Ester Elimination *Versus* Ligand Exchange: the Role of the Solvent in Tin–Oxo Cluster-building Reactions

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Ester elimination between $Sn(OBu^t)_4$ and $Sn(OAc)_4$ in refluxing toluene yields $Sn_6(O)_6(OCMe_3)_6(O_2CMe)_6$ which is characterized in solution and in the solid state by single-crystal X-ray diffraction; reaction of the same species in pyridine results in the formation of the ligand exchange products, $Sn(OBu^t)_x(OAc)_{4-x}$ where x = 1–3.

The field of materials chemistry often involves the application of molecular design principles to the rational synthesis of materials to allow better control over their structure and properties.[1] Hydrolytic sol–gel chemistry has provided a valuable pathway for the synthesis of metal oxide materials with several benefits[2,3] over traditional solid-state synthetic methods such as better control over the evolution of microstructure. The chemistry of sol–gel processing typically involves the hydrolysis and subsequent condensation of metal alkoxide compounds. For metal alkoxides other than silicon, the increased reactivity of the metal centre leads to a high rate of hydrolysis and condensation which makes microstructural control over the resulting sol or gel difficult.[4,5] In an attempt to gain better control over microstructural evolution in metal oxide formation there has been interest in alternative, non-hydrolytic routes to these materials.[6] One way to achieve this is through a bimolecular reaction between two different metal-organic species in which the organic supporting ligands on each complex are designed to be eliminated during the reaction and link the two metal centres, fixing their stoichiometry. This strategy is being studied extensively for formation of semiconductor nanoclusters of Group 13/15 compounds where trimethylsilyl chloride elimination results in formation of a bond between the Group 13 and 15 elements.[7] In the case of metal oxide chemistry, elimination of an ester between a metal alkoxide and a metal carboxylate has been invoked in many cases,[8,9] but the details of this reaction have not been studied.

When a metal alkoxide and metal carboxylate are mixed, a number of different outcomes can be anticipated including no reaction, ligand exchange or ester elimination as described by eqn. (1).

$$M(OR^1)_4 + M'(O_2CR^2)_4 \rightarrow (R^1O)_3M{-}O{-}M'(O_2CR^2)_3 + R^1O(O)CR^2 \quad (1)$$

In the context of materials chemistry, ester elimination is the only fruitful outcome. Bradley *et al.*[10,11] first noticed that reaction between titanium alkoxides and trimethylsilyl acetate yielded, with azeotropic removal of the ester, compounds such as $Ti(OSiMe_3)_4$.

In an attempt to gain further insight into metal oxide cluster formation *via* ester elimination reactions in a systematic and controlled fashion, we have chosen to investigate reactions between tin alkoxide and tin carboxylate compounds. Tin was chosen as a model system due to the presence of two NMR-active isotopes, ^{119}Sn and ^{117}Sn which allow the unambiguous identification of Sn–O–Sn bonds. $Sn(OBu^t)_4$ is monomeric and four-coordinate in solution and in the solid state.[12] $Sn(OAc)_4$ contains an eight-coordinate tin centre in solution and in the solid state.[13] The reaction between $Sn(OBu^t)_4$ and $Sn(OAc)_4$ was carried out in a non-coordinating solvent, toluene, and a coordinating solvent, pyridine, to examine the influence of the solvent.

When the reaction is carried out in pyridine at room temperature, there is no evidence for ester elimination and three distinct products are formed as determined by ^{119}Sn NMR spectroscopy. The three new ^{119}Sn NMR resonances occur at δ −644, −720 and −780 with concomitant disappearance of the resonances due to the starting materials. The new tin resonances show no ^{117}Sn satellites indicating that no Sn–O–Sn bonds have been formed. The three products are identified as $Sn(OBu^t)_3(OAc)$, $Sn(OBu^t)_2(OAc)_2$ and $Sn(OBu^t)(OAc)_3$, by comparison to authentic chemical shifts of these species and are formed as a result of ligand exchange according to eqn. (2).

$$3\ Sn(OBu^t)_4 + 3\ Sn(OAc)_4 \rightarrow 2\ Sn(OBu^t)_3(OAc) + 2\ Sn(OBu^t)_2(OAc)_2 + 2\ Sn(OBu^t)(OAc)_3 \quad (2)$$

