

Formation of a dimeric sulfito-bridged imidotin cubane by oxidation of $(\text{SnNBu}^t)_4$ with SO_2

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Received 17th March 2003, Accepted 6th May 2003

First published as an Advance Article on the web 12th May 2003

The rapid reaction of dry SO_2 gas with $(\text{SnNBu}^t)_4$ in THF at 23 °C produces the dimer $[(\text{SnNBu}^t)_4\mu\text{-OSO}_2]_2(\text{THF})$ in which two imidotin cubanes are linked through one of their tin atoms by a bridging (η^1, η^2) sulfito ligand.

Imidotin(II) cubanes of the type $(\text{SnNR})_4$ represent one of the fundamental building blocks of inorganic cluster chemistry.¹ Although the first example $(\text{SnNBu}^t)_4$ was reported in 1979,² reactions in which the $(\text{SnNR})_4$ cube is retained are scarce. Lewis base properties have been established in the formation of bis-adducts of the type $(\text{SnNR})_4 \cdot 2\text{L}$ ($\text{R} = \text{Bu}^t$, $\text{L} = \text{AlCl}_3$,^{3a} $\text{R} = \text{SiEt}_3$, $\text{L} = \text{Fe}(\text{CO})_4$ ^{3b}) in which two of the Sn(II) centres are coordinated to the Lewis acid. The complex $\{(\text{SnNPh})_4\text{MgCl}_2(\text{THF})_4\}_z$, which has a polymeric structure as a result of weak $\text{Sn} \cdots \text{Cl}$ interactions, has also been reported.⁴ Very recently we found that $(\text{SnNBu}^t)_4$ is oxidized by elemental chalcogens in boiling toluene to produce $\text{Sn}_4\text{Se}_2(\text{NBu}^t)_4$, a complex that contains two Group 14–Group 16 double bonds, or the monochalcogenides $\text{Sn}_4\text{E}(\text{NBu}^t)_4$ ($\text{E} = \text{S}, \text{Te}$).⁵ The controlled hydrolysis of $(\text{SnNBu}^t)_4$ replaces one of the NBu^t cornerstones by the isoelectronic oxo ligand to give $[\text{Sn}_4(\text{NBu}^t)_3\text{O}]_6$, which has a dimeric structure with weak $\text{O} \rightarrow \text{Sn}$ donor interactions.^{2b† ‡}

In the context of our recent finding that the hexameric anilido-magnesium complex $[(\text{THF})\text{MgNPh}]_6$ undergoes insertion of SO_2 molecules into $\text{Mg}-\text{N}$ bonds to give $[(\text{THF})\text{Mg}\{\text{O}_2\text{S}(\mu\text{-NPh})\text{SO}_2\}]_6$,⁷ we have investigated the reaction of SO_2 with $(\text{SnNBu}^t)_4$. Surprisingly, the imidotin cube remains intact in this reaction, while one of the Sn(II) atoms is oxidized to Sn(IV) and SO_2 is converted to a sulfito ligand to give $[(\text{SnNBu}^t)_4\mu, \eta^1, \eta^2\text{-OSO}_2]_2$ (**1**). The dimer **1** is the first example of a complex in which two of these cubic building blocks are linked by bridging ligands.

