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The utility of hypercoordination and secondary bonding for the synthesis of a binary organoelement oxo cluster

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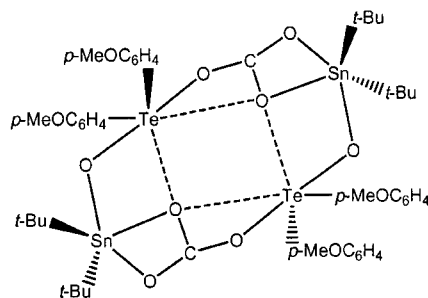
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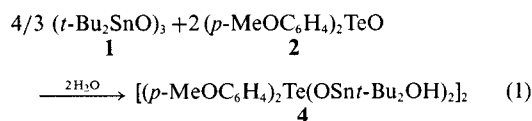
A strategy for the preparation of the otherwise difficult to obtain binary organometallic oxides containing two heavy main group elements is described and exemplified by the synthesis of $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{OSn}t\text{-Bu}_2\text{OH})_2]_2$.

Organotin oxo clusters and polymers have attracted considerable attention in recent years owing to their structural diversity and a variety of interesting applications in material science and catalysis, which stems to a large extent from the high Lewis acidity of the tin atoms.¹ Attempts to incorporate a second heavy element into the structure of organotin oxo clusters are motivated by the possibility to develop more advanced catalysts with multiple active centres. However, so far only a handful of compounds containing Sn–O–M linkages (M = heavy element) are known.² Progress in the field has arguably been delayed by the lack of a generally applicable synthesis strategy. Our recent discovery that solutions of $(t\text{-Bu}_2\text{SnO})_3$ (**1**)³ and $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ (**2**)⁴ readily absorb carbon dioxide from the air to form a unique molecular tellurastannoxane carbonate cluster, $[(p\text{-MeOC}_6\text{H}_4)_2\text{TeOSn}t\text{-Bu}_2\text{CO}_3]_2$ (**3**, Scheme 1),⁵ has prompted us to investigate the reaction between the two rather simple heavy organometallic oxides in greater detail.



Scheme 1 Structure of the tellurastannoxane carbonate cluster **3**.

We have now found that the same reactants in a Sn : Te ratio of 2 : 1 (in the presence of moist air) form a novel molecular tellurastannoxane, $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{OSn}t\text{-Bu}_2\text{OH})_2]_2$ (**4**) (eqn. (1)), with a quite complex molecular structure (Fig. 1).[‡]



The complexity of the structure originates from the concomitant increase of the coordination numbers at tin (from 4 to 5) and tellurium (from 3 to 3 + 2) when compared to the starting materials. As a result the tin and tellurium atoms are involved in hypervalent and (weak) secondary bonding,⁶ whereas these features are absent in the structures of the parent compounds

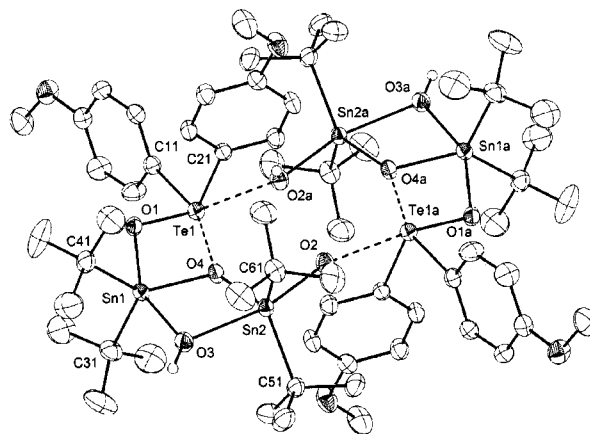


Fig. 1 Molecular structure of **4**. Selected bond parameters (Å,°): Te1–O1 1.898(2), Te1–O2a 2.756(2), Te1–O4 2.595(2), Sn1–O1 2.145(2), Sn1–O3 2.167(2), Sn1–O4 2.007(2), Sn2–O2 2.106(2), Sn2–O3 2.300(2), Sn2–O4 1.996(2); O1–Te1–O2a 172.65(8), O1–Sn1–O3 152.70(8), O1–Sn1–O4 78.92(8), O4–Sn1–O3 74.72(9), O2–Sn2–O3 159.23(9), O2–Sn2–O4 87.32(9), O3–Sn2–O4 71.98(8), Te1–O1–Sn1 113.47(10), Sn1–O3–Sn2 98.01(9), Sn1–O4–Sn2 114.83(10). Symmetry transformation used to generate equivalent atoms: a = 2 – x, –y, 1 – z. Non-hydroxy hydrogens have been omitted for clarity.