For example, the chemical shift of δ −644 is consistent with the chemical shift of $Sn(OBu^t)_3(OAc)(pyridine)$ which has recently

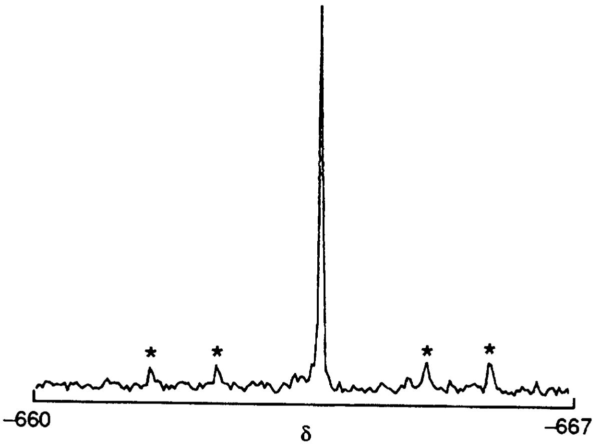

Fig. 1 ^{119}Sn NMR spectrum of **1**. Asterisks denote tin satellites.

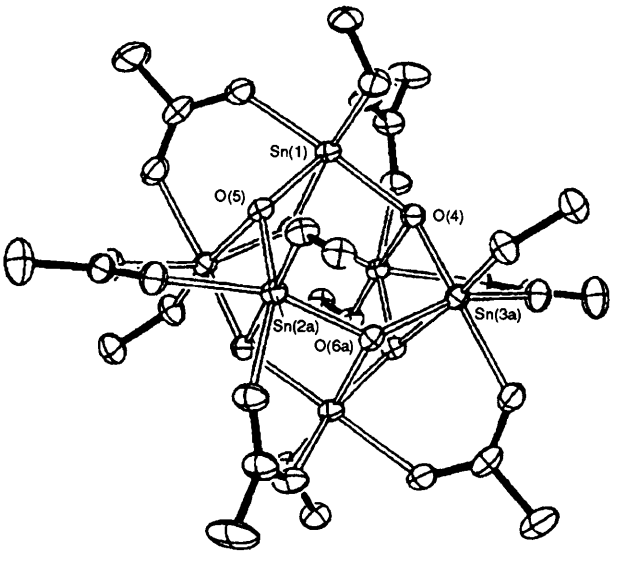

Fig. 2 Solid-state structure of **1** showing only α-carbons of Bu^t groups for clarity. Representative bond lengths/Å Sn(1)–O(5) 2.049(4), Sn(1)–O(4) 2.042(5), Sn(2a)–O(5) 2.049(6), Sn(2a)–O(6a) 2.054(5), Sn(3a)–O(4) 2.055(4). Representative bond angles/° O(5)–Sn(1)–O(4) 103.7(2), Sn(1)–O(5)–Sn(2a) 135.0(3).

been prepared by independent synthesis according to eqn. (3) and structurally characterized in the solid state by single-crystal X-ray diffraction.[14]

$$\mathrm{Me_3Si(OAc) + Sn(OBu^t)_4 \xrightarrow{pyridine} Sn(OBu^t)_3(OAc)(py) + Me_3SiOBu^t} \quad (3)$$

In contrast, when the reaction between $\mathrm{Sn(OBu^t)_4}$ and $\mathrm{Sn(OAc)_4}$ was carried out in refluxing toluene for 12 h, elimination of the ester, $\mathrm{Bu^tOAc}$, was observed as determined by GC–MS with formation of a tin–oxo cluster species, $\mathrm{[SnO(OBu^t)(OAc)]_n}$, **1**,† according to the stoichiometry of eqn. (4).

$$\mathrm{Sn(OBu^t)_4 + Sn(OAc)_4 \rightarrow 2\ [SnO(OBu^t)(OAc)]_n + 2Bu^tOAc} \quad (4)$$

^1H NMR spectroscopy revealed that **1** is highly symmetrical and contains one type of alkoxide and acetate ligand in $[^2H_6]$benzene solution. The ^{119}Sn NMR data revealed a single resonance at δ −663 consistent with one type of six-coordinate tin atom,[15] with two sets of tin satellites as shown in Fig. 1. The $^2J_{^{119}Sn-O-^{117}Sn}$ values of 251 and 411 Hz and integrated areas of 14 and 13%, respectively, are consistent with a structure in which each tin atom is coupled through two non-equivalent oxo-bridges to two nearest neighbour tin atoms. These observations are consistent with the formulation of **1** as a closed-ring oxo-cluster with a degree of oligomerization, *n*, where *n* is an even integer ⩾ 6.