The passage of dry sulfur dioxide gas into a THF solution of $(\text{SnNBu}^t)_4$ at 23 °C results in an immediate reaction to produce **1**, which was identified by ^1H and ^{119}Sn NMR spectra, IR spectrum and an X-ray structural determination. The molecular structure of **1** is depicted in Fig. 1. The molecule is a centrosymmetric dimer with crystallographic $C2/m$ symmetry. Two $(\text{SnNBu}^t)_4$ cubes are bridged by two sulfito ligands. The SO_3^{2-} ligands are O, O' -chelated to a tin atom [Sn(1)] of one cube and linked in an O -monodentate fashion to the symmetry-related tin atom of the second cube. Thus the oxo-anion adopts a μ, η^1, η^2 bonding mode and the oxidized tin atom Sn(1) becomes hexacoordinate. The sulfito ligand subtends an angle of $65.90(15)^\circ$ at Sn(1). The OSO bond angles are $97.8(2)$ and $107.73(14)^\circ$; the lower value is associated with the chelating function of the ligand. As expected,⁵ the mean Sn–N bond length involving the Sn(IV) atom is *ca.* 0.08 Å shorter than the mean Sn(II) bond length. The mean N–Sn(IV)–N bond angle is *ca.* 3.6° wider than $[\text{N}-\text{Sn}(\text{II})-\text{N}]$ despite the difference in coordination numbers (6-coordinate *vs.* 3-coordinate), presumably reflecting the stereochemical influence of the lone pair on the Sn(II) centres. The mean Sn–O bond length of 2.146(3) Å is in the range of values found for hexacoordinate tin.⁸

The NMR data for **1** in CDCl_3 are consistent with retention of the solid-state structure in solution. The ^1H NMR spectrum

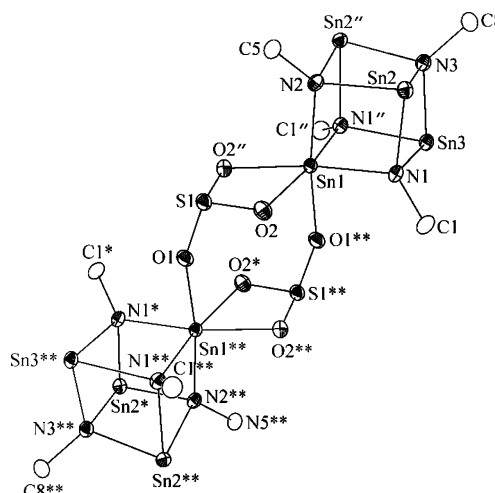


Fig. 1 Structure of **1**. Probability ellipsoids are drawn at the 30% level. Only the α -carbon atoms of Bu^t groups are shown. Selected bond lengths (Å) and angles ($^\circ$): Sn(1)–N(1) 2.130(3), Sn(1)–N(2) 2.162(4), Sn(2)–N(1) 2.240(3), Sn(2)–N(2) 2.216(3), Sn(2)–N(3) 2.196(3), Sn(3)–N(1) 2.231(3), Sn(3)–N(3) 2.192(4), Sn(1)–O(1)* 2.142(4), Sn(1)–O(2) 2.149(3), S(1)–O(1) 1.508(4), S(1)–O(2) 1.551(3), O(2)–Sn(1)–O(2)* $65.90(15)$, O(2)–Sn(1)–O(1)* $88.31(11)$, O(1)–S(1)–O(2) $107.73(14)$, O(2)–S(1)–O(2)* $97.8(2)$. Superscripts refer to symmetry-related atoms: * $x, -y + 1, z$; * $-x, +y, -z$; ** $-x, -y + 1, -z$.

exhibits two resonances in the NBu^t region with relative intensities 3:1; from symmetry considerations the weaker resonance is attributed to the Bu^t group attached to N(3). The ^{119}Sn NMR spectrum shows two resonances at δ 490 and -258 , which can be assigned to the Sn(II) and Sn(IV) atoms, respectively, on the basis of their chemical shifts and relative intensities. The IR spectrum of **1** exhibits strong bands at 1023, 919 and 591 cm^{-1} that are attributed to the sulfite ligand by comparison with the vibrational frequencies of SO_3^{2-} .⁹

