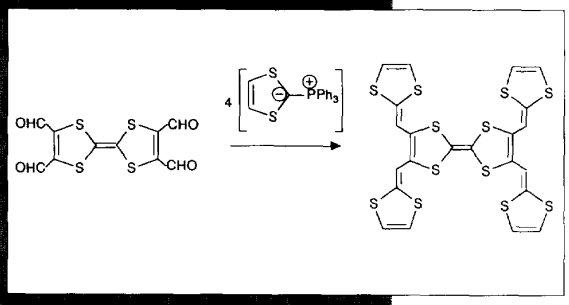
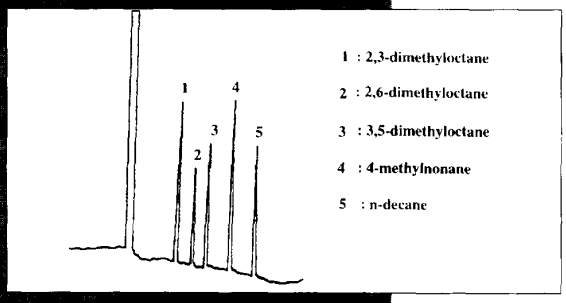


Highly extended, planar and sulfur-rich tetrathiafulvalene derivatives: towards an increased dimensionality of organic metals
Marc Sallé, Alain Gorgues, Michel Jubault, Kamal Boubekeur, Patrick Batail, Roger Carlier (Angers, Nantes, Rennes, France) 417



Étude par chromatographie en phase gazeuse des propriétés de rétention de trois phases stationnaires cristaux liquides substitués latéralement
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Front cover: Fragment of a molecular wall assembled out of a collection of extended cation radical units based on a (green) difunctionalized core. Note the zip-like attachment of the stacks achieved via the neat overlapping of the red (or blue) dithiole units on both faces of the wall (CrystalMaker™). Sallé et al, p 417

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List of authors

TrAC - Trends in Analytical Chemistry: Reference Edition

Volume 14: 1995

TrAC Compendium Series Volume 14

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Table I. Crystal data and structure refinements for compounds **3**, **4** and **5**.

	$(n\text{-}Bu_4N)_2[(SO_4)\{Mo_2O_{10}\}]$, **3**	$(n\text{-}Bu_4N)_2[(SO_4)\{W_2O_{10}\}]$, **4**	$[N(CH_3)_4]_3[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}]$, $3.5H_2O$, **5**
fw	932.88	1 108.67	1 221.14
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Pcnb* (No 60)	*Pcnb* (No 60)	*P21/n* (No 14)
a, Å	14.850 (2)	14.834 (4)	13.604 (4)
b, Å	15.949 (2)	16.005 (3)	15.690 (7)
c, Å	18.892 (2)	18.833 (3)	32.768 (9)
α, deg	90	90	90
β, deg	90	90	101.82 (2)
γ, deg	90	90	90
V, Å^3	4 474 (1)	4 471 (2)	6 628 (33)
Z	4	4	8
ρ, g.cm^{-3}	1.385	1.647	2.447
μ (Mo-K_α), cm^{-1}	6.47	107.08	108.23
Diffractometer	CAD4	CAD4	CAD4
Monochromator	graphite	graphite	graphite
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan range, θ deg	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ
2θ range, deg	2 - 50	2 - 40	2 - 50
Reflctn collected	4 392	2 388	12 614
Reflctn used ($I > 3\sigma(I)$)	1 831	603	6 653
R	0.067		0.068
R_w*	0.068 ($w = 1$)		0.077 ($w = 1$)
Abs corr**	DIFABS		DIFABS
min/max abs	0.95/1.02		0.814/1.089
second extinct param	0.782 10^{-4}		0.957 10^{-4}
ls parameters	304		786

* $R = \Sigma\,(||F_o| - |F_c||)\,/\Sigma|F_o|$ et $R_w = \left[\Sigma w\,(|F_o| - |F_c|)^2\,/\Sigma w F_o^2\right]^{1/2}$

** DIFABS: Walker N and Stuart D, *Acta Cryst* (1983) A39, 158.

Table II. Final atomic coordinates and estimated standard deviations for complex **3**.

Atom	x/a	y/b	z/c	U *(equiv)*	*Occ*
Mo(1)	0.0962(4)	0.3061(5)	0.2287(5)	0.0687	0.5000
Mo(2)	−0.0168(2)	0.2228(1)	0.0808(1)	0.0852	0.5000
S(1)	−0.098(2)	0.205(2)	0.237(2)	0.0982	0.5000
O(1)	−0.014(5)	0.247(9)	0.2653(7)	0.0936	0.5000
O(2)	0.081(3)	0.384(3)	0.272(5)	0.0987	0.5000
O(4)	0.219(1)	0.280(1)	0.231(2)	0.1133	0.5000
O(5)	0.122(1)	0.364(1)	0.141(1)	0.1114	0.5000
O(6)	0.026(1)	0.3463(8)	0.1452(8)	0.0841	0.5000
O(7)	−0.106(1)	0.235(1)	0.1624(9)	0.0899	0.5000
O(8)	−0.048(1)	0.130(1)	0.051(1)	0.1123	0.5000
O(9)	−0.089(2)	0.303(2)	0.035(1)	0.1234	0.5000
O(10)	−0.005(2)	0.288(1)	−0.0016(9)	0.1034	0.5000
O(11)	0.113(2)	0.209(2)	0.081(1)	0.1111	0.5000
O(12)	0.076(1)	0.193(1)	0.1514(9)	0.0715	0.5000
O(13)	−0.106(3)	0.115(5)	0.252(6)	0.1453	0.5000
O(3)	0.164(4)	0.229(4)	0.287(4)	0.1094	0.5000
O(14)	−0.174(4)	0.249(4)	0.270(4)	0.0890	0.5000
N(1)	0.8274(6)	0.5315(5)	0.1541(5)	0.0769	1.0000
C(1)	0.9260(7)	0.5230(7)	0.1277(6)	0.0789	1.0000
C(2)	0.9835(8)	0.6007(7)	0.1441(7)	0.0945	1.0000
C(3)	1.0817(9)	0.5792(9)	0.118(1)	0.1197	1.0000
C(4)	1.140(1)	0.652(1)	0.128(1)	0.1479	1.0000
C(5)	0.7786(7)	0.6064(6)	0.1197(6)	0.0735	1.0000
C(6)	0.769(1)	0.5970(9)	0.0388(7)	0.1096	1.0000
C(7)	0.7217(9)	0.6758(9)	0.0099(8)	0.1153	1.0000
C(8)	0.623(1)	0.679(1)	0.0311(8)	0.1304	1.0000
C(9)	0.8218(7)	0.5494(7)	0.2344(6)	0.0809	1.0000
C(10)	0.8711(8)	0.4814(7)	0.2807(7)	0.0908	1.0000
C(11)	0.8565(9)	0.5070(9)	0.3579(7)	0.1099	1.0000
C(12)	0.903(1)	0.443(1)	0.4075(7)	0.1270	1.0000
C(13)	0.7849(9)	0.4463(7)	0.1351(7)	0.0902	1.0000
C(14)	0.684(1)	0.4438(9)	0.1526(9)	0.1183	1.0000
C(15)	0.662(1)	0.354(1)	0.123(1)	0.1759	1.0000
C(16)	0.579(2)	0.328(2)	0.146(2)	0.2750	1.0000

Table III. Final atomic coordinates and estimated standard deviations for complex **5**.

