

Solvent Dependent Ester Elimination Reactions in the Preparation of Mixed-metal Oxo Clusters: the Synthesis of $\text{PbSn}_2(\mu_3\text{-O})(\text{OBU}^t)_4(\text{OAc})_4$

James Caruso, Mark J. Hampden-Smith* and Eileen N. Duesler

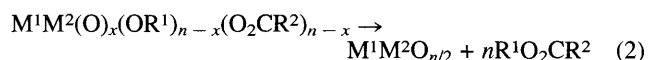
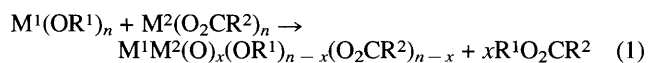
Department of Chemistry and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131, USA

The reaction between $\text{Sn}(\text{OBU}^t)_4$ and $\text{Pb}(\text{OAc})_4$ has been studied as a function of the nature of the reaction solvent: in refluxing toluene, ester elimination results in the quantitative formation of $\text{PbSn}_2(\mu_3\text{-O})(\text{OBU}^t)_4(\text{OAc})_4$ which has been characterized in solution by ^1H , ^{119}Sn and ^{207}Pb NMR and in the solid state by single-crystal X-ray diffraction, whereas in pyridine, reaction of the same two species results in ligand exchange forming $\text{Sn}(\text{OBU}^t)_3(\text{OAc})$ -pyridine and $\text{Pb}(\text{OAc})_3(\text{OBU}^t)$.

The search for molecular routes to metal oxides has become an area of intense scientific interest due to the technological relevance of these materials.¹⁻⁵ Metal oxides exhibit a wide range of interesting properties including ionic and electrical conductivity, piezo-, pyro- and ferro-electricity and magnetism which can be exploited in applications such as sensors, membrane separations and in microelectronic devices.⁶⁻¹² Molecular routes are proving important as a result of the possibility to control the physical and chemical properties of the final materials and particularly the crystal chemistry of the products which is often the basis of the applications of these materials.^{13,14}

In many molecular approaches to extended solids, mixed metal oxo clusters are either invoked as intermediates or used as the starting materials. The systematic construction and assembly of molecular metal oxo clusters or building blocks offers a number of distinct advantages over other methods to prepare mixed metal oxides.¹⁵ In the molecular building block approach, it should be possible to build hierarchical structures with particular stoichiometry and as a result control many of the physical and chemical properties of the final material such as pore structure, density and crystallinity. The key aspect to this approach is to investigate and understand the chemistry associated with the synthesis and assembly of molecular metal oxo clusters.

We have chosen to study the ester elimination reaction between metal alkoxides $[\text{M}(\text{OR})_n]$ and metal carboxylates $[\text{M}(\text{O}_2\text{CR})_n]$ as described by eqns. (1) and (2) as a method to systematically prepare metal oxide materials.¹⁶⁻¹⁸



This reaction scheme accommodates the design criteria set forth above by allowing for: (a) complete elimination of the ligands, and therefore facilitates formation of high purity products, (b) control over stoichiometry of the final product and (c) the isolation of metal oxo clusters as intermediates which could be assembled in a manner to control microstructure of the final material. We have recently proposed some criteria for achieving ester elimination between metal alkoxide and metal carboxylate species¹⁷ and also that an ester elimination reaction between $\text{Sn}(\text{OBU}^t)_4$ and $\text{Sn}(\text{OAc})_4$ results in formation of the molecular cluster $\text{Sn}_6\text{O}_6(\text{OBU}^t)_6(\text{OAc})_6$.¹⁹ This cluster can be considered a small molecular fragment of cassiterite phase SnO_2 (rutile structure) since it possesses all the structural characteristics, namely three-coordinate O and six-coordinate Sn. In this report, we have expanded this investigation to the reaction of heterometallic systems and investigated ester elimination reactions between tin and lead compounds. We chose tin and lead precursors due to the presence of NMR active nuclei of both elements which should allow for the unambiguous identification of oxo bridges in the resulting materials and structural characterization in solution.