The retention of the $(\text{SnNBu}^t)_4$ cube in **1** is noteworthy in view of the facility of SO_2 insertion into $\text{Sn}-\text{NR}_2$ bonds (*e.g.* $\text{Me}_3\text{SnNMe}_2$)¹⁰ and into the $\text{Mg}-\text{NPh}$ bonds of the hexagonal prism $[(\text{THF})\text{Mg}(\text{NPh})]_6$.⁷ Presumably, the oxidation of one of the Sn(II) sites occurs much more rapidly than an insertion process. The conversion of SO_2 into an SO_3^{2-} ligand is also unexpected, although not unprecedented. Oxygen transfer from SO_2 to give sulfite complexes has been reported for both transition-metal and main group element systems.^{11,12} A likely route to **1** involves the formation of the μ -oxo dimer $[(\text{SnNBu}^t)_4(\mu\text{-O})]_2$ (**2**) by oxygen transfer from SO_2 to $(\text{SnNBu}^t)_4$ followed by double insertion of SO_2 into the Sn–O bonds of **2**. Unlike the corresponding sulfide $\text{Sn}_4\text{S}(\text{NBu}^t)_4$, which is monomeric,⁴ the oxo counterpart is expected to be dimeric since the terminal $[\text{Sn}=\text{O}]$ group is unstable with respect to bridging.¹³ Attempts to validate this hypothesis were thwarted by the intractable nature of the product obtained from the oxidation of $(\text{SnNBu}^t)_4$ with pyridine-*N*-oxide.

In summary, the reaction of $(\text{SnNBu}^t)_4$ with SO_2 results in oxidation of one Sn(II) centre to give the first example of a complex in which two cubanes $(\text{SnNR})_4$ are strongly linked.¹⁴

This finding may presage the discovery of macromolecular systems involving this potentially versatile building block.

The financial support of NSERC (Canada) is gratefully acknowledged.

Notes and references

† Synthesis of **1**: Dry sulfur dioxide gas was bubbled through a stirred solution of $(\text{SnNBu})_4$ (0.123 g, 0.162 mmol) in THF (15 mL) under argon at 23 °C for 1 min. The yellow solution turned yellow–orange and then became cloudy. Removal of volatile materials under vacuum and subsequent washing of the pale yellow residue with *n*-hexane (2×5 mL) yielded **1** as a white powder (0.107 g, 0.122 mmol, 75%). Recrystallization by the solvent diffusion method (THF/*n*-hexane) at 23 °C gave X-ray quality crystals. Satisfactory CHN analyses could not be obtained owing to partial loss of lattice THF, but **1** was shown to be pure by NMR. NMR data (CDCl_3 , 23 °C): ^1H NMR: δ 3.75 (m, THF), 1.86 (m, THF), 1.58 (s, 27 H, CMe_3), 1.52 (s, 9 H, CMe_3); ^{119}Sn NMR: δ 490 [Sn(II)], –258 [Sn(IV)] (ref. SnMe_4).

‡ Crystal data for **1**: Molecular formula $\text{C}_{36}\text{H}_{80}\text{N}_8\text{O}_7\text{S}_2\text{Sn}_8$, $M = 1750.72$, monoclinic space group $C2/m$, $a = 26.1198(6)$, $b = 11.5613(3)$, $c = 10.1693(3)$ Å, $\beta = 105.943(1)^\circ$, $V = 2952.8(1)$ Å³, $T = 173(2)$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 3.440$ mm^{–1}. Crystal size $0.12 \times 0.08 \times 0.07$ mm, 16507 reflections measured, 3828 unique ($R_{\text{int}} = 0.0479$), final $R = 0.031$ for 3213 observed data with $I > 2.00 \sigma(I)$. Data were collected on a Nonius Kappa CCD diffractometer and the structure was solved by direct methods (SIR 92) and refined against F^2 using SHELXL97. The atoms Sn(1), Sn(2), Sn(3) and Sn(1'), Sn(2'), Sn(3') are disordered with occupancy factors of 0.955 and 0.045, respectively. The atoms Sn(1–3) were refined anisotropically, whereas Sn(1'–3') were only refined isotropically. The asymmetric unit contains one-half molecule of THF with an O-atom lying on a mirror plane and two C-atoms across the mirror plane. The distances O–C and C–C were constrained using the command DFIX and an overall isotropic thermal displacement parameter was allowed to refine for the O- and C-atoms of THF. CCDC reference

number 206175. See <http://www.rsc.org/suppdata/dt/b3/b302966b/> for crystallographic data in .cif or other electronic format.

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