PO}_2)_2\{\text{WO}_2(\text{O}_2)\}_2\{\text{WO}(\text{O}_2)(\text{OH})(\text{OH}_2)\}] \cdot \text{EtOH} \cdot \text{H}_2\text{O} \cdot 0.5\text{MeOH}$ **2**. The complex was isolated as a colourless crystalline solid from $\text{WO}_3 \cdot \text{H}_2\text{O}$, H_2O_2 , $\text{Ph}_2\text{PO}(\text{OH})$ and

[†] Studies on polyoxo- and polyperoxo-metalates. Part 6.¹

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

W(1)–O(6)	1.666(7)	W(1)–O(8)	1.929(7)	As(3)–C(19)	1.879(11)	As(3)–C(18)	1.897(12)
W(1)–O(7)	1.943(7)	W(1)–O(10)	1.970(6)	As(4)–O(16)	1.697(6)	As(4)–O(9)	1.698(7)
W(1)–O(9)	2.045(7)	W(1)–O(11)	2.056(7)	As(4)–C(21)	1.874(9)	As(4)–C(20)	1.899(10)
W(1)–O(12)	2.279(6)	W(2)–O(13)	1.702(7)	As(5)–O(12)	1.690(6)	As(5)–O(22)	1.750(7)
W(2)–O(10)	1.923(6)	W(2)–O(15)	1.931(7)	As(5)–C(23)	1.873(11)	As(5)–C(24)	1.875(11)
W(2)–O(14)	1.966(7)	W(2)–O(16)	2.029(7)	O(7)–O(8)	1.462(10)	O(14)–O(15)	1.470(9)
W(2)–O(17)	2.041(7)	W(2)–O(12)	2.326(6)				
As(3)–O(11)	1.681(7)	As(3)–O(17)	1.683(7)				
O(6)–W(1)–O(8)	101.0(4)	O(6)–W(1)–O(7)	102.4(4)	O(13)–W(2)–O(12)	172.6(3)	O(10)–W(2)–O(12)	70.3(2)
O(8)–W(1)–O(7)	44.4(3)	O(6)–W(1)–O(10)	101.9(4)	O(15)–W(2)–O(12)	84.3(3)	O(14)–W(2)–O(12)	84.5(3)
O(8)–W(1)–O(10)	148.0(3)	O(7)–W(1)–O(10)	146.8(3)	O(16)–W(2)–O(12)	85.4(3)	O(17)–W(2)–O(12)	83.6(3)
O(6)–W(1)–O(9)	94.8(3)	O(8)–W(1)–O(9)	75.1(3)	O(11)–As(3)–O(17)	110.1(4)	O(11)–As(3)–C(19)	106.2(6)
O(7)–W(1)–O(9)	119.0(3)	O(10)–W(1)–O(9)	80.9(3)	O(17)–As(3)–C(19)	105.1(5)	O(11)–As(3)–C(18)	110.7(5)
O(6)–W(1)–O(11)	94.8(3)	O(8)–W(1)–O(11)	119.2(3)	O(17)–As(3)–C(18)	113.1(5)	C(19)–As(3)–C(18)	111.4(6)
O(7)–W(1)–O(11)	75.0(3)	O(10)–W(1)–O(11)	80.7(3)	O(16)–As(4)–O(9)	107.6(3)	O(16)–As(4)–C(21)	102.3(4)
O(9)–W(1)–O(11)	160.7(3)	O(6)–W(1)–O(12)	172.5(3)	O(9)–As(4)–C(21)	107.8(4)	O(16)–As(4)–C(20)	115.0(4)
O(8)–W(1)–O(12)	86.2(3)	O(7)–W(1)–O(12)	84.3(3)	O(9)–As(4)–C(20)	112.1(4)	C(21)–As(4)–C(20)	111.5(5)
O(10)–W(1)–O(12)	70.6(2)	O(9)–W(1)–O(12)	84.8(3)	O(12)–As(5)–O(22)	104.6(4)	O(12)–As(5)–C(23)	113.6(5)
O(11)–W(1)–O(12)	83.4(3)	O(13)–W(2)–O(10)	102.5(3)	O(22)–As(5)–C(23)	103.9(5)	O(12)–As(5)–C(24)	111.7(5)
O(13)–W(2)–O(15)	101.4(3)	O(10)–W(2)–O(15)	146.5(3)	O(22)–As(5)–C(24)	108.8(5)	C(23)–As(5)–C(24)	113.5(6)
O(13)–W(2)–O(14)	102.9(4)	O(10)–W(2)–O(14)	146.6(3)	O(8)–O(7)–W(1)	67.3(4)	O(7)–O(8)–W(1)	68.3(4)
O(15)–W(2)–O(14)	44.3(3)	O(13)–W(2)–O(16)	95.6(3)	As(4)–O(9)–W(1)	121.9(4)	W(2)–O(10)–W(1)	123.0(3)
O(10)–W(2)–O(16)	80.3(3)	O(15)–W(2)–O(16)	120.1(3)	As(3)–O(11)–W(1)	124.1(4)	As(5)–O(12)–W(1)	130.8(3)
O(14)–W(2)–O(16)	76.0(3)	O(13)–W(2)–O(17)	93.3(4)	As(5)–O(12)–W(2)	128.0(3)	W(1)–O(12)–W(2)	96.0(2)
O(10)–W(2)–O(17)	80.8(3)	O(15)–W(2)–O(17)	74.8(3)	O(15)–O(14)–W(2)	66.6(4)	O(14)–O(15)–W(2)	69.1(4)
O(14)–W(2)–O(17)	118.8(3)	O(16)–W(2)–O(17)	160.5(3)	As(4)–O(16)–W(2)	123.3(4)	As(3)–O(17)–W(2)	124.6(4)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