The reaction between $\text{Sn}(\text{OBU}^t)_4$ and $\text{Pb}(\text{OAc})_4$ in toluene at 50°C after several minutes results in the formation of a new species which gives analytical and spectroscopic data consistent with the empirical formula $\text{PbSn}_2(\text{O})(\text{OBU}^t)_4(\text{OAc})_4$.[†] Analysis of the volatile reaction products by GC-MS reveals the presence of *tert*-butyl acetate as evidenced by the two molecular ion peaks at m/z 59 and 101 corresponding to the fragments $\text{H}_3\text{CC}(\text{O})\text{O}^+$ and $\text{C}_4\text{H}_9\text{OC}(\text{O})^+$, respectively, consistent with an authentic sample of this ester. The solid state structure of this compound[‡] was determined by single-crystal X-ray diffraction (Fig. 1) and revealed a trinuclear structure with one μ_3 -oxo bridge. The molecular structure contains one approximate mirror plane containing the lead, the μ_3 -oxo bridge and which bisects the Sn- μ_3 -O-Sn' bond. It contains 4 bridging acetate ligands and 4-*tert*-butoxy ligands, 2 bridging and 2 terminal. The strongest evidence for retention of this structure in solution comes from its ^{119}Sn and ^{207}Pb NMR spectra. The ^{119}Sn NMR spectrum (Fig. 2) of this compound in pyridine reveals a single

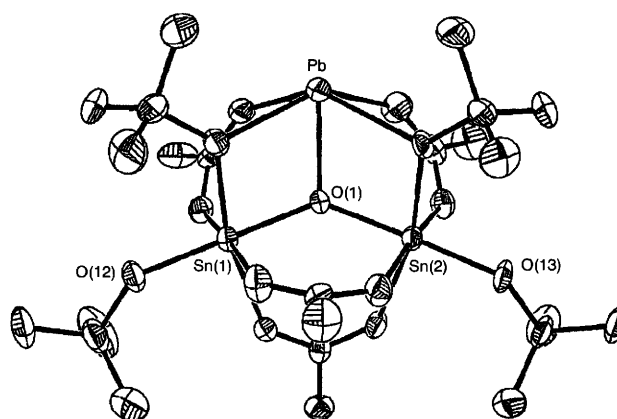


Fig. 1 Molecular structure of $\text{PbSn}_2(\mu_3\text{-O})(\text{OBU}^t)_4(\text{OAc})_4$. Relevant bonds lengths (Å): Pb-O(1) 2.228 (6), Sn(1)-O(1) 2.001 (5), Sn(2)-O(1) 1.994 (4), Sn(1)-O(12) 1.937(5), Sn(2)-O(13) 1.937(4). Relevant bond angles ($^\circ$): Pb-O(1)-Sn(1) 108.9 (2), Pb-O(1)-Sn(2) 110.0 (2), Sn(1)-O(1)-Sn(2) 129.0 (6), O(1)-Sn(2)-O(13) 178.0 (2), O(1)-Sn(1)-O(12) 179.5 (2).

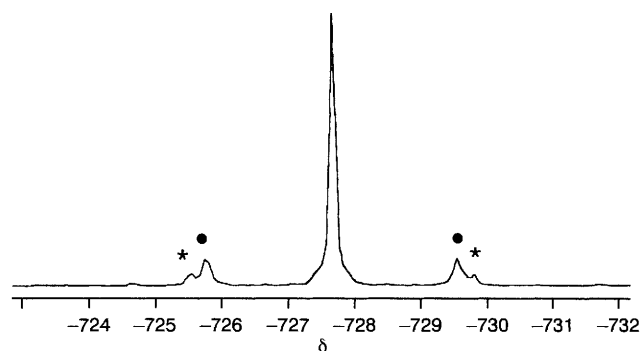


Fig. 2 Solution ^{119}Sn $\{^1\text{H}\}$ NMR spectrum of $\text{PbSn}_2(\mu_3\text{-O})(\text{OBU}^t)_4(\text{OAc})_4$ showing the two different couplings to ^{117}Sn (•) and ^{207}Pb (*).

