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Cluster Compounds

Carbon Dioxide Fixation by the Cooperative Effect of Organotin and Organotellurium Oxides

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Dedicated to Professor Alwyn G. Davies

The recent interest in carbon dioxide fixation by organometallic species has occurred for two reasons:[1] First, the increasing industrial emission of the "greenhouse gas" CO_2 into the atmosphere has been widely accepted as one of the main causes for global warming and climate changes, and therefore efficient solutions for the recovery of CO_2 are highly sought after. Second, being an inexpensive, nontoxic commodity, CO_2 holds considerable potential as a C_1 feedstock for the preparation of key intermediates required by the chemical industry on a multitonne scale, such as urea and dimethyl carbonate (DMC). In this regard, organometallic complexes play a vital role for the activation of the comparatively inert C–O bonds in CO_2. Whilst a vast variety of transition-metal compounds are able to form complexes with CO_2, main-group organometallic species known to bind CO_2 are rare.[1] Notable exceptions include triorganotin oxides, $(R_3Sn)_2O$, and triorganotin hydroxides, R_3SnOH, which react with gaseous CO_2 to give rise to the formation of polymeric triorganotin carbonates, $(R_3Sn)_2CO_3$ (R = alkyl).[2] Industrially, triorganotin carbonates are used as catalysts for the preparation of organic carbonates from alkyl halides and potassium carbonate.[1c] Di- and triorganotin alkoxides, $R_nSn(OR')_{4-n}$ (R = alkyl, R′ = alkyl, aryl; $n = 2, 3$) react with gaseous or supercritical CO_2 to give di- and triorganotin (alkoxy) carbonates, $R_3Sn(O_2COR')$ and $R_2Sn(OR')(O_2COR')$, some of which produce DMC upon thermolysis.[3]

We have now found that solutions containing of di-*tert*-butyltin oxide, $(t\text{Bu}_2\text{SnO})_3$,[4] and di-*p*-anisyltellurium oxide, $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$,[5] (Sn/Te ratio = 1:1) readily absorb gaseous CO_2 to produce a unique molecular tellurastannoxane,[6] $[\{(p\text{-MeOC}_6\text{H}_4)_2\text{TeOSn}(t\text{Bu}_2)\text{CO}_3\}_2]$ (**1**) as an air-stable crystalline material [Eq. (1)]. The formation of this material is rapid (less than 15 min) at room temperature and almost quantitative when the solution is purged with an excess of CO_2. Smaller amounts of the same material were also formed

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serendipitously, for the first time, when such a $(t\mathrm{Bu_2SnO})_3$/$(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$ solution was exposed for several days to air.

$$\tfrac{2}{3}(t\mathrm{Bu_2SnO})_3 + 2\,(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO} \xrightarrow{2\,\mathrm{CO_2}} [\{(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeOSn}(t\mathrm{Bu_2})\mathrm{CO_3}\}_2]\ (\mathbf{1}) \qquad (1)$$

The molecular structure of **1** (Figure 1),[7] displays an almost planar inorganic $\mathrm{Sn_2Te_2C_2O_8}$ core (largest deviation from the ideal plane: 0.393(2) Å), which lies across a crystallographic center of inversion. The geometry of the tin atom is best described as a distorted trigonal bipyramid, in which two oxygen atoms are situated in the axial positions and two carbon atoms and one oxygen atom occupy the equatorial positions. The distortion seems to originate from the chelating coordination mode of the carbonate.

