

Synthesis, reactivity, X-ray crystal and molecular structures of a novel dimeric tungsten(vi) polyoxoperoxo complex: $[\text{PPh}_4]_2[\text{Ph}_2\text{SiO}_2\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]$ and of a molybdenum(vi) analogue

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Tungsten and molybdenum complexes containing a diphenylsilanediolato ligand are structurally characterised; the overall structures of the anions are conserved in organic solvents.

The chemistry of heteropolyoxoperoxo metalates has received much attention in recent years.^{1–8} In the course of systematic investigations of peroxidic d⁰ transition-metal complexes involving different assembling ligands, model complexes with silicon-based anionic moieties were considered, in relation to attempts to prepare metal complexes supported on and/or inserted in silica. Monomeric silicic acid, $\text{Si}(\text{OH})_4$, exists only in dilute aqueous solution; since this polymerizes,⁹ $[\text{SiO}_4]^{4-}$ or hydrogenosilicates may be thought difficult to use as assembling ligands in the same way as $[\text{HPO}_4]^{2-}$,⁶ $[\text{HASO}_4]^{2-}$,⁷ $[\text{SO}_4]^{2-}$,⁸ etc. In some cases, $\text{Si}(\text{OH})_4$ reacts directly and oligomeric species are known to depolymerize *e.g.* in the synthesis of $\text{H}_4[\text{SiM}_{12}\text{O}_{40}](\text{aq})$ ($\text{M} = \text{Mo}, \text{W}$).¹⁰ The corresponding silicopolyoxoperoxo-molybdates or -tungstates, $[\text{SiO}_4\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{4-}$, have been synthesized, but in our hands, are not easily purified. Organodisilanols can model geminal hydroxy groups which are much more reactive on silica surfaces than single silanols. Preliminary results obtained with diphenylsilanediol, $\text{Ph}_2\text{Si}(\text{OH})_2$, are presented here. This compound is known as a chelating agent, either in mono- or in di- to tetra-meric forms.^{11–14} The complexes $[\text{PPh}_4]_2[\text{Ph}_2\text{SiO}_2\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]$ ($\text{M} = \text{W}$ **1** or Mo **2**) can be isolated from water-ethanol mixtures.

' $\text{WO}_3\cdot\text{H}_2\text{O}$ ' (or ' $\text{MoO}_3\cdot\text{H}_2\text{O}$ ') was first reacted with a 30% m/v solution of hydrogen peroxide and this solution was then added to ethanolic $\text{Ph}_2\text{Si}(\text{OH})_2$. After 45 min, slow addition of ethanolic PPh_4Cl precipitated **1** (or **2**) in good yield. The white (yellow) precipitate was filtered off, washed with water and diethyl ether and then air-dried (yields: 75–90%).[‡] Crystals of **1** and **2** were grown by slow evaporation of acetonitrile solutions.

1 and **2** are isomorphous compounds. A representation[§] of the dinuclear anion, $[\text{Ph}_2\text{SiO}_2\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$, is shown in Fig. 1. It consists of an assembling anion, $[\text{Ph}_2\text{SiO}_2]^{2-}$, and of a dimeric moiety, $\{\text{W}_2\text{O}_{10}\}$, resulting from the association of two pentagonal bipyramids sharing one edge, $\text{O}(6)\cdots\text{O}(12)$, of the non-basal planes. Each of these atoms is on the girdle axis of a bipyramid with a typical lengthening of the M–O distances, the other axial positions being occupied by oxo ligands with normal bond lengths.^{1–3,6–8} The W atoms are located outside the mean equatorial plane defined by the five O atoms corresponding to two peroxo groups and to the oxygen atom of the assembling ligand {0.375 [0.392] for W(1) [Mo(1)] and 0.366 [0.382] Å for W(2) [Mo(2)], respectively}. There is one non-bridging peroxo group with η^2 side-bound configuration and one bridging $\mu\text{-}\eta^2$: η^1 peroxo group. The Si–O and Si–C bond distances are similar to those found in cyclic siloxanes.