resonance at $\delta -728$ which is consistent with a six-coordinate Sn^{IV} centre. Furthermore, the resonance exhibits two sets of satellites with coupling constants (and integrated areas) of 326 Hz (24%) and 382 Hz (10%). This area of integration corresponds to one ^{119}Sn nucleus coupled to both a ^{117}Sn (8%) and ^{207}Pb (22%) isotope with similar two-bond Sn–O–M coupling constants. The ^{207}Pb NMR spectrum shows a single resonance at $\delta -302$ with one set of satellites with an area of integration of 36%. This data corresponds to a ^{207}Pb centre coupled to two equivalent $^{117,119}\text{Sn}$ metal centres where ^{117}Sn and ^{119}Sn both have ca. 8% natural abundance. The ^1H and ^{13}C NMR data also support the retention of the solid state structure in solution through the existence of two types of alkoxide ligands in a 1 : 1 ratio (one type terminal, one type bridging) and two different types of acetate ligands in a 1 : 1 ratio.²⁰ The reduction of lead(IV) to form a lead(II) product is not uncommon in this type of reaction and we presume the oxidation product is likely to be an organic species.²¹

When the reaction between $\text{Sn}(\text{O}i\text{Bu})_4$ and $\text{Pb}(\text{OAc})_4$ is carried out in pyridine as solvent, there is no evidence for ester elimination and instead a ligand exchange reaction occurs at temperatures up to 80 °C. The ^{119}Sn NMR of this reaction mixture shows a single resonance at $\delta -644$ which corresponds to the mixed tin alkoxide carboxylate, $\text{Sn}(\text{O}i\text{Bu})_3(\text{OAc})\cdot\text{pyridine}$, which has been independently synthesized and structurally characterized in the solid state.¹⁷ The ^1H NMR data of the reaction mixture also reveal several overlapping resonances both at $\delta 1.5$ and 2.0 consistent with the ligand exchange product $\text{Sn}(\text{O}i\text{Bu})_3(\text{OAc})\cdot\text{pyridine}$. The ^{207}Pb NMR data of this reaction mixture reveal a single resonance at $\delta -1740$ consistent with the presence of a pyridine adduct of $\text{Pb}(\text{OAc})_3(\text{O}i\text{Bu})$.²² Similar observations were made when $\text{Sn}(\text{O}i\text{Bu})_4$ and $\text{Sn}(\text{OAc})_4$ were reacted in pyridine, resulting in ligand exchange rather than ester elimination.

Although a number of questions concerning the generality of ester elimination reactions remain unanswered, it is clear that this is a useful strategy to prepare both homo- and heterometallic metal oxo clusters in high yields.

We thank the AFOSR for financial support of this work and the NSF chemical instrumentation program for the purchase of a low field NMR spectrometer.

Received, 23rd February 1995; Com. 5/01123J

Footnote

† Synthesis of $\text{PbSn}_2(\mu_3\text{-O})(\text{O}i\text{Bu})_4(\text{OAc})_4$ **1**: a 50 ml Schlenk flask was charged with 1.94 g (4.72 mmol) $\text{Sn}(\text{O}i\text{Bu})_4$ and 2.09 (4.72 mmol) $\text{Pb}(\text{OAc})_4$. Then 50 ml dry toluene was added and the resulting bright-yellow solution was stirred at 50–70 °C for 3 h. The volatile components were removed under vacuum resulting in a pale-yellow powder. The compound can be recrystallized from concentrated pyridine to give crystals suitable for single crystal X-ray diffraction at room temperature over several days. Yield: 1.95 g (42%). ^1H NMR ($\text{C}_5\text{D}_5\text{N}$) δ 1.53 (s, 9H), 1.58 (s, 9H), 2.09 (s, 4H), 2.1 (s, 2H). ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$) δ 25.1, 26.2, (s, O_2CMe), 32.8, 33.4 (s, OCMe_3), 73.7, 73.8 (s, OCMe_3), 178 (s, O_2CMe). ^{119}Sn NMR ($\text{C}_5\text{D}_5\text{N}$) δ -728 (s, $^2J_{119\text{Sn}-\text{O}-117\text{Sn}}$ 382, $^2J_{119\text{Sn}-\text{O}-207\text{Pb}}$ 326 Hz), total

integrated area of satellites with respect to main peak = 34%). ^{207}Pb NMR ($\text{C}_5\text{D}_5\text{N}$) δ -302 (s, $^2J_{207\text{Pb}-\text{O}-117,119\text{Sn}}$ 342 Hz, total integrated area of satellites with respect to main peak = 36%).

