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Communications

Synthesis and Characterization of $[Tl_2Sn(OEt)_6]_n$, a One-Dimensional Polymer in the Solid State

The mild thermal and photochemical decompositions of molecular species are emerging as viable routes for the formation of ceramic materials, alloys, and metals. Materials prepared as thin films by chemical vapor deposition from molecular precursors include CoSi,[1] Mn_2Si,[2] ZrB_2,[3] HgTe,[4] HgCdTe,[5] TiS,[6] TiC,[7] Al,[8] Sn[9], Pt,[10] and Au.[11] Other ceramic materials prepared from molecular precursors include a large variety of metal oxides via sol-gel routes,[12] SiC,[13] Si_3N_4,[14] GaAs,[15] and BN,[16] as powders, fibers, components of composites, or monolithic materials. However, many of these materials can be obtained by traditional methods, and much less attention has been directed toward the preparation of new binary ceramic materials by such routes. We are currently exploring ways to prepare new metastable tin oxide phases $Sn^{II}{}_xSn^{IV}{}_yO_{x+2y}$[17] at low temperatures from mixed-valence tin alkoxide precursors, $Sn^{II}{}_xSn^{IV}{}_yOR_{2x+4y}$. A number of studies have indicated that pure tin(IV) oxide can be prepared from

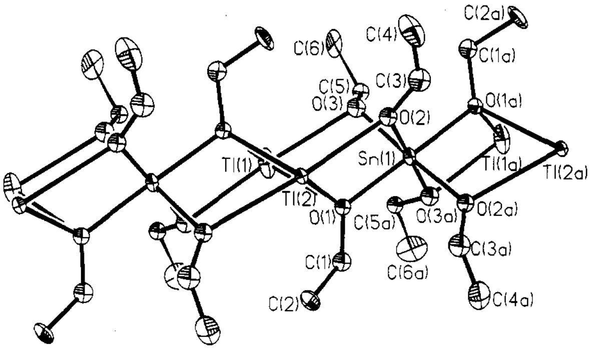

Figure 1. Thermal ellipsoid plot of the structure of $[Tl_2Sn(OEt)_6]_n$. Relevant distances (Å): Sn-O(1) = 2.11 (2), Sn-O(2) = 2.203 (3), Sn-O(3) = 2.05 (4), Tl(1)-O(1) = 2.70 (3), Tl(1)-O(3) = 2.71 (3), Tl(2)-O(1) = 2.60 (3), Tl(2)-O(2) = 2.66 (4). Relevant angles (deg): Sn-O(2)-Tl(2) = 107.4 (2), Sn-O(1)-Tl(2) = 106.3, Sn-O(3)-Tl(1) = 105.0 (2), O(1)-Tl(2)-O(2) = 62.9 (9), O(1)-Tl(1)-O(3) = 64 (1), O(2)-Tl(2)-O(2a) = 157 (1), O(3)-Tl(1)-O(3a) = 154 (1). Angles around Sn vary between 83 and 96°.

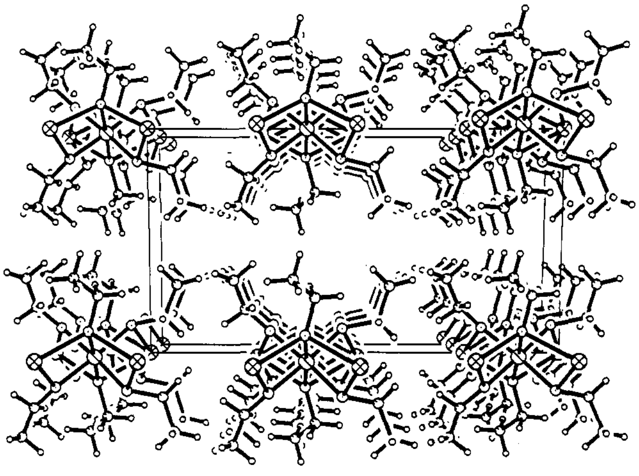

Figure 2. A view, looking down the *c* axis of III, showing the columnar nature of the polymer and the spatial orientation of the adjacent stacks.

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tin(IV) alkoxide precursors.[18] In order to incorporate both oxidation states of tin into a single species, we are preparing tin(IV) alkoxide salts for subsequent metathesis reactions with tin(II) halides. Tin(II) alkoxide salts are relatively well-known,[19] whereas tin(IV) alkoxide salts are much less common.[20] During this study, we have isolated and structurally characterized the first example of a homoleptic alkoxide salt of tin(IV), $[Tl_2Sn(OEt)_6]_n$, that exists as a one-dimensional polymer in the solid state.