W(1)–O(1)	1.699(7)	W(1)–O(2)	1.923(7)	W(3)–O(14)	1.701(7)	W(3)–O(12)	1.920(7)
W(1)–O(3)	1.930(6)	W(1)–O(4)	2.023(6)	W(3)–O(15)	1.934(7)	W(3)–O(16)	1.947(8)
W(1)–O(6)	2.042(6)	W(1)–O(5)	2.069(6)	W(3)–O(5)	2.025(6)	W(3)–O(6)	2.078(6)
W(1)–O(7)	2.144(6)	W(2)–O(8)	1.688(7)	W(3)–O(17)	2.217(6)	O(2)–O(3)	1.463(10)
W(2)–O(9)	1.938(7)	W(2)–O(10)	1.941(8)	O(4)–P(18)	1.536(7)	O(7)–P(31)	1.519(7)
W(2)–O(12)	1.952(7)	W(2)–O(5)	2.041(6)	O(9)–O(10)	1.472(11)	O(11)–P(18)	1.522(7)
W(2)–O(11)	2.057(6)	W(2)–O(13)	2.305(7)	O(15)–O(16)	1.465(11)	O(17)–P(31)	1.508(7)
O(1)–W(1)–O(2)	99.7(3)	O(1)–W(1)–O(3)	100.2(3)	O(14)–W(3)–O(12)	97.1(3)	O(14)–W(3)–O(15)	100.0(4)
O(2)–W(1)–O(3)	44.6(3)	O(1)–W(1)–O(4)	94.9(3)	O(12)–W(3)–O(15)	83.9(3)	O(14)–W(3)–O(16)	98.0(4)
O(2)–W(1)–O(4)	123.5(3)	O(3)–W(1)–O(4)	79.2(3)	O(12)–W(3)–O(16)	127.8(3)	O(15)–W(3)–O(16)	44.4(3)
O(1)–W(1)–O(6)	96.6(3)	O(2)–W(1)–O(6)	80.3(3)	O(14)–W(3)–O(5)	96.3(3)	O(12)–W(3)–O(5)	74.7(3)
O(3)–W(1)–O(6)	124.3(3)	O(4)–W(1)–O(6)	151.1(3)	O(15)–W(3)–O(5)	154.5(3)	O(16)–W(3)–O(5)	151.1(3)
O(1)–W(1)–O(5)	92.1(3)	O(2)–W(1)–O(5)	150.3(3)	O(14)–W(3)–O(6)	94.4(3)	O(12)–W(3)–O(6)	145.1(3)
O(3)–W(1)–O(5)	158.3(3)	O(4)–W(1)–O(5)	82.0(2)	O(15)–W(3)–O(6)	126.2(3)	O(16)–W(3)–O(6)	82.6(3)
O(6)–W(1)–O(5)	71.2(3)	O(1)–W(1)–O(7)	173.4(3)	O(5)–W(3)–O(6)	71.4(2)	O(14)–W(3)–O(17)	176.4(3)
O(2)–W(1)–O(7)	86.7(3)	O(3)–W(1)–O(7)	85.3(3)	O(12)–W(3)–O(17)	84.4(3)	O(15)–W(3)–O(17)	83.4(3)
O(4)–W(1)–O(7)	82.6(2)	O(6)–W(1)–O(7)	83.0(3)	O(16)–W(3)–O(17)	83.6(3)	O(5)–W(3)–O(17)	80.9(2)
O(5)–W(1)–O(7)	81.6(2)	O(8)–W(2)–O(9)	101.1(4)	O(6)–W(3)–O(17)	82.6(2)	O(3)–O(2)–W(1)	67.9(4)
O(8)–W(2)–O(10)	100.3(4)	O(9)–W(2)–O(10)	44.6(3)	O(2)–O(3)–W(1)	67.4(4)	P(18)–O(4)–W(1)	129.8(4)
O(8)–W(2)–O(12)	101.4(3)	O(9)–W(2)–O(12)	79.4(3)	W(3)–O(5)–W(2)	102.0(3)	W(3)–O(5)–W(1)	109.2(3)
O(10)–W(2)–O(12)	122.7(3)	O(8)–W(2)–O(5)	95.7(3)	W(2)–O(5)–W(1)	148.5(3)	W(1)–O(6)–W(3)	108.2(3)
O(9)–W(2)–O(5)	150.5(3)	O(10)–W(2)–O(5)	153.6(3)	P(31)–O(7)–W(1)	129.3(4)	O(10)–O(9)–W(2)	67.8(4)
O(12)–W(2)–O(5)	73.6(3)	O(8)–W(2)–O(11)	94.7(3)	O(9)–O(10)–W(2)	67.6(4)	P(18)–O(11)–W(2)	136.1(4)
O(9)–W(2)–O(11)	121.3(3)	O(10)–W(2)–O(11)	77.1(3)	W(3)–O(12)–W(2)	109.3(3)	O(16)–O(15)–W(3)	68.3(4)
O(12)–W(2)–O(11)	150.8(3)	O(5)–W(2)–O(11)	80.8(2)	O(15)–O(16)–W(3)	67.3(4)	P(31)–O(17)–W(3)	127.1(4)
O(8)–W(2)–O(13)	172.9(3)	O(9)–W(2)–O(13)	84.5(3)	O(11)–P(18)–O(4)	114.0(4)	O(11)–P(18)–C(30)	109.5(4)
O(10)–W(2)–O(13)	80.7(3)	O(12)–W(2)–O(13)	83.7(3)	O(17)–P(31)–O(7)	114.5(4)		
O(5)–W(2)–O(13)	81.0(2)	O(11)–W(2)–O(13)	78.5(3)				

