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Preparation and X-Ray Crystal Structure of $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}O_2)]_2$, a Rare Example of a Bis(1,2-μ-peroxo)-bridged Metal Complex[†]

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The crystalline binuclear bis(amido)tin(IV) complex $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}O_2)]_2$ has been characterised by X-ray diffraction; the molecule possesses a structural feature highly unusual for metal complexes, in which the two tin atoms are doubly-bridged by 1,2-μ-peroxo ligands [⟨Sn–O⟩ 1.987(7), ⟨O–O⟩ 1.501(10) Å; ⟨O–Sn–O⟩ 99.7(3), ⟨Sn–O–O⟩ 100.0(4)°].

We report the synthesis[‡] [eqn. (1)] and X-ray characterisation[§] of the crystalline binuclear (1,2-μ-peroxo)tin(IV) amide $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}O_2)]_2$ **1**. The molecule (Fig. 1) has a structure involving an Sn_2O_4 six-membered ring, in which the tin atoms are linked by two 1,2-μ-peroxo ligands. Structurally-authenticated examples of main-group element 1,2-μ-peroxides are scarce, $[SiMe_2(\mu\text{-}O_2)]_3$[2] and $[Sn\{CH(SiMe_3)_2\}_2]_2(\mu\text{-}O)(\mu\text{-}O_2)$[3] being the only cases of which we are aware. The type of double-bridging found in **1**, analogous to that in 1,2,4,5-tetraoxanes[4] of organic chemistry, is very rare, and possibly unique, for a metal complex.

$$2Sn[N(SiMe_3)_2]_2 + 2O_2 \rightarrow [Sn\{N(SiMe_3)_2\}_2(\mu\text{-}O_2)]_2 \quad (1)$$

There is a well-established oxidative addition chemistry of divalent silicon, germanium and tin compounds, involving a very wide range of addenda,[5] including dioxygen and oxygen-atom donors.[6] In tin chemistry, two recent reports have described crystal structures of $[Sn\{CH(SiMe_3)_2\}_2]_2(\mu\text{-}O)(\mu\text{-}O_2)$[3] and $[Sn\{CH(SiMe_3)_2\}_2(\mu\text{-}O)]_2$,[7] both derived by oxidation of the tin(II) alkyl $[Sn\{CH(SiMe_3)_2\}_2]_2$. An early report on the reaction of dioxygen and $Sn[N(SiMe_3)_2]_2$ suggested that the product was an infusible bis(amido)tin(IV) oxide,[8] but this is not borne out by the present results.

The Sn_2O_4 ring in **1** is puckered, the sum of the internal angles equalling 599° (*cf.* 720° for a planar arrangement). The ring possesses a near-symmetrical twist-boat configuration; the relative conformation of the amido groups on each tin atom appears to minimise transannular steric interactions of the *cis*-ligands. These amido groups effectively encapsulate the Sn_2O_4 core; this may account not only for the kinetic stability of **1**, but also for the adoption of a dimeric rather than a polymeric structure. The two peroxo-bridges have similar O–O bond lengths of 1.504(9) and 1.498(10) Å, values towards the upper end of the range observed in other 1,2-μ-peroxo complexes, longer than in solid H_2O_2 (1.453 Å),[9] but similar to that in $[SiMe_2(\mu\text{-}O_2)]_3$ (1.49 Å).[2] The Sn–O bond lengths [⟨Sn–O⟩ = 1.987(7) Å] are shorter than typical for tin(IV) complexes (2.15 Å[10]), and more nearly match those found in $Sn^{II}(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2$ [Sn–O = 1.995(4) and 2.022(4) Å][11] or $[Sn(\mu\text{-}OBu^t)(OBu^t)]_2$ [$\langle Sn\text{–}O_t\rangle$ = 1.97(2) Å].[12]

The puckered ring contains O–Sn–O angles [99.7(3) and 99.6(3)°] which are considerably smaller than the tetrahedral angle, and N–Sn–N angles which are larger [120.5(3) and 122.2(3)°]. The latter angles are unusually large for a tin compound containing the $Sn[N(SiMe_3)_2]_2$ fragment (*cf.*[3] the exceptional C–Sn–C angles in $[Sn\{CH(SiMe_3)_2\}_2]_2(\mu\text{-}O)(\mu\text{-}O_2)$; and the Sn–N bonds are short [⟨Sn–N⟩ = 2.015(7) Å]. The origin of the large N–Sn–N angles and short Sn–N bonds cannot be entirely steric in nature, since these structural features are expected to lead to increased repulsion between the *cis*-amido ligands across the ring, and also because the tin atoms experience less crowded environments than exist in