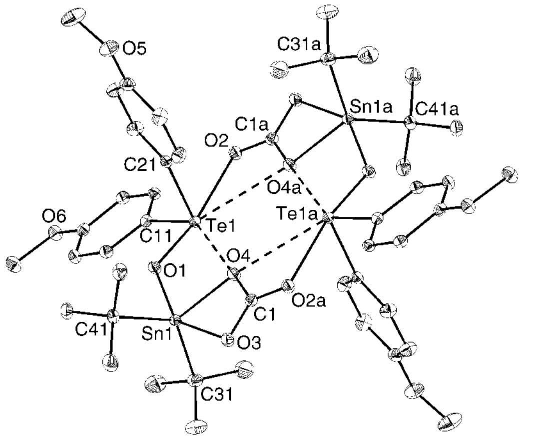

Figure 1. The X-ray crystal structure of **1**, thermal ellipsoids set at 30% probability. Selected interatomic separations [Å] and angles [°]: Te1-O1 1.921(2), Sn1-O3 2.307(2), Te1-O2 2.481(2), Sn1-O4 2.094(2), Te1···O4 3.279(2), Sn1-C31 2.166(3), Te1···O4a 3.059(2), Sn1-C41 2.166(3), Te1-C11 2.112(2), C1-O2a 1.259(3), Te1-C21 2.107(2), C1-O3 1.278(3), Sn1-O1 2.043(2), C1-O4 1.329(3); O1-Te1-O2 170.25(7), O1-Sn1-C31 102.18(9), O1-Te1-O4 59.32(7), O1-Sn1-C41 98.06(9), O1-Te1-O4a 138.14(7), O3-Sn1-O4 59.47(7), O1-Te1-C11 91.16(8), O3-Sn1-C31 97.27(9), O1-Te1-C21 93.11(9), O3-Sn1-C41 92.60(8), O2-Te1-O4 126.00(6), O4-Sn1-C31 113.94(9), O2-Te1-O4a 46.52(6), O4-Sn1-C41 115.82(8), O2-Te1-C11 84.55(8), C31-Sn1-C41 126.96(10), O2-Te1-C21 78.83(8), O2a-C1-O3 124.7(2), O4-Te1-O4a 79.51(5), O2a-C1-O4 120.9(2), O4-Te1-C11 149.18(7), O3-C1-O4 114.4(2), O4-Te1-C21 93.01(8), Te1-O1-Sn1 128.28(9), O4a-Te1-C11 130.67(7), C1-O2a-Te1a 110.26(15), O4a-Te1-C21 81.01(8), C1-O3-Sn1 88.94(14), C11-Te1-C21 97.62(9), C1-O4-Sn1 97.20(14), O1-Sn1-O3 145.36(7), C1-O4-Te1 172.53(16), O1-Sn1-O4 86.35(7), Sn1-O4-Te1a 171.65(9) (Symmetry operation used to generate equivalent atoms: $a = -x, -y, -z$).

Taking into account the stereochemically active lone pair, the geometry of the tellurium atom may be described as a distorted octahedron with two carbon atoms mutually *cis* and two oxygen atoms mutually *trans*, and a deficiency in the primary coordination sphere along the vector defined by the two tellurium atoms (Te1···Te1a 4.875(1) Å). The O-Te-O linkage is rather asymmetric (Te1-O1 1.921(2), Te1-O2 2.481(2) Å) as opposed to the O-Te-O linkage in the polymeric parent compound, $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$ (Te1-O1 2.100(2) Å, Te1-O1a 2.025(2) Å). Differences are also found in the secondary bonding; while $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$ lacks such interactions, two significant intramolecular secondary Te···O bonds are observed for the tellurium atoms of **1**, which involve O4 of the carbonate moiety.[8]

Consistent with the molecular structure established by X-ray crystallography and the pentacoordinate geometry of the tin atoms, the ^{119}Sn magic angle spinning (MAS) NMR spectrum of **1** shows an isotropic chemical shift at $\delta_{\mathrm{iso}} = -262.4$ ppm, which differs from that of $(t\mathrm{Bu_2SnO})_3$ ($\delta_{\mathrm{iso}} = -84.3$ ppm), which has tetracoordinate tin atoms.[9] The ^{125}Te MAS NMR spectrum of **1** reveals an isotropic chemical shift at $\delta_{\mathrm{iso}} = 1179$ ppm similar to that of the dimeric $\mathrm{Ph_2TeO}$ ($\delta_{\mathrm{iso}} = 1103/1133$ ppm), but rather different to that of the polymeric $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$ ($\delta_{\mathrm{iso}} = 903$ ppm), which is apparently a reflection of the asymmetric O-Te-O linkage and the presence of secondary Te···O interactions in **1** and $\mathrm{Ph_2TeO}$, as opposed to the rather symmetric O-Te-O linkage and the absence of secondary interactions in $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$.[5] At a MAS frequency of 9 kHz, both the ^{119}Sn and the ^{125}Te isotropic chemical shifts were accompanied by a set of spinning sidebands that were indicative for large shielding anisotropies (SA) and utilized for tensor analyses.[10]

For solutions of **1** in $\mathrm{CDCl_3}$, the ^{119}Sn and ^{125}Te NMR spectra show signals at $\delta = -258.3$ and 1194.3 ppm, respectively, which suggest, by comparison with the respective solid-state NMR chemical shifts, that the molecular structure is retained in solution. Both signals show two identical pairs of satellites giving rise to two $^2J(^{119}\mathrm{Sn}\text{-O-}^{125}\mathrm{Te})$ couplings of 113 and 66 Hz, which unambiguously supports the idea that the secondary Te···O interactions also exist in solution.[8] Independent evidence for the configurational stability of **1** in solution stems from osmometric molecular-weight determination in $\mathrm{CHCl_3}$ at 40 °C (1282 Da found, 1301 Da calculated). The presence of the carbonate moiety is evident from the ^{13}C NMR spectra which show a signal at $\delta = 165.4$ ppm (in $\mathrm{CDCl_3}$) and $\delta_{\mathrm{iso}} = 165.6$ ppm (in the solid state), which increases significantly in intensity when using ^{13}C-labeled carbon dioxide for the preparation.