[NMe₄]Cl in a water–methanol–ethanol mixture followed by cooling at 0 °C for 3 weeks. On subsequent standing at room temperature for 3 d fine prismatic needles of **2** were formed.

The crystal structure (Fig. 2) reveals three pentagonal-bipyramidal WO₇ units linked *via* a μ₃-oxo [O(5)], two μ-oxo [O(6) and O(12)] and two diphenylphosphinate ligands. All three tungsten atoms bear an axial oxide ligand, an equatorial symmetric η²-peroxide [W–O bond lengths in the range 1.923(7)–1.947(8) Å, O–O in the range 1.463(10)–1.472(11) Å, O–W–O angles in the range 44.4(3)–44.6(3)°], a common equatorial μ₃-oxo and a shared equatorial μ-oxo (Table 2). The remaining equatorial sites on W(1) and W(2) are occupied by a

binucleating Ph₂PO₂ ligand [based on P(18)], the second of which [based on P(31)] occupies the other axial sites on W(1) and W(3). An aqua ligand [O(13)]* occupies the remaining axial site on W(2). In all three cases the tungsten atom is displaced out of the plane of its equatorial substituents towards the oxo ligand [by 0.22, 0.29 and 0.24 Å for W(1), W(2) and W(3) respectively], the equatorial atoms being coplanar to within 0.03 Å.