Atom	x/a	y/b	z/c	U *(equiv)*	*Occ*
S(1)	0.4068(7)	0.2545(7)	0.0896(3)	0.0467	1.0000
S(2)	0.0964(5)	0.2538(7)	0.0075(3)	0.0362	1.0000
W(3)	0.3007(1)	0.12530(9)	0.01318(4)	0.0337	1.0000
W(4)	0.23690(9)	0.25142(9)	−0.06427(4)	0.0316	1.0000
W(5)	0.2966(1)	0.38424(9)	0.01539(4)	0.0366	1.0000
O(2)	−0.005(2)	0.255(2)	0.013(1)	0.0543	1.0000
O(3)	0.420(1)	0.104(2)	0.0102(7)	0.0171	1.0000
O(4)	0.352(2)	0.260(2)	−0.0788(8)	0.0495	1.0000
O(5)	0.409(2)	0.415(2)	0.0097(8)	0.0420	1.0000
O(10)	0.303(1)	0.257(1)	0.0007(6)	0.0145	1.0000
O(11)	0.500(2)	0.258(2)	0.0748(9)	0.0577	1.0000
O(12)	0.414(2)	0.255(2)	0.1332(7)	0.0546	1.0000
O(13)	0.346(2)	0.199(2)	0.0704(7)	0.0377	1.0000
O(15)	0.342(2)	0.333(2)	0.0742(7)	0.0447	1.0000
O(23)	0.152(1)	0.177(2)	0.0259(7)	0.0273	1.0000
O(24)	0.092(1)	0.254(2)	−0.0376(7)	0.0321	1.0000
O(25)	0.149(2)	0.330(2)	0.0254(7)	0.0386	1.0000
O(31)	0.277(2)	0.031(2)	0.047(1)	0.0629	1.0000
O(32)	0.241(3)	0.010(1)	0.0045(9)	0.0399	1.0000
O(34)	0.239(2)	0.132(1)	−0.0472(7)	0.0356	1.0000
O(41)	0.147(2)	0.199(2)	−0.1123(8)	0.0657	1.0000
O(42)	0.143(2)	0.298(2)	−0.1117(7)	0.0467	1.0000

O(45)	0.233(1)	0.378(1)	−0.0476(6)	0.0300	1.0000
O(51)	0.271(2)	0.479(2)	0.0494(9)	0.0230	1.0000
O(52)	0.226(3)	0.495(2)	0.0068(9)	0.0603	1.0000
S(101)	−0.1713(6)	0.2245(5)	0.1609(2)	0.0345	1.0000
S(102)	0.1383(5)	0.2126(5)	0.2424(2)	0.0253	1.0000
W(103)	−0.05295(8)	0.35514(7)	0.23300(4)	0.0232	1.0000
W(104)	0.00021(8)	0.22833(8)	0.31557(4)	0.0247	1.0000
W(105)	−0.07425(9)	0.09856(7)	0.24002(4)	0.0252	1.0000
O(102)	0.236(2)	0.204(2)	0.2340(8)	0.0458	1.0000
O(103)	−0.166(1)	0.392(2)	0.2378(8)	0.0279	1.0000
O(104)	−0.112(2)	0.243(2)	0.3313(7)	0.0443	1.0000
O(105)	−0.196(2)	0.088(2)	0.2413(7)	0.0383	1.0000
O(110)	−0.068(1)	0.231(1)	0.2496(6)	0.0244	1.0000
O(111)	−0.266(2)	0.231(2)	0.1738(8)	0.0502	1.0000
O(112)	−0.178(2)	0.221(2)	0.1169(7)	0.0521	1.0000
O(113)	−0.104(2)	0.301(1)	0.1741(6)	0.0341	1.0000
O(115)	−0.114(2)	0.145(1)	0.1791(6)	0.0236	1.0000
O(123)	0.088(1)	0.291(1)	0.2220(5)	0.0155	1.0000
O(124)	0.146(1)	0.220(1)	0.2884(6)	0.0289	1.0000
O(125)	0.080(1)	0.137(2)	0.2273(7)	0.0384	1.0000
O(131)	0.023(2)	0.462(1)	0.2386(7)	0.0357	1.0000
O(132)	−0.024(2)	0.443(1)	0.1964(8)	0.0294	1.0000
O(134)	0.009(1)	0.351(1)	0.2964(6)	0.0282	1.0000
O(141)	0.098(2)	0.276(2)	0.3618(6)	0.0406	1.0000
O(142)	0.088(2)	0.176(2)	0.3646(7)	0.0517	1.0000
O(145)	−0.010(2)	0.106(1)	0.3008(7)	0.0290	1.0000
O(151)	−0.056(2)	0.000(1)	0.2085(9)	0.0489	1.0000
O(152)	−0.028(2)	−0.022(2)	0.252(1)	0.0632	1.0000
N(1)	−0.670(2)	−0.247(2)	0.0166(9)	0.0352	1.0000
C(11)	−0.596(8)	−0.186(7)	0.034(2)	0.0971	1.0000
C(12)	−0.744(4)	−0.249(6)	0.043(2)	0.0886	1.0000
C(13)	−0.594(7)	−0.318(5)	0.027(2)	0.1290	1.0000
C(14)	−0.707(5)	−0.235(5)	−0.028(2)	0.1087	1.0000
N(2)	−0.391(2)	0.002(2)	0.1242(9)	0.0378	1.0000
C(21)	−0.436(6)	0.071(6)	0.150(3)	0.1213	1.0000
C(22)	−0.307(4)	−0.045(4)	0.147(2)	0.0888	1.0000
C(22)	−0.468(4)	−0.060(4)	0.104(2)	0.0805	1.0000
C(24)	−0.361(5)	0.053(4)	0.091(2)	0.0941	1.0000
N(3)	−0.432(2)	0.240(2)	0.2672(8)	0.0317	1.0000
C(31)	−0.334(3)	0.285(3)	0.285(2)	0.0586	1.0000
C(32)	−0.510(3)	0.271(3)	0.290(1)	0.0310	1.0000
C(33)	−0.414(4)	0.144(3)	0.278(2)	0.0846	1.0000
C(34)	−0.461(3)	0.261(3)	0.223(1)	0.0627	1.0000
N(4)	−0.358(2)	0.481(2)	0.1270(9)	0.0301	1.0000
C(41)	−0.286(3)	0.540(4)	0.148(1)	0.0715	1.0000
C(42)	−0.390(3)	0.419(3)	0.159(1)	0.0586	1.0000
C(43)	−0.309(4)	0.416(4)	0.100(2)	0.0390	1.0000
C(44)	−0.444(3)	0.521(2)	0.100(1)	0.0446	1.0000
N(5)	0.742(2)	0.038(2)	0.672(1)	0.0382	1.0000
C(51)	0.766(5)	0.060(5)	0.715(1)	0.0761	1.0000
C(52)	0.677(5)	0.103(4)	0.649(2)	0.0506	1.0000
C(53)	0.830(5)	0.023(7)	0.656(2)	0.0878	1.0000
C(54)	0.681(5)	−0.044(5)	0.661(3)	0.1314	1.0000
N(6)	0.519(2)	0.483(2)	0.5926(9)	0.0456	1.0000
C(61)	0.587(5)	0.426(7)	0.620(2)	0.1419	1.0000
C(62)	0.558(5)	0.536(6)	0.563(3)	0.0853	1.0000
C(63)	0.50(1)	0.553(7)	0.620(3)	0.0976	1.0000
C(64)	0.459(7)	0.431(7)	0.561(3)	0.1583	1.0000
O(201)	−0.073(3)	0.354(2)	0.078(1)	0.0669	1.0000
O(202)	−0.080(2)	0.530(2)	0.077(1)	0.0583	1.0000
O(203)	0.073(3)	0.584(4)	0.038(2)	0.1247	1.0000
O(204)	0.074(2)	0.710(4)	0.105(1)	0.1117	1.0000
O(205)	0.195(2)	0.817(2)	0.165(1)	0.0753	1.0000
O(206)	0.342(2)	0.943(2)	0.170(1)	0.0660	1.0000
O(207)	0.328(2)	1.118(2)	0.1761(9)	0.0548	1.0000