The addition of 2 equiv of thallium(I) ethoxide to tin(IV) ethoxide, prepared by ethanolysis of tin(IV) *tert*-butoxide in toluene solution at room temperature, results in a homogeneous exothermic reaction with formation of $[Tl_2Sn(OEt)_6]_n$ according to eq 1. Addition of less than 2 equiv of TlOEt to II results in

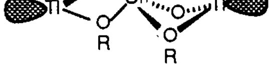
$$\underset{\text{I}}{Sn(O\text{-}t\text{-}Bu)_4} \xrightarrow{\text{excess EtOH}} \underset{\text{II}}{(1/n)[Sn(OEt)_4]_n} \xrightarrow{\text{2TlOEt}} \underset{\text{III}}{[Tl_2Sn(OEt)_6]_n} \quad (1)$$

the formation of a mixture of II and III; no evidence for the formation of $TlSn(OEt)_5$ has been observed. III was obtained in quantitative yield, gave satisfactory combustion analysis[21] and mass spectroscopic[22] data, and was crystallized from toluene at −30 °C to give long, transparent needles. The relatively high solubility of III in nonpolar solvents was unexpected and is consistent with a covalent structure. III exhibits one type of ethoxide ligand in the ^1H NMR spectrum[23] that is temperature invariant when cooled to −90 °C. The methylenic proton resonance exhibits coupling to ^{119}Sn ($I = {}^1/_2$; 8.58% nat abun) and ^{117}Sn ($I = {}^1/_2$; 7.61% nat abun) typical for $^3J_{H-Sn}$. III exhibits a single resonance at −596.2 ppm in the proton-decoupled ^{119}Sn NMR spectrum.[24] The NMR data are therefore consistent with the presence of an octahedral tin moiety in which all six ethoxide ligands are equivalent (i.e., $[Sn(OEt)_6]^{2-}$). However, the presence of solvent-separated ion pairs is clearly inconsistent with the solubility data.

To gain further insight, a single-crystal X-ray diffraction study of III was performed.[25] This study revealed that $[Tl_2Sn(OEt)_6]$ exists as a one-dimensional polymer in the solid state containing tin(IV) atoms octahedrally coordinated by ethoxide ligands and distorted-trigonal-bipyramidal thallium(I) atoms with the lone pair occupying the vacant equatorial coordination site (see Figures 1 and 2). There are two types of ethoxide ligands: one containing a triply bridging oxygen atom (bridging one tin and two thallium atoms) and one containing a doubly bridging oxygen atom (bridging one tin and one thallium atom). The structural architecture of III is analogous to that adopted by the dimers $[MSn(O\text{-}t\text{-}Bu)_2]_2$ (M = Li, Na), in which the two types of alkoxide ligands are doubly and triply bridging.[19] The Sn–O and Tl–O distances in III are in the range expected on the basis of the available structural data for these compounds.

The solid-state structural data appear inconsistent with the spectroscopic data obtained in solution. Indeed, a cryoscopic molecular weight determination revealed that III is *monomeric* in benzene solution.[26] It is interesting to consider possible solution structures for III. The observation of a single type of ethoxide ligand by NMR spectroscopy could be explained by a solution dynamic process. However, the existence of a fluxional process involving rapid ethoxide ligand exchange in benzene and toluene solutions is unlikely for the following reasons. (i) When thallium(I) ethoxide is added to a benzene solution of III, new ethoxide resonances appear at chemical shifts identical with those of pure TlOEt in benzene. (ii) When ethanol is added to a benzene solution of III, new ethoxide resonances appear at chemical shifts identical with those of pure ethanol in benzene. (iii) The ^1H NMR resonances of III are temperature invariant when toluene solutions are cooled to −90 °C.[27] The possibility that $[Tl_2Sn(OEt)_6]$ exists in rapid equilibrium with $[TlOEt]_n$ and $[Sn(OEt)_4]_n$ in solution on the NMR time scale can therefore be eliminated. The observation that no exchange occurs upon addition of ethanol provides evidence that the metal atoms present are coordinatively saturated.[28]

To obtain more information concerning the solution structure of III, solid-state and solution IR data were recorded and compared to data for homoleptic tin alkoxides with known structures. $Sn(O\text{-}t\text{-}Bu)_4$ has recently been structurally characterized[29] and is a flattened tetrahedral monomer in the solid state that exhibits a terminal Sn–O stretch at 602 cm^{-1}. $[Sn(O\text{-}t\text{-}Bu)_2]_2$ exists as an alkoxide-bridged dimer[30] and exhibits two bands in the IR spectrum attributable to Sn–O stretches at 580 and 550 cm^{-1} in the solid state. $[Tl_2Sn(OEt)_6]_n$ in the solid state exhibits a single, broad stretch at 528 cm^{-1} that, in toluene solution, moves to 541 cm^{-1}. These data are consistent with the presence of bridging alkoxide ligands only in solutions of III. Although the solution structure of $[Tl_2Sn(OEt)_6]$ cannot be unequivocally established at this stage, the data available are consistent with a covalent structure such as that shown below, which is analogous to the solid-state structure of $TlSn(O\text{-}t\text{-}Bu)_3$.[31]



$[Tl_2Sn(OEt)_6]$ reacts with tin(II) chloride in tetrahydrofuran solution, according to eq 2, to give $[Sn_2(OEt)_6]$. IV is isolated as an involatile, oligomeric oil from this reaction, gives satisfactory

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(21) Anal. Calcd for $C_{12}H_{30}O_6SnTl_2$: C, 18.05; H, 3.76. Found: C, 18.40; H, 3.68.