* The assignment of O(13) as an aqua ligand is evident from its noticeably long W–O distance of 2.305(7) Å.

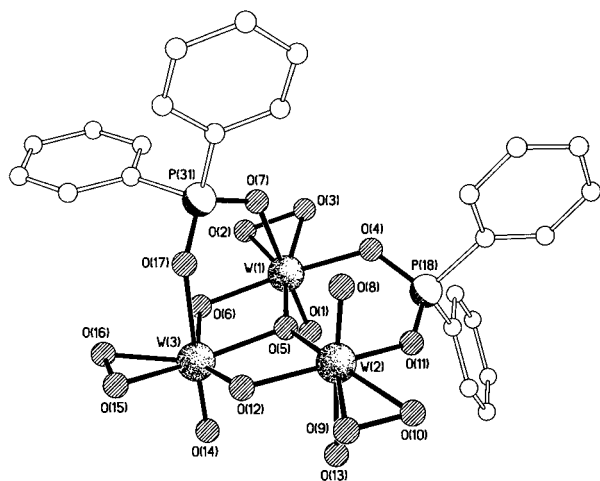


Fig. 2 Molecular structure of the anion in complex **2**

The asymmetry of the equatorial bridges between the three tungsten centres (two μ -oxo and one binucleating Ph_2PO_2) produces a significant asymmetry in the geometry at the central μ_3 -oxo, O(5). This is confined, however, to the angles with W(1)–O(5)–W(2) being noticeably enlarged at $148.5(3)^\circ$, *cf.* $102.0(3)$ and $109.2(3)^\circ$ for the other two angles. (The three tungsten atoms and the μ_3 -oxo are coplanar to within 0.04 Å.) The differences in the W–O bond lengths are not so marked, ranging between 2.025(6) Å for W(3)–O(5) to 2.069(6) Å for W(1)–O(5).

Although both μ -oxo bridges are symmetric and subtend essentially identical angles of $108.2(3)$ at O(6) and $109.3(3)^\circ$ at O(12), the O(6) bridge is significantly longer (average 2.06 Å) than that involving O(12) (average 1.94 Å). The reason for this is not immediately apparent, though it is probably related to the axial Ph_2PO_2 bridge between W(1) and W(3) not present between W(2) and W(3).

The difference in bridging roles of the two Ph_2PO_2 units produces an asymmetry in the non-bonded W...W distances which range between 3.16 and 3.96 Å, subtending angles at tungsten in the range 51 – 75° . This is accompanied by significant differences in the W–O (Ph_2PO_2) distances, with those *trans* to oxo [2.144(6) and 2.217(6) Å] being longer than those *trans* to equatorial μ -oxo [2.023(6) and 2.057(6) Å]. Deviations from tetrahedral geometry at the two phosphorus centres are small, with angles ranging between $105.4(3)$ and $114.0(4)^\circ$ at P(18) and $107.3(3)$ and $114.5(4)^\circ$ at P(31).

Although the hydrogen atoms of the aqua ligand were not located, this atom lies within hydrogen-bonding distance (2.88 Å) of the oxo oxygen atom O(14), the two W–O bonds being tilted towards each other. The crystals are fairly heavily solvated, the solvent molecules being disordered, and there is no evidence for any dominant intermolecular interactions other than normal van der Waals.

Vibrational spectra

The infrared and Raman spectra of complexes **1** and **2** show features comparable with those observed for $[\text{NMe}_4]_2[\text{Ph}_2\text{PO}_3]\{\text{WO}(\text{O}_2)_2\}_2\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})\}]^1$ and $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{XO}_4]\{\text{MO}(\text{O}_2)_2\}_4$ ($M = \text{Mo}$ or W , $X = \text{P}$ or As).⁸ Bands near 960 – 980 cm^{-1} are assigned to the stretch $\nu(\text{M}=\text{O})$, those near 830 – 880 cm^{-1} to stretching modes $\nu(\text{O}-\text{O})$ of the η^2 -peroxide ligands and those around 590 and 540 cm^{-1} as asymmetric and symmetric $[\text{M}(\text{O}_2)]$ stretches respectively. For **1** the latter features are partly obscured by bands from the cacodylate ligand, $[\text{Me}_2\text{AsO}_2]^-$; for **2** P=O stretches of the diphenylphosphinate ligands appear near 1080 cm^{-1} and there are also bands due to the cation $[\text{NMe}_4]^+$. The complexes were not sufficiently soluble to allow the Raman spectra of solutions to be recorded. Complex **2** slowly dissolved in hot D_2O and ^{31}P NMR spectroscopy

showed a peak at δ 28.6 and a smaller peak at δ 38.9, but decomposition may have occurred.