Stoichiometric oxidation of (R)-(+)limonene ((R)-1-methyl-4-(1-methylethenyl)cyclohexene) with **2**, **3**, **4**, **5** *and [(n-$C_4H_9)_4N]_2[(HXO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, ($X^{n+}$ = P(V) or As(V))*

Oxidations were conducted under nitrogen using Schlenk techniques and deaerated solvents. To a thermostated (20 °C) solution of the complex ($O_{peroxo} \approx 1$ mmol) in 5 mL dry CH_2Cl_2 was rapidly added 1.5 mmol (*R*)-(+) limonene. The solution was stirred under pure nitrogen. GC analysis was performed with *n*-decane as internal standard. Organic products were identified by gas chromatography–mass spectroscopy (GC-MS) [16].

Catalytic tests. Experimental procedure

Preparation of oxidant solution: *t*-BuOH (300 mL) was mixed with 30% H_2O_2 (30 mL). The solution was stirred with anhydrous $MgSO_4$ (30 g) for 2 h and then filtered. The oxidant solution was stored in a refrigerator.

A typical epoxidation procedure was as follows: *trans*-oct-2-ene (0.5 mL, 3 mmol) was added to the oxidant solution (H_2O_2/*t*-BuOH; 1 mL, 2 mmol H_2O_2) and mixed with $CHCl_3$ (5 mL) and **4** (37 mg, 0.033 mmol). *trans*-2,3-Epoxyoctane was obtained as the only product when the mixture was stirred at 60 °C for 1 h under reflux. The reaction mixture showed a single phase throughout the reaction. GC analysis was usually performed directly on the liquid phase.

Analysis and identification of products. GC-MS data system: see ref [14-16]

- *Preparation of polyperoxometalates*

$Na_2MoO_4 \cdot 2H_2O$ (3.39 g, 14 mmol) was dissolved in 10 mL water. Then 2M H_2SO_4 (5 mL) was added and the solution reacted with a 30% w/w solution of hydrogen peroxide (8.5 mL, 76.5 mmol) at 20 °C to give a yellow liquid. The complex $[(n\text{-}C_4H_9)_4N]_2[(SO_4)\{Mo_2O_2(O_2)_4\}]$ **3** was formed by slow addition of an aqueous solution of tetrabutylammonium hydrogenosulfate (10 mL, 5.09 g, 15 mmol). The yellow precipitate was filtered off, washed thoroughly with water (3 × 5 mL) and diethylether (2 × 10 mL), then dried in a desiccator over P_4O_{10} (yield: 6.20 g, 95%). After dissolving in dichloromethane/diethyl ether (2:1), single crystals suitable for X-ray measurements were obtained by slow evaporation. Anal calc for $C_{32}H_{72}N_2O_{14}SMo_2$: C, 41.20; H, 7.78; N, 3.00; S, 3.44; Mo, 20.57. Found: C, 41.22; H, 7.73; N, 3.05; S, 3.22; Mo, 21.10.

Powdered samples and crystals of $[(n\text{-}C_4H_9)_4N]_2[(SO_4)\{W_2O_2(O_2)_4\}]$ **4** were formed by an analogous procedure using H_2WO_4 (yield: 40%). Anal calc for $C_{32}H_{72}N_2O_{14}SW_2$: C, 34.67; H, 6.54; N, 2.53; S, 2.89; W, 33.16. Found: C, 34.90; H, 6.54; N, 2.58; S, 3.04; W, 33.04.

The preparation of $[(CH_3)_4N]_3[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}] \cdot 3.5H_2O$ **5** complements a previous study [23] devoted to the synthesis and X-ray structure determination of $[(CH_3)_4N]_4[\{(HSO_4)W_3O_7(O_2)_2\}_2O]$. To a solution of $Na_2WO_4 \cdot 2H_2O$ (5 g, 15 mmol) in 8 mL H_2O, 4 mL H_2O_2 (35 mmol) and 1 mL 98% H_2SO_4 (18 mmol) were slowly added simultaneously. The solution was stirred for 10 min at room temperature. Then tetramethylammonium hydrogenosulfate (5 g, 26 mmol) in 5 mL water was added. Crystals were obtained within a few days at 5 °C (yield: 3.41 g, 45%).