To unambiguously determine the nuclearity of this cluster, a single-crystal X-ray diffraction study was carried out. The solid state structure of **1**‡ is shown in Fig. 2. The molecule has approximately C_3 molecular symmetry which is consistent with the solution spectroscopic data. The structure of the tin–oxo core (bond lengths and angles) is similar to other tin–oxo clusters reported previously. Holmes and coworkers[16–18] have synthesized a variety of small oxo clusters of tin by condensation of tin carboxylates and tin hydroxides. In some of these cases a $Sn_6O_6^{12-}$ core 'drum' structure exists similar to that found in **1**.

We believe that the coordinating solvent, pyridine, in the reaction of eqn. 3 competes successfully with the acetate ligand for the vacant coordination sites at the $\mathrm{Sn(OBu^t)_4}$ centre which may inhibit ester elimination. We have previously observed that pyridine reduces the rate of alcohol/alkoxide exchange in the $\mathrm{Sn(OBu^t)_4 + HOBu^t}$ system.[19] Coordinative saturation at the tin centre may also explain why **1** does not undergo further ester elimination reaction with itself to form tin oxide under these conditions. These observations clearly demonstrate the importance of the solvent in ester elimination reactions.

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Footnotes

† Synthesis of **1**: A 500 ml dry Schlenk flask was charged with 2.08 g (5.86 mmol) of $\mathrm{Sn(OAc)_4}$ and 2.41 g (5.86 mmol) of $\mathrm{Sn(OBu^t)_4}$. Then, 200 ml of dry toluene was added and the solution was refluxed for 12 h. The volatile components were removed under vacuum to produce a pale-yellow powder. The compound can be recrystallized from concentrated cold (10 °C) toluene solution over one week. Crystals suitable for single crystal X-ray diffraction were grown from a cold (10 °C) dilute toluene solution. ^1H NMR (C_6D_6), 250 MHz: δ 1.79 (s, 9H), 1.68 (s, 3H). ^{119}Sn NMR (C_6D_6, 93.3 MHz) δ −663 (s, $^2J_{^{119}Sn-O-^{119}Sn}$ 251 and 411 Hz), integrated area of satellites with respect to main peak ≈ 27%.

‡ *Crystal data* for **1**: $Sn_6C_{36}H_{72}O_{24}\cdot 0.5C_7H_8$, triclinic, $P\bar{1}$, a = 14.101 (2), b = 14.412 (2), c = 18.878 (3) Å, α = 103.59 (2), β = 93.33 (2), γ = 118.79 (2)°, U = 3201.4 (8) $Å^3$; Z = 2; D_c = 1.709 g cm^{-3}; μ(Mo-Kα) = 23.73 cm^{-1}; T = 25 °C, Siemens P4, Mo-Kα. Of 12895 data ($4 \leqslant 2\theta \leqslant 50°$), 12494 were independent, and 8906 were observed $[5\sigma(F_o)]$. The structure was solved by direct methods. Two independent but chemically equivalent compound molecules and one toluene solvent molecule, each centred on an inversion point, were located in the asymmetric unit. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized, $R(F)$ = 3.71%, $R(wF)$ = 4.60%, GOF = 0.97, N_o/N_v = 13.5, $\Delta(\rho)$ = 0.96 e $Å^{-3}$, $\Delta/\sigma_{(max)}$ = 0.020. SHELXL software used for all computations (G. Sheldrick, Siemens XRD, Madison, WI, USA). An empirical (ψ-scan) correction was performed. The ratio of the transmission coefficients was 1.60. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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