Solutions of $(t\mathrm{Bu_2SnO})_3$ and $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$ were treated separately with gaseous $\mathrm{CO_2}$. While the $(p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeO}$ was recovered unchanged, solutions of $(t\mathrm{Bu_2SnO})_3$ also absorb $\mathrm{CO_2}$ to produce $t\mathrm{Bu_2SnCO_3}$ (**2**), albeit at a slower rate than in the formation of **1**. Owing to the virtual insolubility in all common organic solvents, we tentatively assign **2** a polymeric structure, thus acknowledging the fact that all known triorganotin carbonates, $(\mathrm{R_3Sn})_2\mathrm{CO_3}$ (R = alkyl) are also polymeric.[2] This assignment is supported by ^{119}Sn MAS NMR spectroscopy of **2**, which shows an isotropic chemical shift at $\delta_{\mathrm{iso}} = -285.5$.[10]

Applications of organometallic species for the fixation and recovery of $\mathrm{CO_2}$ require the reversibility of the absorption process, preferably at a low temperature to save energy costs.[1] A thermographic analysis of **1** indicates mass loss between 90–145 °C (7.0 % found, 6.8 % calculated) associated with the liberation of $\mathrm{CO_2}$. It is well known that inorganic bases, such as aqueous KOH also absorb $\mathrm{CO_2}$ from air, however these absorption processes are generally irreversible (e.g. $\mathrm{K_2CO_3}$ is stable up to more than 900 °C).[11] A bulk sample of **1** (300 mg) was heated at 145 °C for 60 min and the released CO_2 was determined gravimetrically as $BaCO_3$ (recovery 80 %). The residual material was free of carbonate by indication of ^{13}C NMR spectroscopy and the related ^{119}Sn and ^{125}Te MAS NMR spectra exhibit signals at $\delta_{iso} = -228.3$ and 834 ppm, respectively, which are significantly different from those of **1** and the starting materials. The residual material was completely soluble in $CDCl_3$ and was used for the reabsorption of CO_2, after which the ^{119}Sn and ^{125}Te NMR spectra of the crude product indicated the renewed quantitative formation of **1**.

In summary, we have demonstrated that solutions of $(t\mathrm{Bu}_2\mathrm{SnO})_3$ and $(p\text{-}\mathrm{MeOC}_6\mathrm{H}_4)_2\mathrm{TeO}$ (Sn/Te ratio = 1:1) rapidly absorb CO_2 to form an air-stable molecular tellurastannoxane $[\{(p\text{-}\mathrm{MeOC}_6\mathrm{H}_4)_2\mathrm{TeOSn}(t\mathrm{Bu}_2)\mathrm{CO}_3\}_2]$ (**1**) showing significant intramolecular Te···O interactions in both solution and the solid state. In contrast, the absorption of CO_2 by $(t\mathrm{Bu}_2\mathrm{SnO})_3$ or triorganotin oxo species[2] provides only polymeric organotin carbonates. The desorption of CO_2 occurs at rather low temperatures, which suggests applications of **1** for instance as phase-transfer catalyst[12] or as precursor for the preparation of organic carbonates.[3]

Experimental Section

1: A magnetically stirred solution of $(t\mathrm{Bu}_2\mathrm{SnO})_3$ (995 mg, 1.33 mmol)[4] and $(p\text{-}\mathrm{MeOC}_6\mathrm{H}_4)_2\mathrm{TeO}$ (1.43 g, 4.00 mmol)[5] in $CHCl_3$ (30 mL), was slowly purged with CO_2 for 15 min at room temperature. The solvent was removed in vacuo and the solid residue recrystallized from CH_2Cl_2/hexane to give colorless crystals. These crystals were dried in vacuum at 50 °C for 1 h to remove cocrystallized CH_2Cl_2. Single crystals suitable for X-ray diffraction were grown from a $CHCl_3$ solution, yield: 2.58 g, 1.98 mmol, 99 %. M.p. 198 °C (decomp.) (crystals turn opaque at 120 °C). Elemental analysis (%) calcd for $C_{23}H_{32}O_6SnTe$ (1301.74): C 42.44, H 4.96; found: C 42.39, H 5.03. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.02$ (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H}) = 9$ Hz, 8 H), 6.92 (d, $^3J(^1\mathrm{H}\text{-}^1\mathrm{H}) = 9$ Hz, 8 H), 3.81 (s, 12 H), 1.18 ppm (s, $^3J(^1\mathrm{H}\text{-}^{119}\mathrm{Sn}) = 109$ Hz, 36 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.4$ (CO_3), 161.5 (*p*-C), 133.6 (*o*- or *m*-C), 129.5 ($^1J(^{13}\mathrm{C}\text{-}^{125}\mathrm{Te}) = 323$ Hz; *i*-C), 114.7 (*o*- or *m*-C), 55.3 (OCH_3), 39.4 ($^1J(^{13}\mathrm{C}\text{-}^{119}\mathrm{Sn}) = 562$ Hz; $\mathit{C}CH_3$), 29.3 ppm ($C\mathit{C}H_3$).

2: A solution of $(t\text{-}\mathrm{Bu}_2\mathrm{SnO})_3$ (249 mg, 0.33 mmol)[4] in $CHCl_3$ (20 mL), was slowly purged with CO_2 for 30 min at room temperature. The colorless amorphous precipitate formed was collected by filtration and air dried. Yield: 228 mg, 0.78 mmol, 78 %. M.p. 250 °C (decomp.) Elemental analysis (%) calcd for $C_9H_{18}O_3Sn$ (292.97): C 36.90, H 6.19; found: C 36.91, H 6.20.

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