Results and discussion

Crystal structure of **3**: *bis(tetrabutylammonium)di-μ-peroxo-μ-sulfato di[oxoperoxomolybdate](2-)*

Single crystal X-ray analyses show that **3** and the previously described complexes $[(n\text{-}C_4H_9)_4N]_2[(HXO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (where X = P [16] or As [17]) are structurally very similar (fig 1). Selected bond distances and angles are given in table IV. The anionic structure in all cases consists of an assembling anion ($[SO_4]^{2-}$ in **3**) and a neutral moiety, $M_2O_2(\mu\text{-}O_2)_2(O_2)_2$ (M = Mo [this work] or W [16–17]). Recently, an analogue of these dinuclear species, $(NH_4)_5[(PO_4)\{V_2O_2(O_2)_4\}] \cdot H_2O$, has been reported [24].

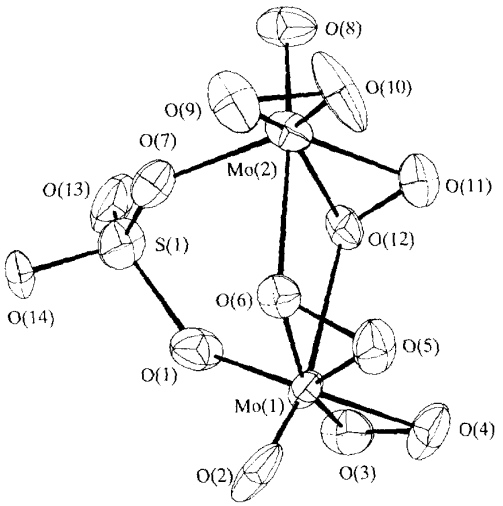


Fig 1. Cameron view of the $[(SO_4)\{Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ anion in **3** with the atom numbering scheme.

The Mo atoms are seven-coordinated by oxygen atoms in a pentagonal bipyramidal arrangement (*PBPY-7*) with an average Mo–O distance of 1.95 Å in the equatorial plane, axial positions being occupied by oxo ligands [Mo(1)–O(2) 1.50(7) and Mo(2)–O(8) 1.65(2) Å] and by the μ_2-O atom of an unsymmetrical bridging peroxo group [Mo(1)–O(12) 2.34(2) and Mo(2)–O(6) 2.40(1) Å]. As expected, these bonds, *trans* to the oxo ligands [O(2) and O(8)], are substantially longer than the equatorial Mo–O bonds; distances Mo(1)–O(12) and Mo(2)–O(6) are as long as the carbonyl oxygen–Mo bond distance of 2.402(7) Å found in MoO_2Cl_2L [L = (1*R*)-*endo*-(+)-3-(diethoxyphosphorylcamphor)] [25]. Two kinds of peroxo ligands are thus observed in these complexes: the usual side-bonded mode and the less common unsymmetrical bridge which has been found in other *peroxide-rich* (O_2^{2-}/Mo > 1) anionic structures [15, 25], such as $[(PO_4)\{Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$ and $[Mo_{10}O_{22}(O_2)_{12}]^{8-}$. The disulfide ion ($S_2^{2-}$) may also, like O_2^{2-}, coordinate as an unsymmetrical bridge (see, for example, ref [27]). When a peroxo oxygen atom forms a bridge to a second molybdenum atom, the bond to the first molybdenum atom is slightly weakened. The two associated pentagonal bipyramids share one edge, O(6)···O(12), not belonging to the basal plane. The Mo atoms are located slightly above the mean equatorial plane defined by the five equatorial O atoms [0.32 and 0.41 Å for Mo(1) and Mo(2) respectively]; such distances are also found for other structural units [4]. There is also a bend in the O(2)–Mo(1)–O(12) and O(6)–Mo(2)–O(8) axes [163.1(22)° and 169.8(9)° respectively].

Table IV. Selected bond distances (Å) and angles (°) for complex **3**.

Mo(1)–O(1)	2.02(2)	Mo(1)–O(2)	1.50(7)
Mo(1)–O(4)	1.88(2)	Mo(1)–O(5)	1.94(2)
Mo(1)–O(6)	2.00(2)	Mo(1)–O(12)	2.34(2)
Mo(1)–O(3)	1.94(6)		
Mo(2)–O(6)	2.40(1)	Mo(2)–O(7)	2.04(2)
Mo(2)–O(8)	1.65(2)	Mo(2)–O(9)	1.88(3)
Mo(2)–O(10)	1.88(1)	Mo(2)–O(11)	1.94(2)
Mo(2)–O(12)	1.98(1)		
S(1)–O(1)	1.52(2)	S(1)–O(7)	1.48(3)
S(1)–O(13)	1.47(8)	S(1)–O(14)	1.47(5)
O(4)–O(3)	1.57(8)	O(5)–O(6)	1.46(2)
O(9)–O(10)	1.44(3)	O(11)–O(12)	1.46(3)
O(1)–Mo(1)–O(2)	94.5(40)	O(2)–Mo(1)–O(4)	108.5(20)
O(2)–Mo(1)–O(5)	95.9(30)	O(2)–Mo(1)–O(6)	95.0(31)
O(5)–Mo(1)–O(6)	43.6(7)	O(1)–Mo(1)–O(12)	75.3(30)
O(2)–Mo(1)–O(12)	163.1(22)	O(4)–Mo(1)–O(12)	88.2(8)
O(5)–Mo(1)–O(12)	82.1(8)	O(6)–Mo(1)–O(12)	71.9(6)
O(2)–Mo(1)–O(3)	106.6(36)	O(4)–Mo(1)–O(3)	48.4(22)
O(12)–Mo(1)–O(3)	86.3(20)		
O(6)–Mo(2)–O(8)	169.8(9)	O(7)–Mo(2)–O(8)	99.0(9)
O(6)–Mo(2)–O(9)	80.1(10)	O(8)–Mo(2)–O(9)	106.5(12)
O(6)–Mo(2)–O(10)	86.6(9)	O(8)–Mo(2)–O(10)	103.6(13)
O(9)–Mo(2)–O(10)	45.1(9)	O(6)–Mo(2)–O(11)	80.4(8)
O(8)–Mo(2)–O(11)	100.4(10)	O(6)–Mo(2)–O(12)	70.9(6)
O(8)–Mo(2)–O(12)	102.4(8)	O(10)–Mo(2)–O(12)	128.9(11)
O(11)–Mo(2)–O(12)	43.8(8)		
O(1)–S(1)–O(7)	105.1(26)	O(1)–S(1)–O(13)	114.8(58)
O(7)–S(1)–O(13)	119.8(46)	O(1)–S(1)–O(14)	105.6(58)
O(7)–S(1)–O(14)	101.3(32)	O(13)–S(1)–O(14)	108.6(42)
Mo(1)–O(1)–S(1)	138.9(12)	Mo(2)–O(7)–S(1)	129.4(15)

• **3** *and* **4** *are isomorphous compounds*

Single crystals of **4** were not suitable for crystal structure determination. Cell parameters (table I) and chemical analysis (see the *Experimental section*) strongly suggest that **3** and **4** are isomorphous. This is also supported by their vibrational spectra (fig 2) which suggest that the anionic moieties of these crystals have the same symmetry (vide infra).