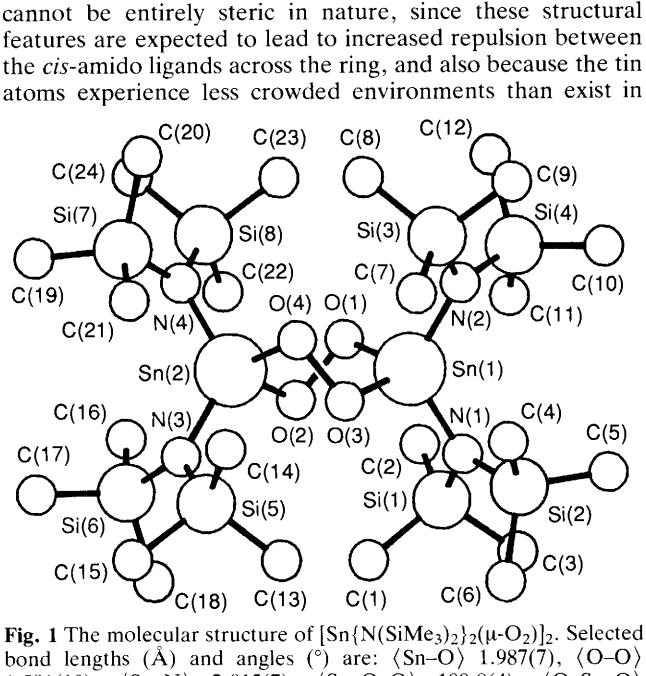

Fig. 1 The molecular structure of $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}O_2)]_2$. Selected bond lengths (Å) and angles (°) are: ⟨Sn–O⟩ 1.987(7), ⟨O–O⟩ 1.501(10), ⟨Sn–N⟩ 2.015(7); ⟨Sn–O–O⟩ 100.0(4), ⟨O–Sn–O⟩ 99.7(3), ⟨N–Sn–N⟩ 121.4(3).

[†] No reprints available.

[‡] *Preparation of* **1**: A solution of orange $Sn[N(SiMe_3)_2]_2$[1] (4.99 g, 11.4 mmol) in pentane (30 ml) was shaken in an atmosphere of dioxygen gas until decolourisation was complete. After filtration to remove an insoluble gel-like coproduct, volatiles were removed from the reaction vessel *in vacuo*, affording a white waxy solid (4.28 g) of crude **1** [by $^{119}Sn\{H\}$ NMR spectroscopy]. Colourless crystals of **1** were obtained from this by recrystallisation from pentane at −30 °C, m.p. 151 °C (decomp.), satisfactory elemental analyses were obtained; ^1H NMR ($[^2H_8]$toluene, 305 K) δ 0.36 (s), $^{13}C\{^1H\}$ NMR ($[^2H_8]$toluene, 305 K) δ 5.48 (s), $^{119}Sn\{^1H\}$ NMR (toluene + $[^2H_8]$toluene, 305 K) δ −268 s (s).

some other complexes with smaller N–Sn–N angles, for example $Sn(Br)[N(SiMe_3)_2]_3$.[13] It seems likely that the high electronegativity of the peroxo ligands results in a polarisation of the tin–oxygen bonds in the sense $^{\delta+}Sn–O^{\delta-}$, increasing the occupancy of the O–O antibonding set. Associated with this polarisation, $N(p_\pi)$-$Sn(p/d_\pi)$ interaction may be increased, to maintain charge balance at tin, strengthening and reducing in length the Sn–N bonds. This shortening of the Sn–N bonds accounts for the wide N–Sn–N angle, as it reduces steric repulsions between geminal amido groups.§

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§ *Crystal data* [T 295 K, Enraf-Nonius CAD-4 diffractometer, no absorption correction, structural solution by heavy-atom methods (SHELXS-86)]: **1** $C_{24}H_{72}N_4O_4Si_8Sn_2$, M = 942.9, monoclinic, space group $P2_1/n$, a = 11.442(3), b = 24.064(4), c = 17.279(5) Å, β = 90.29(2)°, U = 4757.6 Å^3, Z = 4, D_c = 1.32 g cm^{-3}, μ(Mo-Kα) = 12.8 cm^{-1}, specimen 0.3 × 0.3 × 0.2 mm, 4568 unique reflections for $2 < \theta < 20°$, 2216 reflections with $|F^2| > 3\sigma(F^2)$ used in the refinement; R = 0.036, R_w = 0.046.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895.

2 G. A. Razuvaev, V. A. Yablokov, A. V. Ganyushkin, V. E. Shklover, I. Tsinker and Yu. T. Struchkov, *Dokl. Akad. Nauk, SSSR*, 1978, **242**, 132; V. E. Shklover, P. Ad'Yaasuren, I. Tsinker, V. A. Yablokov, A. V. Ganyushkin and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1980, **211**, 12.

3 C. J. Cardin, D. J. Cardin, M. M. Devereux and M. A. Convery, *J. Chem. Soc., Chem. Commun.*, 1990, 1461.

4 J. Z. Gougoutas, in *The Chemistry of Peroxides*, ed. S. Patai, Wiley, Chichester, 1983, p. 391; C.-Y. Chiang, W. Butler and R. L. Kuczkowski, *J. Chem. Soc., Chem. Commun.*, 1988, 465.

5 M. F. Lappert and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1985, 51; M. F. Lappert, *Rev. Silicon, Germanium, Tin, Lead Cpds.*, 1986, **9**, 130.

6 T. T. Sumuraya, S. A. Batcheller and S. Masamune, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 930.

7 M. A. Edelman, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1990, 1116.

8 C. D. Schaeffer and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1974, **96**, 7160.

9 W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 1965, **42**, 3054.

10 P. G. Harrison, in *The Chemistry of Tin*, ed. P. G. Harrison, Blackie, Glasgow, 1989, p. 9.

11 B. Çetinkaya, I. Gümrüçkü, M. F. Lappert, J. L. Atwood, R. D. Rogers and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1980, **102**, 2088.

12 T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, S. J. Smith and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1985, 939.

13 R. D. Rogers and J. L. Atwood, *J. Cryst. Spectrosc. Res.*, 1983, **13**, 1; M. F. Lappert, M. C. Misra, M. Onyszchuk, R. S. Rowe, P. P. Power and M. J. Slade, *J. Organomet. Chem.*, 1987, **330**, 31.