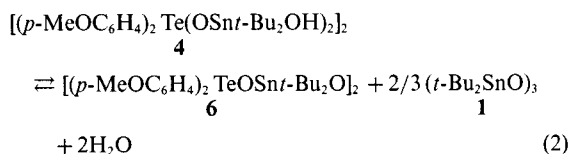
1³ and **2**.⁴ The structure lies across a crystallographic centre of inversion and comprises two almost planar inorganic Sn_2TeO_4 moieties (largest deviation from the ideal plane: 0.280(1) Å), that are part of two fused four-membered ring systems.[§]

The geometry of the two crystallographically independent tin atoms is distorted trigonal bipyramidal with the expected occupancies of two carbon atoms and one oxygen atom in the equatorial positions and two oxygen atoms in the axial positions (geometrical goodness $\Delta\sigma(\theta)$: 89.7 for Sn1 and 76.4 for Sn2). The Sn–O bond lengths of **4**, ranging from 1.996(2) to 2.300(2) Å, are slightly longer than in **1** (Sn–O 1.965(2) Å).³ Consistent with the pentacoordinated geometry, the ¹¹⁹Sn MAS NMR spectrum of **4** shows two signals of equal intensity at δ_{iso} –238.2 and –243.5. The signals were accompanied by sets of spinning sidebands, which are indicative for large shielding anisotropies (SA).⁷ The geometry of the tellurium atom of **4** is best described as distorted octahedral when taking into account all significant carbon and oxygen contacts and the stereochemically active lone pair. The primary Te–O1 bond length of 1.898(2) Å is comparable to the elongated ‘double’ bond lengths (1.871(18) and 1.909(8) Å) in the unsymmetric dimers of Ph_2TeO (**5**)⁸ and shorter than the ‘single’ bond lengths (2.025(2) and 2.100(2) Å) in the rather symmetric polymer $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ (**2**).⁴ Besides the primary Te–O bond there are two secondary Te···O contacts of 2.595(2) and 2.756(2) Å that are shorter than the sum of the van der Waals radii (3.58 Å). Notably, the latter contact is reasonable for the weak association of the two crystallographically related $\text{Sn}_2\text{TeO}_5(\text{OH})_2$ moieties. From comparison of the tellurium geometries of **2**–**5** it can be surmised that the coordination of the oxygen atoms is rather flexible in

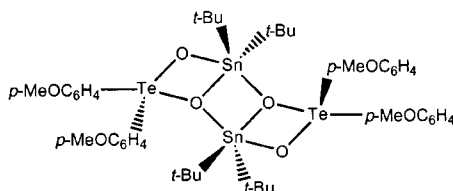
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regard to the number, directionality and length of Te–O bonds. The ^{125}Te MAS NMR spectrum of **4** shows one signal at δ_{iso} 1176 that compares well with those of **3** (1179) and **5** (1103/1133), but differs from that of **2** (903). The difference originates most probably from the presence (**3–5**) and absence (**2**) of secondary Te...O interactions. The signal was also accompanied by a set of spinning sidebands, pointing to a large shielding anisotropy (SA).⁷ The IR spectrum of **4** (KBr pellet) reveals two sharp absorptions at 3650 and 3576 cm^{-1} , that were indicative for the presence of two inequivalent hydroxy groups. The two associated hydrogen atoms, attached to the oxygen atoms O2 and O3, were identified and refined with constrained bond lengths and position (H3 only) in the last refinement cycle of the X-ray structure analysis. The O3–H3 hydroxy group is involved in weak intermolecular hydrogen bonding with the oxygen atom of an adjacent organic substituent (O3...O5 3.536(4) Å).

In solution $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{OSn}t\text{-Bu}_2\text{OH})_2]_2$ (**4**) lacks configurational stability and undergoes a reversible condensation/rearrangement process into $[(p\text{-MeOC}_6\text{H}_4)_2\text{TeOSn}t\text{-Bu}_2\text{O}]_2$, ($t\text{-Bu}_2\text{SnO}$)₃ (**1**) and water, as evidenced by ^{119}Sn and ^{125}Te NMR spectroscopy (eqn. (2)). This process is a result of the kinetic lability of both the Sn–O and the Te–O bonds and is presumably entropy driven.