Crystal structure of **5**: *tris(tetramethylammonium)-hydrogenodi-μ2-oxo-μ3-oxo-μ2-sulfato-μ3-sulfato-tris[oxoperoxotungstate](3-)*

The unit cell of **5** contains two independent anions $[(\mu\text{-}HSO_4)(\mu\text{-}SO_4)\{W_3O_3(\mu_2\text{-}O)_2(\mu_3\text{-}O)(O_2)_3\}]^{3-}$ which have the same overall structure based on three

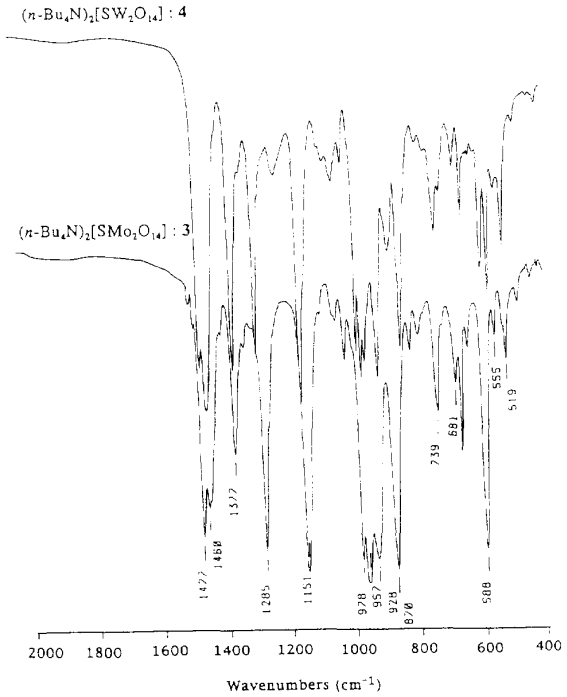


Fig 2. IR spectra of **3** and **4** (solid sample with Nujol).

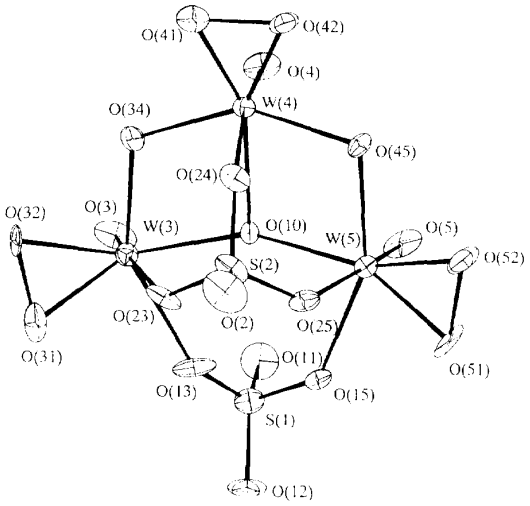


Fig 3. Cameron view of one of the $[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}]^{3-}$ anions in **5** with the atom numbering scheme; the hydrogen atom is omitted.

$WO_5(O_2)$ pentagonal bipyramids (fig 3) linked through bridging oxo, μ-$[SO_4]^{2-}$ and μ-$[HSO_4]^-$ groups. One of these sulfato groups is protonated, but the location of this hydrogen atom has not been determined. Selected interatomic distances and bond angles are given in table V.

Each tungsten atom is ligated to only one side-bond peroxo group. The equatorial plane (girdle) of the tungsten atom W(4) (fig 3), is defined by a peroxo group with O(41)–O(42) 1.50(4) Å, one μ_3-oxo [O(10)] and two μ_2-oxo ligands [O(34) and O(45)], with an average W–O bond length of 2.00(2) Å. One of the apical positions of the girdle axis is occupied by a terminal oxo-ligand (with an average W=O length of 1.725(20) Å), and the other by a μ-O atom [O(24)] of a bridging sulfato (or hydrogenosulfato) group with a rather long W–O bond (2.325(20) Å) and a small bend of the O(4)–W(4)–O(24) line (171.9(10)°, and 173.4(10)° for the second anion). The two other tungsten atoms [W(3) and W(5)] and their analogues in the independent anionic species have the same overall geometry: W–O: 1.99–2.00 Å in the girdle, W=O: 1.660–1.675(20) Å, and the W–O bonds *trans* to the oxo ligands are substantially longer [2.265–2.280(20) Å] than their equatorial counterparts. The S(2) atom is connected to three $WO_5(O_2)$ moieties (*PBPY-7*) through three O atoms, while S(1) is connected to only two $WO_5(O_2)$ units. Hydrogen atoms of the $[HSO_4]^-$ anion and the water molecules were not located in Fourier difference maps. However, O···O distances shorter than 3 Å suggest hydrogen bonding between two O atoms of water molecules. Moreover, several sets of hydrogen bonds between oxygen atoms of the sulfato groups, O(2) or O(12) or their analogues O(112) or O(102) might exist in the crystal ($2.80(3) \leqslant O_{sulfato}\cdot O_w \leqslant 2.91(4)$ Å (see the supplementary material).

Table V. Selected bond distances (Å) and angles (°) for complex **5**.