The IR spectra of complexes **1** and **2** show features comparable to those observed for other dinuclear species;^{6–8} in addition a strong band at 1586 cm^{-1} is assigned as $\nu(\text{C}-\text{C}, \text{phenyl})$,^{12,15} and a very sharp band at 1107 cm^{-1} is due to an in-plane deformation of the phenyl ring with some $\nu(\text{Si}-\text{C})$ character.^{12,15} The phenyl vibrations occur in expected positions. Consistent with the structural data and the existence of two distinct M=O bonds, there are strong $\nu(\text{M}=\text{O})$ bands at 978s and 964s for **1** and at 968s and 955s for **2**; Si–O stretches appear at *ca.* 926 cm^{-1} as a very strong maximum for both compounds. Bands at 862s for **2** and 841s for **1** are assigned to $\nu(\text{O}-\text{O})$ of the peroxo ligands and bands at *ca.* 580 and 530 cm^{-1} are assigned to asymmetric and symmetric $[\text{M}(\text{O}_2)]$ stretches, respectively. For **1** and **2**, comparison of the $\nu(\text{O}-\text{O})$ and $\nu(\text{Si}-\text{O})$ vibrations (IR and Raman) in the solid state and MeCN solution suggests that the overall structures of the two anions are conserved in solution.

Epoxidation of cycloalkenes by **1** was markedly more successful than for linear analogues; the larger the cycloalkene ring, the greater the degree of conversion to epoxide. In all

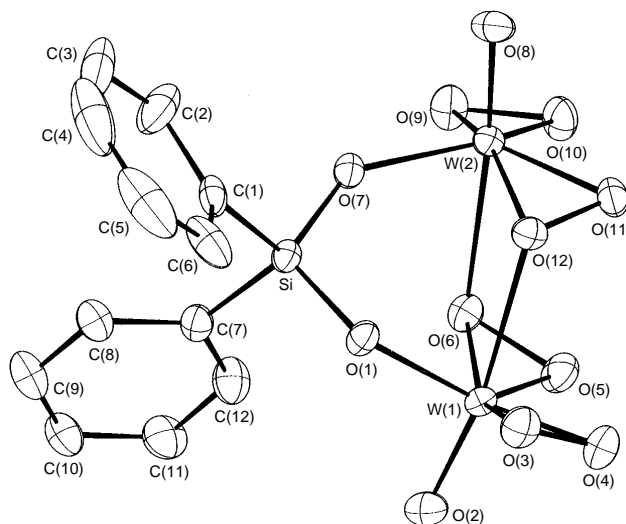


Fig. 1 CAMERON representation of $[\text{Ph}_2\text{SiO}_2\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ showing the atom labelling scheme. Selected bond lengths (Å) for **1** [**2**]: M(1)–O(1) 1.954(3) [1.964(2)], M(1)–O(2) 1.701(4) [1.681(2)], M(1)–O(3) 1.926(4) [1.928(2)], M(1)–O(4) 1.922(4) [1.931(2)], M(1)–O(5) 1.934(4) [1.927(2)], M(1)–O(6) 2.031(4) [2.006(2)], M(1)–O(12) 2.398(4) [2.444(2)], M(2)–O(6) 2.408(4) [2.459(2)], M(2)–O(7) 1.951(3) [1.959(2)], M(2)–O(8) 1.691(4) [1.672(2)], M(2)–O(9) 1.938(4) [1.937(2)], M(2)–O(10) 1.932(4) [1.929(2)], M(2)–O(11) 1.937(4) [1.927(2)], M(2)–O(12) 2.031(4) [2.014(2)], Si–O(1) 1.618(4) [1.619(2)], Si–O(7) 1.616(4) [1.620(2)], Si–C(1) 1.871(5) [1.874(3)], Si–C(7) 1.871(6) [1.884(3)], O(3)–O(4) 1.505(6) [1.481(4)], O(5)–O(6) 1.491(5) [1.470(3)], O(9)–O(10) 1.503(5) [1.473(3)], O(11)–O(12) 1.496(5) [1.468(3)].

cases, the order of increasing activity of PTC systems was $[\text{Ph}_2\text{SiO}_2(\text{Mo}_2\text{O}_{10})]^{2-} \ll [\text{Ph}_2\text{SiO}_2(\text{W}_2\text{O}_{10})]^{2-} < [\text{HAsO}_4(\text{W}_2\text{O}_{10})]^{2-}$, which confirms the assembling anion effect, but there is also a dramatic influence of the onium moiety.¹⁶ Spectral data show that the diphenylsilanediolato compounds are recovered without any change if, at the end of the reaction, there is an excess of H_2O_2 . Work is in progress to optimize conversions and selectivities.