Oxidation studies

Unfortunately insolubility of the complexes in all common solvents precluded detailed studies on their oxidative properties. However when **1** was used as a catalyst for the oxidation of cyclooctene with hydrogen peroxide as co-oxidant a yield of 93% epoxide was obtained. The complex itself was insoluble in the reaction mixture and may be acting as a heterogeneous catalyst. Although **2** dissolved slowly in hot aqueous peroxide and gave a yield of 88% of cyclooctene oxide it is likely that decomposition had occurred since the ^{31}P NMR spectrum of the reaction mixture showed several peaks.

Experimental

X-Ray crystallography

Crystal data. Complex **1**, $\text{C}_6\text{H}_{19}\text{As}_3\text{O}_{13}\text{W}_2 \cdot \text{H}_2\text{O}$, $M = 909.7$, triclinic, space group $P\bar{1}$, $a = 8.009(1)$, $b = 8.161(1)$, $c = 14.773(2)$ Å, $\alpha = 80.96(1)$, $\beta = 86.05(1)$, $\gamma = 85.66(1)^\circ$, $U = 949.3(2)$ Å³, $Z = 2$, $D_c = 3.18 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 173.6 \text{ cm}^{-1}$, $F(000) = 832$. A clear plate of dimensions $0.42 \times 0.23 \times 0.08 \text{ mm}$ was used. Complex **2**, $\text{C}_{28}\text{H}_{35}\text{NO}_{17}\text{P}_2\text{W}_3 \cdot \text{EtOH} \cdot \text{H}_2\text{O} \cdot 0.5\text{MeOH}$, $M = 1351.2$, triclinic, space group $P\bar{1}$, $a = 11.042(1)$, $b = 12.350(1)$, $c = 16.546(1)$ Å, $\alpha = 81.03(1)$, $\beta = 83.48(1)$, $\gamma = 80.75(1)^\circ$, $U = 2190.7(3)$ Å³, $Z = 2$, $D_c = 2.05 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 80.0 \text{ cm}^{-1}$, $F(000) = 1286$. A clear prismatic needle of dimensions $0.50 \times 0.10 \times 0.10 \text{ mm}$ was used.

Data for both compounds were measured on a Siemens P4/PC diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator) using ω scans. 3182 (5723) Independent reflections were measured for **1** and **2** respectively ($2\theta \leq 50^\circ$ for **1** and 45° for **2**) of which 2869 and 4802 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz polarisation factors, and semi-empirical absorption corrections (based on ψ scans) were applied; the maximum and minimum transmission factors were 0.606 and 0.138 for **1** and 0.613 and 0.438 for **2**.

The structures were solved by the heavy-atom method for complex **1** and by direct methods for **2**. In both structures the major-occupancy non-hydrogen atoms were refined anisotropically with the phenyl rings in **2** being treated as idealised rigid bodies. The positions of the CH hydrogen atoms were idealised, assigned isotropic thermal parameters, [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $1.5U_{\text{eq}}(\text{CMe})$], and allowed to ride on their parent atoms. Refinements were by full-matrix least squares based on F^2 to give $R1 = 0.040$, $wR2 = 0.106$ for **1** and 0.035, 0.088 for **2** for the observed data and 231 and 471 parameters respectively. The maximum and minimum residual electron densities in the final ΔF maps were 2.15 and -1.81 e \AA^{-3} for **1** and 0.95 and -0.88 e \AA^{-3} for **2**. Computations were carried out on 50 MHz 486 personal computers using the SHELXTL PC program system.¹¹

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/269.