W(3) O(3)	1.68(2)	W(3) O(10)	2.04(2)
W(3) O(13)	2.16(2)	W(3) O(23)	2.29(2)
W(3) O(31)	1.88(3)	W(3) O(32)	1.93(2)
W(3) O(34)	1.99(2)		
W(4) O(4)	1.73(2)	W(4) O(10)	2.14(2)
W(4) O(24)	2.31(2)	W(4) O(34)	1.90(2)
W(4) O(41)	1.95(3)	W(4) O(42)	1.94(2)
W(4) O(45)	2.00(2)		
W(5) O(5)	1.65(2)	W(5) O(10)	2.00(2)
W(5) O(15)	2.05(2)	W(5) O(25)	2.26(2)
W(5) O(45)	2.07(2)	W(5) O(51)	1.89(2)
W(5) O(52)	1.92(3)		
S(1) O(11)	1.44(2)	S(1) O(12)	1.41(2)
S(1) O(13)	1.26(3)	S(1) O(15)	1.51(3)
S(2) O(2)	1.43(2)	S(2) O(23)	1.45(2)
S(2) O(24)	1.47(2)	S(2) O(25)	1.42(2)
O(31) O(32)	1.42(4)	O(41) O(42)	1.50(4)
O(51) O(52)	1.42(4)		
W(103) O(103)	1.67(2)	W(103) O(110)	1.99(2)
W(103) O(113)	2.09(2)	W(103) O(123)	2.24(2)
W(103) O(131)	1.91(2)	W(103) O(132)	1.89(2)
W(103) O(134)	2.08(2)		
W(104) O(104)	1.72(2)	W(104) O(142)	1.97(2)
W(104) O(110)	2.17(2)	W(104) O(134)	1.98(2)
W(104) O(124)	2.34(2)	W(104) O(141)	1.94(2)
W(104) O(145)	1.91(2)		
W(105) O(105)	1.67(2)	W(105) O(110)	2.03(2)
W(105) O(115)	2.08(2)	W(105) O(125)	2.30(2)
W(105) O(145)	2.01(2)	W(105) O(151)	1.86(2)
W(105) O(152)	1.96(3)		
S(101) O(111)	1.44(2)	S(101) O(112)	1.43(2)
S(101) O(113)	1.48(2)	S(101) O(115)	1.50(2)
S(102) O(102)	1.42(2)	S(102) O(123)	1.46(2)
S(102) O(125)	1.42(2)	S(102) O(124)	1.49(2)
O(142) O(141)	1.53(4)	O(131) O(132)	1.43(3)
O(151) O(152)	1.45(4)		

O(3)	W(3)	O(10)	97.2(11)	O(3) W(3) O(13)	92.5(11)
O(3)	W(3)	O(23)	168.4(12)	O(10) W(3) O(23)	75.4(7)
O(13)-	W(3)	O(23)	76.6(8)	O(3) W(3) O(31)	99.7(12)
O(23)-	W(3)	O(31)	83.9(10)	O(3) W(3) O(32)	101.5(15)
O(23)-	W(3)	O(32)	88.7(12)	O(31) W(3) O(32)	43.6(12)
O(3)	W(3)	O(34)	99.8(10)	O(23) W(3) O(34)	87.4(8)
O(4)	W(4)	O(10)	93.0(9)	O(4) W(4) O(24)	171.9(10)
O(4)	W(4)	O(34)	101.3(12)	O(24) W(4) O(34)	82.3(9)
O(4)	W(4)	O(41)	105.0(12)	O(24) W(4) O(41)	82.7(10)
O(4)	W(4)	O(42)	103.8(11)	O(24) W(4) O(42)	79.7(9)
O(41)	W(4)	O(42)	45.4(10)	O(4) W(4) O(45)	94.4(11)
O(24)	W(4)	O(45)	78.9(8)	O(10) W(4) O(24)	80.7(7)
O(5)	W(5)	O(10)	99.5(12)	O(5) W(5) O(15)	95.9(13)
O(5)	W(5)	O(25)	174.6(14)	O(10) W(5) O(25)	76.2(7)
O(15)	W(5)	O(25)	80.4(9)	O(5) W(5) O(45)	96.3(11)
O(25)	W(5)	O(45)	85.7(8)	O(5) W(5) O(51)	97.7(14)
O(25)	W(5)	O(51)	85.4(11)	O(5) W(5) O(52)	100.2(17)
O(25)	W(5)	O(52)	85.1(13)	O(51) W(5) O(52)	43.8(11)
O(11)	S(1)	O(12)	116.9(17)	O(11) S(1) O(13)	112.8(17)
O(12)	S(1)	O(13)	114.3(18)	O(11) S(1) O(15)	110.5(16)
O(12)	S(1)	O(15)	104.5(16)	O(13) S(1) O(15)	95.1(14)
O(2)	S(2)	O(23)	112.8(16)	O(2) S(2) O(24)	107.5(15)
O(23)	S(2)	O(24)	109.3(14)	O(2) S(2) O(25)	110.6(18)
O(23)	S(2)	O(25)	107.6(14)	O(24) S(2) O(25)	108.9(13)
W(3)	O(10)	W(4)	98.2(7)	W(3) O(10) W(5)	153.7(10)
W(4)	O(10)	W(5)	104.2(8)	S(1) O(13) W(3)	145.1(16)
S(1)	O(15)	W(5)	131.1(14)	S(2) O(23) W(3)	127.4(11)
S(2)	O(24)	W(4)	121.5(11)	S(2) O(25) W(5)	128.9(13)
W(3)	O(34)	W(4)	108.5(10)	W(4) O(45) W(5)	106.9(9)
O(103)	W(103)	O(110)	98.2(10)	O(103) W(103) O(113)	94.6(10)
O(103)	W(103)	O(123)	172.5(10)	O(110) W(103) O(123)	76.8(7)
O(113)	W(103)	O(123)	79.3(7)	O(103) W(103) O(131)	101.3(11)
O(123)	W(103)	O(131)	85.6(8)	O(103) W(103) O(132)	97.8(10)
O(123)	W(103)	O(132)	85.0(8)	O(131) W(103) O(132)	44.2(9)
O(103)	W(103)	O(134)	96.3(10)	O(123) W(103) O(134)	87.9(7)
O(104)	W(104)	O(142)	103.7(11)	O(104) W(104) O(110)	93.9(9)
O(104)	W(104)	O(134)	95.0(10)	O(124) W(104) O(145)	83.0(8)
O(104)	W(104)	O(124)	173.4(10)	O(142) W(104) O(124)	82.5(9)
O(104)	W(104)	O(141)	103.0(10)	O(142) W(104) O(141)	46.1(10)
O(110)	W(104)	O(141)	149.1(8)	O(134) W(104) O(141)	79.8(9)
O(124)	W(104)	O(141)	79.5(8)	O(104) W(104) O(145)	100.3(10)
O(105)	W(105)	O(110)	95.6(10)	O(105) W(105) O(115)	89.6(9)
O(105)	W(105)	O(125)	166.9(10)	O(151) W(105) O(152)	44.4(11)
O(110)	W(105)	O(125)	76.5(8)	O(115) W(105) O(125)	78.7(8)
O(105)	W(105)	O(145)	102.3(9)	O(125) W(105) O(145)	86.5(8)
O(105)	W(105)	O(151)	100.4(11)	O(125) W(105) O(151)	82.9(9)
O(105)	W(105)	O(152)	100.9(12)	O(125) W(105) O(152)	90.4(11)
O(111)	S(101)	O(112)	114.8(15)	O(111) S(101) O(113)	113.0(15)
O(112)	S(101)	O(113)	103.7(14)	O(111) S(101) O(115)	111.7(14)
O(112)	S(101)	O(115)	107.0(13)	O(113) S(101) O(115)	105.9(11)
O(102)	S(102)	O(123)	111.4(13)	O(102) S(102) O(125)	109.3(14)
O(123)	S(102)	O(125)	108.5(12)	O(102) S(102) O(124)	108.9(14)
O(123)	S(102)	O(124)	109.0(11)	O(125) S(102) O(124)	109.7(13)
W(103)	O(110)	W(104)	104.0(9)	W(104) O(145) W(105)	107.7(10)
W(103)	O(110)	W(105)	154.1(11)	W(104) O(110) W(105)	97.5(8)
S(101)	O(113)	W(103)	130.6(12)	S(101) O(115) W(105)	131.8(12)
S(102)	O(123)	W(103)	128.2(10)	S(102) O(125) W(105)	127.3(13)
W(103)	O(134)	W(104)	107.7(9)	S(102) O(124) W(104)	119.7(11)