‡ Crystal data for **1**: $\text{PbSn}_2\text{C}_{24}\text{H}_{48}\text{O}_{13}$, triclinic, $P\bar{1}$, $a = 11.871$ (8), $b = 13.069$ (8), $c = 13.689$ (8) Å, $\alpha = 1187.47$ (3), $\beta = 92.32$ (3), $\gamma = 94.09$ (4)°, $V = 1855$ (3) Å³; $Z = 2$; $D_c = 1.771$ g cm⁻³; $\mu(\text{Mo-K}\alpha) = 5.913$ mm⁻¹; $T = 25$ °C, Siemens R3m/v, Mo-K α . Of 7130 data ($7 \leq 2\theta \leq 25^\circ$), 6147 were independent, and 4525 were observed [$3\sigma(F_o)$]. The structure was solved by the Patterson method. Two independent but chemically equivalent compound molecules were located in the asymmetric unit. Refinement: all non-hydrogen atoms anisotropic, all hydrogen atoms idealized, $R(F) = 3.29\%$, $R(wF) = 2.92\%$, GOF = 1.16, $N_o/N_v = 12.5$, $D(r) = 0.96$ e Å⁻³, $D/s(\text{max}) = 0.001$. SHELXL software used for all computations (G. Sheldrick, Siemens XRD, Madison, WI, USA). 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.

References

- J. Livage, M. Henry and C. Sanchez, *C. Prog. Solid State Chem.*, 1989, **18**, 259.
- L. C. Klein, *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes*, Noyes Publications, Park Ridge, 1988.
- C. J. Brinker and G. W. Scherer, *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*, Academic, San Diego, 1990.
- L. G. Hubert-Pfalzgraf, *New J. Chem.*, 1987, **11**, 663.
- K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
- Manufacturing with Materials*, ed. L. Edwards and M. Endean, Butterworth, London, 1990.
- Materials Principles and Practice*, ed. C. Newey and G. Waever, Butterworth, London, 1990.
- Structural Materials*, ed. G. Weidmann, P. Lewis and N. Reid, Butterworth, London, 1990.
- Electronic Materials*, ed. N. Braithwaite and G. Weaver, Butterworth, London, 1990.
- A. P. Davidson, *Materials World*, 1994, 381.
- F. S. Galasso, *Structure, Properties and Preparation of Perovskite-type Compounds*, Pergamon, London, New York, 1969.
- F. Jona and G. Shirane, *Ferroelectric Crystals*, Macmillan, New York, 1962.
- R. E. Newham, *Structure-Property Relations*, Springer-Verlag, New York, 1975.
- C. D. Chandler, C. Roger and M. J. Hampden-Smith, *Chem. Rev.*, 1993, **93**, 1205.
- V. W. Day, T. A. Eberspacher, W. G. Klempner and C. W. Park, *J. Am. Chem. Soc.*, 1993, **115**, 8469.
- J. Caruso, T. M. Alam and M. J. Hampden-Smith, *J. Am. Chem. Soc.*, submitted.
- J. Caruso, C. Roger, F. Schwertfegger, M. J. Hampden-Smith, A. L. Rheingold, and G. Yap, *Inorg. Chem.*, 1995, **34**, 449.
- C. D. Chandler, J. Caruso, M. J. Hampden-Smith and A. L. Rheingold, *Polyhedron* 1994, in press.
- J. Caruso, M. J. Hampden-Smith, A. L. Rheingold and G. Yap, *J. Chem. Soc., Chem. Commun.*, 1995, 157.
- T. A. Wark, E. A. Gulliver, M. J. Hampden-Smith and A. L. Rheingold, *Inorg. Chem.*, 1990, **29**, 4360.
- J. March, *Advanced Organic Chemistry*, Wiley, New York, 1985.
- B. Wrackmeyer and K. Horchler, *Ann. Rep. on NMR Spectroscopy*, 1990, vol. 22, pp. 249.