General

Infrared spectra of the solids were measured over the range 4000 – 400 cm^{-1} using KBr discs on a Perkin-Elmer 1720 Fourier-transform spectrometer, Raman spectra of the solids (as powders in melting-point tubes) on a Perkin-Elmer 1760X FT-IR instrument fitted with a 1700X NIR FT-Raman accessory using a Nd-YAG laser (1064 nm excitation). Micro-

analyses were carried out by the Microanalytical Laboratories at Imperial College.

The compound $\text{MoO}_3 \cdot \text{H}_2\text{O}$ was supplied by BDH and $\text{WO}_3 \cdot \text{H}_2\text{O}$ was obtained from Fluka Chemie. Hydrogen peroxide was obtained from BDH as a 30% w/v aqueous solution and used as supplied. Diphenylphosphinic acid and cacodylic acid were from Aldrich.

Syntheses

$[(\text{Me}_2\text{AsO})_2\{\text{Me}_2\text{AsO}(\text{OH})\}\{\text{WO}(\text{O}_2)\}_2\text{O}] \cdot \text{H}_2\text{O}$ 1. The compound $\text{WO}_3 \cdot \text{H}_2\text{O}$ (1.5 g, 5.0 mmol) was suspended in aqueous hydrogen peroxide solution (4 cm³, 30% w/v) and stirred at 50 °C until a colourless solution was obtained. This was centrifuged to remove any insoluble material then $\text{Na}[\text{Me}_2\text{AsO}_2]$ (0.40 g, 2.5 mmol) in ethanol (5 cm³) was added followed dropwise by $[\text{NMe}_4]\text{Cl}$ (0.27 g, 2.5 mmol) in water (5 cm³). Ethanol (5 cm³) was added and the mixture cooled to 4 °C. The colourless crystalline solid was filtered off, washed with cold ethanol (2 × 5 cm³) and diethyl ether (10 cm³) and then air dried. Yield 0.8 g, 0.88 mmol, 35% (Found: C, 7.9; H, 2.0; O_2^{2-} , 14.2. Calc. for $\text{C}_6\text{H}_{21}\text{As}_3\text{O}_{14}\text{W}_2$: C, 7.9; H, 2.2; O_2^{2-} , 14.1%). IR: $\nu(\text{W}=\text{O})$ 986, $\nu(\text{O}-\text{O})$ 854, $\nu_{\text{asym}}[\text{W}(\text{O}_2)]$ 565 and $\nu_{\text{sym}}[\text{W}(\text{O}_2)]$ 536 cm⁻¹.

$[\text{NMe}_4][(\text{Ph}_2\text{PO})_2\{\text{WO}_2(\text{O}_2)\}_2\{\text{WO}(\text{O}_2)(\text{OH})(\text{OH}_2)\}] \cdot \text{EtOH} \cdot \text{H}_2\text{O} \cdot 0.5\text{MeOH}$ 2. The compound $\text{WO}_3 \cdot \text{H}_2\text{O}$ (1.5 g, 5.0 mmol) was suspended in aqueous hydrogen peroxide solution (4 cm³, 30% w/v) and stirred at 50 °C until a colourless solution was obtained. This was centrifuged to remove any insoluble material then $\text{Ph}_2\text{PO}(\text{OH})$ (0.55 g, 2.5 mmol) in ethanol (5 cm³) was added, followed dropwise by $[\text{NMe}_4]\text{Cl}$ (0.27 g, 2.5 mmol) in water (5 cm³). Ethanol (5 cm³) was added and the mixture cooled to 4 °C. The colourless crystalline solid was filtered off, washed with cold ethanol (2 × 5 cm³) and diethyl ether (10 cm³) and air dried. Yield 1.4 g, 1.01 mmol, 40% (Found: C, 3.2; H,

27.3; N, 1.0; O_2^{2-} , 6.9. Calc. for $\text{C}_{31}\text{H}_{45}\text{NO}_{20}\text{P}_2\text{W}_3$: C, 3.3; H, 27.3; N, 1.0; O_2^{2-} , 7.0%). IR: $\nu(\text{W}=\text{O})$ 951, $\nu(\text{O}-\text{O})$ 880, $\nu_{\text{asym}}[\text{W}(\text{O}_2)]$ 555 and $\nu_{\text{sym}}[\text{W}(\text{O}_2)]$ 541 cm⁻¹.

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