Hydrogen bonds between anionic species and water molecules

The ^{1}H MAS NMR spectrum of a polycrystalline sample of **5** (fig 4) is clearly dominated by a signal at 3.1 ppm, corresponding to the isotropic chemical shift of hydrogen atoms of methylammonium ions and of water molecules; spinning side bands, a little more than 8.8 ppm apart, are easily identified. The spectrum also contains a well-defined, relatively narrow signal at 6.1 ppm which can be attributed to the $[HSO_4]^-$ group. The value of 6.1 ppm may be considered typical of a hydrogen-bonded hydrogenosulfato group [28]. It can also be compared with the value of 5.4 ppm obtained with a polycrystalline sample of $(n\text{-}Bu_4N)_2[HPW_2O_{14}]$ (see [16]). The value of the chemical shift is not significantly higher than that reported for sulfated zirconia catalysts which are highly acidic — this comparison is perhaps unjustified. Simulation of the spectrum (fig 4) shows that these HSO_4 protons contribute ca 2% of the total H atoms, in good agreement with the expected value. All these hydrogen bonds contribute to the stability of the crystals. The infrared spectrum in the 6 μm region has two maxima (1 710 and 1 650 cm^{-1}), which indicates that there are at least two kinds of hydrogen bond involving water molecules.

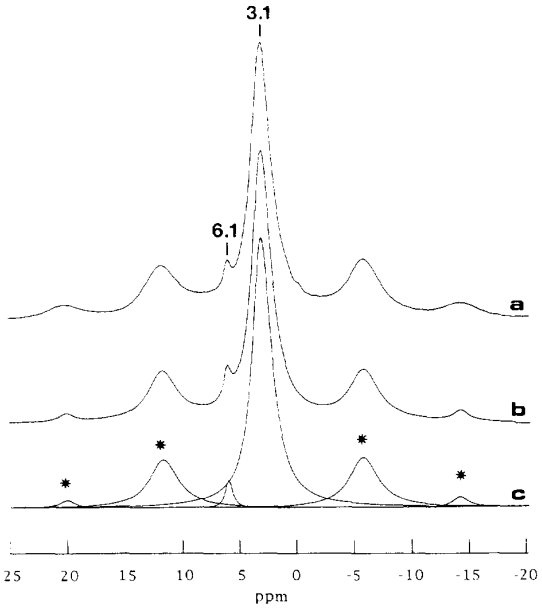


Fig 4. Room-temperature ^{1}H MAS NMR spectrum of a polycrystalline sample of $[(CH_3)_4N]_3[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}]\cdot 3.5H_2O$ **5**. **a**: Experimental spectrum; **b**: simulated spectrum; **c**: weighted contributions.

IR spectra of **3**, **4** *and* **5**

The infrared spectra of **3** and **4** in the solid state are very similar (fig 2). The ν(M=O) vibrations at 978–957 and 988–974 cm^{-1} are related to the existence of two distinct M=O bonds, ν(O–O) at 870 and 841 cm^{-1}. The $\nu_{as}[M(O_2)]$ vibrations at 588–555 and 598–577 cm^{-1} and $\nu_s[M(O_2)]$ at 519 and 525 cm^{-1} for **3** and **4** respectively, are consistent with the vibrational data for other comparable peroxocomplexes containing the $M_2O_2(\mu\text{-}O_2)_2(O_2)_2$ moiety [12, 14–17]. Bands at 588(vs) and 598(s)–575(s) cm^{-1} may also

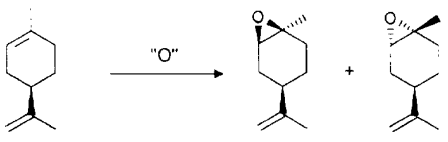
Table VI. Selected infrared data for **3**, **4** and **5**.

3: $[(C_4H_9)_4N]_2[(SO_4)\{Mo_2O_2(O_2)_4\}]$	***4:*** $[(C_4H_9)_4N]_2[(SO_4)\{W_2O_2(O_2)_4\}]$	***5:*** $[(CH_3)_4N]_3[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}] \cdot aq$	*assignment*
		1 710 m	$\nu_2(H_2O)$
		1 650 m	
1 285 vs	1 308 vs	1 277 m	$\nu_3(SO_4)$
1 270 sh	1 280 sh	1 219 m	
1 151 vs	1 167 vs	1 150 s	
		1 080 s	
		1 067 sh	
978 vs	988 vs	968 vs	ν(M=O)
957 vs	974 vs	949 vs	
923 vs	922 vs	995 m	$\nu_1(SO_4)$
		980 s	
870 vs	841 vs	887 s	ν(O–O)
		870 m	
588 vs	598 s	639 m	$\nu_4(SO_4)$ and/or
555 w	577 s	611 m	$\nu_{as}[M(O_2)]$
		554 s	
519 m	525 m	525 w	$\nu_s[M(O_2)]$

be assigned to vibrations of the metal–oxygen heteropolyoxoperoxo framework with a possible contribution of $\nu_4(SO_4)$. The three bands (1 285, 1 270 and 1 151 cm^{-1} for $[(SO_4)\{Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$; 1 308, 1 280, 1 167 cm^{-1} for $[(SO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$), all very strong, are tentatively attributed to the sulfur–oxygen stretching ($\nu_3(SO_4)$). These high frequencies are very probably related to the unusual coordination mode of the sulfato group, $\nu_1(SO_4)$ being at 922 cm^{-1} (vs) in both cases. The general similarity of the infrared spectra of **3** and **4**, as well as that of their crystal data, suggests that the salts are isomorphous. In table VI, the main infrared bands for complexes **3**–**5** are listed with tentative assignments for the vibrational modes. Bands due to water (ν_2 mode) are quite clear for the S_2W_3 salt but are not present for **3** or **4**, indicating again the absence of water of crystallization in the SM_2 (M = Mo or W) salts. Vibrational spectroscopy was also used to show that the anions of **3**, **4**, and **5** exist in organic solvents (CH_3CN) at room temperature [16].

