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μ-Peroxo-μ-oxo-bis[bis(trimethylsilylmethyl)tin]: The First Structurally Characterised Main-group Metal η²-Peroxide, a Formal Tin Analogue of an Ozonide

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The title compound is the first μ-η²-peroxodimetallic species to be characterised for a main group metal, possessing a long peroxo O–O bond, and large C–Sn–C angles, and is an unexpected product from the oxidation of $[SnR_2]$ [R = $CH(SiMe_3)_2$], with a structure analogous to an organic ozonide.

Bridged peroxo compounds of the first-row transition metals are well established,[1] but for the main-group metals reports are sparse, and none has been adequately characterised.[2] We now report structural and spectroscopic data on the first such derivative of a metal of the main groups, produced in low yield from the oxidation of $[SnR_2]$ in the presence of $[Mo_2(OAc)_2(MeCN)_6][BF_4]$. This unexpected product was obtained from mixing solutions of the two reagents in hexane at room temperature under an atmosphere of dry nitrogen. The red colour of the Mo species was rapidly replaced by orange, which slowly faded (*ca.* 2 h, at −20 °C) to colourless. Colourless crystals formed on standing for *ca.* 200 hours at −20 °C.

X-Ray analysis† of the crystals established the structure shown, togther with salient bond lengths and angles, in Fig. 1.

The essential features are (i) a long peroxo O–O distance, (ii) an unusually large C–Sn–C angle at each tin atom, (iii) a symmetrical μ-oxo bridge, and (iv) a dihedral angle of *ca.* 40° between the peroxo O–O vector and the plane containing Sn(1), O(1) and Sn(2). The last feature is common in the well known structural relatives of the type $[L_4Co(\mu\text{-}NH_2)(\mu\text{-}O\text{-}O)CoL_4]$.[1] In this case, the long O(2)–O(3) distance is presumably not associated with any specifically electronic effect (there are no orbitals on tin appropriate for populating the O–O antibonding set) and is probably a consequence of the bulky alkyl substituents on tin. Thus the distance [1.543(12) Å] is significantly longer than normally found for similar transition metal species (1.44–1.49 Å)[3] and greater than that in H_2O_2 (1.47 Å). The C–Sn–C angles [123.3(5),

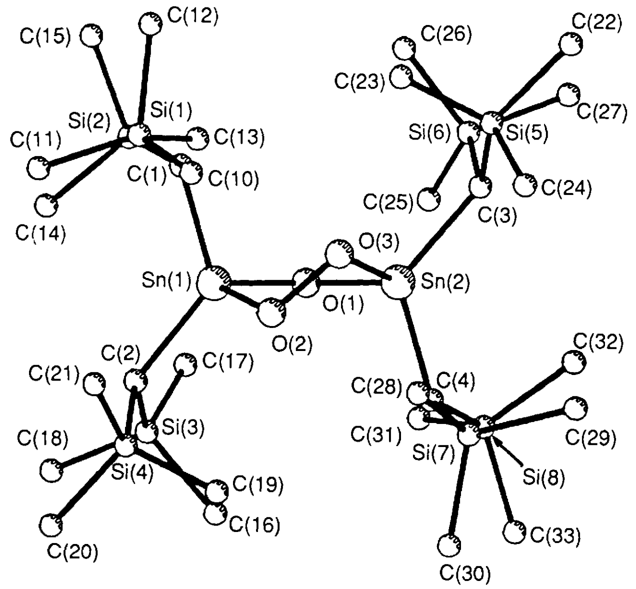

Fig. 1 A single molecule of $[R_2Sn(\mu\text{-}O)(\mu\text{-}O\text{-}O)SnR_2]$ viewed down the bisector of the Sn(1)–O(1)–Sn(2) angle. Selected bond lengths (Å) and bond angles (°): Sn(1)–O(1) 1.991(9), Sn(2)–O(1) 1.959(9), Sn(1)–O(2) 2.009(9), Sn(2)–O(3) 2.012(9), O(2)–O(3) 1.543(12), C(2)–Sn(1)–C(1) 123.3(5), C(4)–Sn(2)–C(3) 124.2(5), Sn(2)–O(1)–Sn(1) 110.3(4), O(2)–O(3)–Sn(2) 104.7(6), O(3)–O(2)–Sn(1) 102.0(6). The Sn(1)–Sn(2) vector is 3.241(4) Å (non-bonded)

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† *Crystal data* for $C_{28}H_{76}O_3Si_8Sn_2$: M = 922.973, triclinic, $P\bar{1}$, a = 9.660(3), b = 12.450(2), c = 21.881(3) Å, α = 79.79(1), β = 84.13(2), γ = 68.59(2)°, U = 2384.9(9) Å^3, D_c = 1.285 g cm^{-3}. A colourless platelet of dimensions approx. 0.3 × 0.2 × 0.1 mm was used for measurement. Z = 2, $F(000)$ = 960, μ(Mo-Kα) = 11.54 cm^{-1}. No. of data measured 6046, of which 4929 had $|F_o| \geq 5\sigma|F_o|$. Refinement converged at R = 0.0634 (unit weights were used). Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation. Data were corrected for Lorentz, polarisation, decay and absorption effects, and the structure was solved using SHELXS-86 and SHELX-76, courtesy of G. M. Sheldrick, University of Göttingen. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Spectroscopic data: ^1H NMR ($CDCl_3$) δ 0.238 and 0.213 (diastereotopic methyls, relative intensity 18) and 0.069 (CH groups, relative intensity 1) with respect to internal Me_4Si; IR ν_{max}/cm^{-1} (CsI disc) 2953m, 2899w, 1405w, 1250s, 1011m, 989s, 968m, 843vs, 777m, 761w, 689w, 666m and 646m.

124.2(5)°] in the present compound are larger than any previously observed values, including those reported for uncoordinated $[SnR_2]$,[4] or the stannylene as either terminal[5] or bridging ligand.[6] These trends can most readily be rationalised on the basis of valence shell electron pair repulsions: the oxygen atoms of the present system being the most electronegative ligands yet studied in this context. The single oxo-bridge is characterised by Sn–O bonds slightly longer and more symmetrical than previously observed,[7] the latter being a rather uncommon feature.

The mode of formation of the peroxo-bridged species is not at present understood. However, the reagents were mixed under pure, dry nitrogen and in dried, degassed solvents required for the handling of the tin reagent. It has been shown that $[SnR_2]$ reacts with oxygen to give $[(R_2SnO)_n]$,[8] and it thus appears that the product results from either a stoichiometric tin–molybdenum intermediate, which we have so far been unable to isolate, or a molybdenum-containing catalyst. We have established that dioxygen (adventitious oxygen, possibly from the glass, can never be totally excluded) is the oxidant, and the yield is modestly improved by the admission of the gaseous dioxygen.

As with $[SnR_2]$, the related diarylstannylenes give either oxygenated oligomeric species or partially oxygenated oligomers, *e.g.*, $[Ar_6Sn_3O]$ or $[Ar_6Sn_3(\mu\text{-}O)_3]$, (Ar = 2,4,6-triisopropylphenyl or 2,6-diethylphenyl respectively) both having been structurally characterised.[9] Work is currently in progress to investigate the effect of the molybdenum reagent on these processes, and to establish the mode of formation of the alkyltin ozonide.

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