Two novel anionic polyoxoperoxo species have been synthesized with $\text{Ph}_2\text{Si}(\text{OH})_2$, $\text{H}_2\text{O}_2\text{-H}_2\text{O-EtOH}$ and 'WO₃-H₂O' or 'MoO₃-H₂O'. They should be useful to model grafted polyoxoperoxo species which can be obtained on silica surfaces with geminal or single silanols or siloxane bridges and analogous complexes.^{16,17}

Footnotes

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‡ All new complexes gave satisfactory elemental analyses (C, H, P, Si, Mo/W).

§ *Crystal data and collection parameters:* C₆₀H₅₀O₁₂P₂SiW₂ **1**, $M = 1420.78$, monoclinic, space group C2/c (no. 15), $a = 46.380(5)$, $b = 13.345(5)$, $c = 18.988(2)$ Å, $\beta = 113.259(9)^\circ$, $U = 10797(7)$ Å³ (by least-squares refinement on diffractometer angles from 25 centred reflections, $11.5 < 2\theta < 12.5$), $T = 290$ K, graphite-monochromated Mo-K α radiation, $\lambda = 0.71073$ Å, $Z = 8$, $D_c = 1.75$ Mg m⁻³, $F(000) = 5564$, yellow parallelepiped with dimensions $0.30 \times 0.45 \times 0.65$ mm, $\mu(\text{Mo-K}\alpha) = 44.92$ cm⁻¹, Nonius CAD4 four-circle diffractometer, ω - 2θ scans, data collection range $1.0 < \theta < 28.0^\circ$, three standard reflections showed no significant variation in intensity; 13009 unique data collected of which 8923 with $(F_o)^2 > 3\sigma(F_o)^2$ were used in all calculations. Corrections were made for Lorentz and polarisation effects, extinction correction was also applied¹⁸ and absorption correction based on DIFABS program¹⁹ applied before anisotropic refinements (min. 0.81, max. 1.24).

C₆₀H₅₀Mo₂O₁₂P₂Si **2**, $M = 1244.96$, monoclinic, space group C2/c (no. 15), $a = 46.331(5)$, $b = 13.343(3)$, $c = 19.027(4)$ Å, $\beta = 113.35(1)^\circ$, $U = 10799(7)$ Å³ (by least-squares refinement on diffractometer angles from 25 centred reflections, $11.5 < 2\theta < 12.5$), $T = 290$ K, graphite-monochromated Mo-K α radiation, $Z = 8$, $D_c = 1.53$ Mg m⁻³, $F(000) = 5045$, colourless parallelepiped with dimensions $0.40 \times 0.30 \times 0.40$ mm, $\mu(\text{Mo-K}\alpha) = 5.94$ cm⁻¹, Nonius CAD4 four-circle diffractometer with ω - 2θ scans, collection range $1.0 < \theta < 28^\circ$, two standard reflections showed no significant variation in intensity; 13005 unique reflections measured, 8945 with $(F_o)^2 > 3\sigma(F_o)^2$ were used in all calculations. Lorentz and polarisation effects with extinction correction as above for **1**; absorption correction based on DIFABS program¹⁹ was applied before anisotropic refinements (min. 0.85, max. 1.12).

Structure solution and refinement: atomic form factors for neutral W (or Mo), Si, P, O, C and H were taken from ref. 20. Real and imaginary parts of anomalous dispersion were taken into account. The structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically. Refinements were carried out in four blocks by minimising the function $\sum_w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors (program CRYSTALS).²¹ All hydrogen atoms were found on difference Fourier maps; their positions were not refined and they were considered with an overall isotropic thermal

parameter $0.9_0 < \text{C-H} < 1.0_5$ Å for both **1** and **2**, $U_{\text{iso}} = 0.074(3)$ for **1** and $0.075(2)$ for **2**. The final R factors as defined in ref. 21 were $R = 0.034$, $R_w = 0.037$ for **1** and $R = 0.032$, $R_w = 0.034$ for **2** for 697 parameters, and unit weighting scheme, GOF = 2.21 for **1** and 2.04 for **2**, maximum $\Delta\rho = 0.77$ and 0.40 e Å⁻³ for **1** and **2** respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/352.

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