Stoichiometric oxidation reactions

These results led us to choose the stoichiometric reaction of **2**, **3**, **4**, **5** and two binuclear W(VI) peroxo complexes with olefins at room temperature; the (*R*)-(+) limonene test [15–17], which can be performed at 21 °C, is very useful for comparing the activity of these di- or trinuclear species. (+)-Limonene oxide (mixture of *cis* and *trans*) was isolated and identified by MS and ^1H and ^{13}C NMR spectroscopy [16].



Stoichiometrically one would expect 1 mmol of complex **3** or **4** to oxidize four mmol of substrate. However, at room temperature the results are not in agreement with expectation. Figure 5 shows that half the peroxide oxygen is transferred to the olefinic substrate not only by the PW_2 complex $[(n\text{-}C_4H_9)_4N]_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ [16] and the arsenato analogue [17], but also by **3** and **4**. Surprisingly, the oxoperoxosulfato tungstate species **4** is more efficient than the other dinuclear complexes; moreover, with the SMo_2 complex **3** the experimental curve (fig 5) compares well with that of PW_2. On the other hand, the trinuclear species **5** is inefficient at room temperature, as are other tetranuclear species with side-bonded peroxo groups which are being studied [29]. The order of increasing activity towards epoxidation of (*R*)-(+)-limonene was found to be:

$[(CH_3)_4N]_3[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}]$ (S_2W_3)
<< $[(n\text{-}C_4H_9)_4N]_3[(PO_4)\{Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (PMo_4)
< $[(n\text{-}C_4H_9)_4N]_2[(SO_4)\{Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (SMo_2)
< $[(n\text{-}C_4H_9)_4N]_2[(HPO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (PW_2)
< $[(n\text{-}C_4H_9)_4N]_2[(HAsO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (AsW_2)
< $[(n\text{-}C_4H_9)_4N]_2[(SO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (SW_2).

It appears that the sulfato group has a promoting effect for both tungsten and molybdenum complexes with the $M_2O_2(\mu\text{-}O_2)_2(O_2)_2$ moiety.

Preliminary results of catalytic tests

We found that compound **4** is an active catalyst for the epoxidation by H_2O_2 of more demanding substrates than (*R*)-(+)-limonene, such as linear alkenes. Typical catalytic experiments with two-phase systems involving **4**, 10–30% aqueous H_2O_2 and oct-1-ene or *trans*-oct-2-ene are not easily optimized: the tetrabutylammonium group is not an appropriate cation for phase-transfer catalysis with the $[(SO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ anion. Attempts to isolate and characterize other salts

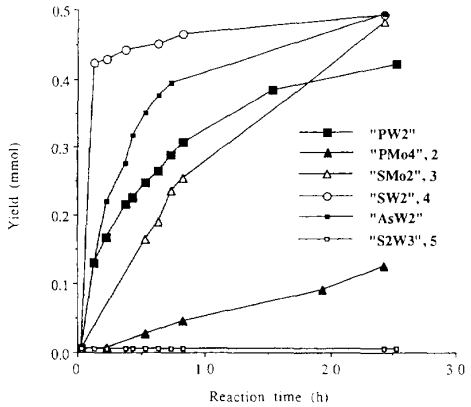


Fig 5. Stoichiometric oxidation of (*R*)-(+)-limonene under nitrogen using $(n\text{-}Bu_4N)_3[(PO_4)\{Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$, PMo_4, **2** (0.125 mmol); $(n\text{-}Bu_4N)_2[(SO_4)\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, SMo_2, M = Mo, **3** (0.250 mmol); SW_2, M = W, **4** (0.250 mmol); $(Me_4N)_3[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}] \cdot 3.5H_2O$, S_2W_3 **5** and $(n\text{-}Bu_4N)_3[(HXO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$, PW_2: X = P (0.250 mmol) and AsW_2: X = As (0.250 mmol). Epoxide yield is plotted versus time: O_{peroxo} = 1 mmol; (*R*)-(+)-limonene = 1.5 mmol, temperature = 20 °C; solvent (CH_2Cl_2) = 5 mL; yields are determined by GC using *n*-decane as internal standard.

with large lipophilic quaternary ammonium cations are in progress [30].

A typical procedure for the epoxidation of *trans*-oct-2-ene with an oxidant solution (H_2O_2/*t*-BuOH/$CHCl_3$ — see the *Experimental section*) gives pure *trans*-2,3-epoxyoctane with a yield of 40% in 1 h. The catalytic activity was observed to fall off, due to the partial breakdown of the heteropolyoxoperoxotungstate framework and to the formation of less active species such as S_2W_3, oxoalkoxoperoxo species: O-transfer by SW_2 causes the structure of the dinuclear species to collapse.

In the same way, oxidations of primary or secondary alcohols at room temperature in benzene or toluene, with H_2O_2 as cooxidant, result in poor yields of aldehydes or ketones due to the formation of tetranuclear alkoxoperoxo species which are under study [29].

Conclusion

The reactivity of the $W_2O_2(\mu\text{-}O_2)_2(O_2)_2$ moiety in **4** is rather unique, as is that of $Mo_2O_2(\mu\text{-}O_2)_2(O_2)_2$ in the sulfato complex **3**. These novel peroxide-rich (O_2^{2-}/M = 2) species can be active intermediates for the catalytic epoxidation of alkenes or other reactions like *N*-oxidation by aqueous hydrogen peroxide [29]. The key role of the pairs of bridging peroxo ligands is being studied theoretically, as are the experimental parameters which favor the generation and regeneration of the anionic species [30] and the hydrophilicity/hydrophobicity characteristics of the ion pairs. These results complement a previous study [23]; they show that several anionic species may exist in the $WO_3 \cdot H_2O$ or $[WO_4]^{2-}/H_2O_2\text{-}H_2O/H_2SO_4/Q^+X^-$ system. Unfortunately they cannot be identified spectroscopically.

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Supplementary material available

Tables of least-squares planes for **3** and **5**, anisotropic thermal parameters of all non-hydrogen atoms and interatomic distances and bond angles in the cations have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication N° = SUP 90412 and are available on request from the Document Supply Centre.

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