The ^{119}Sn NMR spectrum (CDCl_3) of an analytical pure sample of **4** shows two signals of equal intensity at δ –82.4 ($^2J(^{119}\text{Sn}\text{--O}\text{--}^{117}\text{Sn})$ 365 Hz) and –237.5 ($^2J(^{119}\text{Sn}\text{--O}\text{--}^{125}\text{Te})$ 102 and $^2J(^{119}\text{Sn}\text{--O}\text{--}^{125}\text{Te})$ 200 Hz) that were unambiguously assigned to ($t\text{-Bu}_2\text{SnO}$)₃ (**1**)³ and $[(p\text{-MeOC}_6\text{H}_4)_2\text{TeOSn}t\text{-Bu}_2\text{O}]_2$ (**6**), respectively. The ^{125}Te NMR spectrum (CDCl_3) of the same sample reveals one signal at δ 1198 ($^2J(^{125}\text{Te}\text{--O}\text{--}^{119/117}\text{Sn})$ 189 and $^2J(^{125}\text{Te}\text{--O}\text{--}^{119/117}\text{Sn})$ 94 Hz). The fact that there is only one ^{125}Te NMR signal, but two different $^2J(^{119}\text{Sn}\text{--O}\text{--}^{125}\text{Te})$ couplings, allows the conclusion that **6** is most probably a dimer. $[(p\text{-MeOC}_6\text{H}_4)_2\text{TeOSn}t\text{-Bu}_2\text{O}]_2$ (**6**) was also formed as the sole product in solution when ($t\text{-Bu}_2\text{SnO}$)₃ (**1**)³ and $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ (**2**)⁴ were reacted in a Sn : Te ratio of 1 : 1. From the ^{119}Sn NMR chemical shift, a pentacoordinate environment can be safely deduced. A proposed structure that is consistent with the NMR data and resembles part of the solid-state structure of **4** (e.g. the ring defined by Te1Sn1O1O4) comprises a ladder-type arrangement featuring a tricyclic Sn₂Te₂O₄ ring system (Scheme 2). Similar ladder-type structures are well documented



Scheme 2 Proposed structure of the ladder-type tellurastannoxane **6**.

for dimeric tetraorganodistannoxanes, $\text{R}_2(\text{X})\text{SnOSn}(\text{Y})\text{R}_2$ (R = alkyl, aryl; X, Y = Hal, OH, OSiMe₃, O₂CR, O₃SR), a common class of organotin compounds.⁹

In summary, the molecular tellurastannoxane $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}(\text{OSn}t\text{-Bu}_2\text{OH})_2]_2$ (**4**), prepared from rather simple organoelement oxides, ($t\text{-Bu}_2\text{SnO}$)₃ (**1**) and $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ (**2**), demonstrates for the first time the utility of hypercoordination and (weak) secondary interactions for the synthesis of binary organoelement oxide clusters featuring heavy elements, such as tin and tellurium, which are otherwise difficult to obtain. Studies are underway to extend the concept to other heavy main group elements.

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Notes and references

‡ *Synthesis*: A solution of **1** (1.50 g, 2.00 mmol) and **2** (1.08 g, 3.00 mmol) in diethyl ether (100 mL) was stirred at 30 °C for 2 h. Hexane (50 mL) was added and the solvent slowly evaporated in the presence of moist air. After 2 d, colourless crystals of **4** were deposited (2.23 g, 85%), mp 275–280 °C (decomp.). Anal. Calc. for C₆₀H₁₀₄O₁₂Sn₄Te₂ (1747.68): C, 41.24; H, 6.00. Found: C, 41.05; H, 5.95%.

§ *Crystal data* for **4**: C₆₀H₁₀₄O₁₂Sn₄Te₂, $M = 1747.68$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.8078(9)$, $b = 22.6307(18)$, $c = 13.7604(11)$ Å, $\beta = 105.4640(10)^\circ$, $U = 3543.9(5)$ Å³, $T = 293$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 2.25$ mm⁻¹, 8067 reflections measured, 7256 unique ($R_{\text{int}} = 0.032$) which were used in all calculations. The final $wR(F^2)$ was 0.076 (all data). CCDC reference number 252236. See <http://www.rsc.org/suppdata/dt/b5/b502677f/> for crystallographic data in CIF or other electronic format.

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- (a) The tensor analyses were performed according to the method of Herzfeld and Berger: J. Herzfeld and X. Chen, in *Encyclopedia of Nuclear Magnetic Resonance*, ed. D. M. Grant and R. K. Harris, John Wiley & Sons, Chichester, 1996, vol. 7, p. 4362; (b) Computer program used: DmFit 2002: D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70; (c) Definitions: δ_{iso} (ppm) = $-\sigma_{\text{iso}} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) = $\sigma_{33} - \sigma_{\text{iso}}$ and $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\text{iso}})$ where σ_{11} , σ_{22} and σ_{33} (ppm) are the principal tensor components of the shielding anisotropy (SA), sorted as follows $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$; (d) Results obtained: ^{119}Sn ($\delta_{\text{iso}} = -238.2$): $\zeta = -385$, $\eta = 0.85$; $\sigma_{11} = 594$, $\sigma_{22} = 267$, $\sigma_{33} = -147$; ($\delta_{\text{iso}} = -243.5$): $\zeta = -364$, $\eta = 0.90$; $\sigma_{11} = 589$, $\sigma_{22} = 262$, $\sigma_{33} = -120$. ^{125}Te ($\delta_{\text{iso}} = 1176$): $\zeta = -463$, $\eta = 0.90$; $\sigma_{11} = -736$, $\sigma_{22} = -1153$, $\sigma_{33} = -1639$.
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