(22) Mass spectra were measured in the positive ion mode by electron impact. Only a very weak (<1%) molecular ion mass was observed (m/e = 797), but a fragment at m/e = 713 (~75% of the base mass at m/e = 205; ^{205}Tl) corresponding to $Tl_2Sn(OEt)_5$ exhibited the expected isotope distribution pattern.

(23) $[Tl_2Sn(OEt)_6]$ ^1H NMR data (benzene-d_6, 19 °C, 360 MHz): OCH_2CH_3, 1.47 ppm, t, 3 H, J_{H-H} = 6.9 Hz; OCH_2CH_3, 4.45 ppm, q, 2 H, $J_{H-^{117}Sn}$ = 35.6 Hz, $J_{H-^{119}Sn}$ = 36.8 Hz (total observed intensity of tin satellites = 17.7%; calculated = 16.2%).

(24) ^{119}Sn NMR spectra were recorded at 93.28 MHz. The chemical shift of III is quoted relative to that of $SnMe_4$ (downfield = positive sign convention): no coupling to ^{205}Tl was observed.

(25) Long colorless needles were grown from toluene at −30 °C. The crystal used for the X-ray study was 0.23 × 0.46 × 0.80 mm and was sealed in a glass capillary. Crystal data: empirical formula $C_{12}H_{30}O_6SnTl_2$, monoclinic space group $C2$, a = 6.487 (3) Å, b = 16.831 (9) Å, c = 9.293 (5) Å, β = 101.88 (4)°, Z = 2. A total of 1757 independent reflections were measured in the range $2 \lesssim 2\theta < 50°$ ($h,k,\pm l, -h,-k,\pm l$) on a Nicolet R3m/V diffractometer (293 K) using graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, with $\pm$–2θ scan mode, $2\theta_{max}$ = 50°. The crystal quality deteriorated during data collection as shown by the 25% drop in standard intensities. An empirical correction for severe absorption effects had to be applied. The agreement factors on azimuthal scans before and after this correction were 36.6% and 6.3%, the corresponding transmission range was 0.917–0.128. The structure was solved by direct methods using SHELXTL PLUS and was refined by using full-matrix least-squares techniques. Hydrogen atoms were omitted from the refinement. The final agreement factors were R = 0.084 and R_W = 0.091 for 1217 reflections having $F > 3.0\sigma(F)$.

(26) The molecular weight of III was determined by the freezing-point depression of benzene. Measurements were made at two different concentrations: 0.20 and 0.41 M solutions gave molecular weights of 780 and 860, respectively (calcd for $Tl_2Sn(OEt)_6$ = 808). Each value is the average of three measurements. Attempts to measure the molecular weight at higher concentration were hampered by precipitation of III before the benzene froze.

(27) If $[Tl_2Sn(OEt)_6]$ undergoes a fluxional process that is rapid at 90 °C, then, assuming coalescence of two types of alkoxide ligands at −110 °C, with frequency separation up to 360 Hz (1 ppm), an activation barrier, ΔG^*, of 7–8 kcal/mol can be calculated. We feel that such a process is unlikely.

(28) Coordinatively unsaturated metal alkoxide compounds often undergo rapid exchange with added alcohol; see, e.g., Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 574.

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$$\underset{\text{III}}{Tl_2Sn(OEt)_6} + SnCl_2 \rightarrow \underset{\text{IV}}{Sn_2(OEt_6)} + 2TlCl \qquad (2)$$

combustion analysis, and exhibits physical properties similar to $[Sn(OEt)_4]_4$, as expected.

Further studies are in progres to aid the structural assignment in solution and characterization of the hydrolysis products of III and IV. Knowledge of the solution structure of such species is essential to determine the fundamental steps involved in the pyrolytic and hydrolytic conversion of tin alkoxides to tin oxides (via oxotin alkoxides), especially since tin species containing oxygen ligands exhibit a vast structural chemistry.[32]

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Supplementary Material Available: Table 1 (atomic coordinates and thermal parameters), Tables 2 and 3 (bond lengths and angles), and tables 4 and 5 (anisotropic displacement coefficients and H atom coordinates (5 pages); Table 6 (observed and calculated structure factors) (7 pages). Ordering information is given on any current masthead page.

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(32) Oxo-tin compounds have recently been reported in the form of cubes, double cubes, drums, and oxygen-capped clusters. For a recent review, see: Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Schmid, C. G.; Swamy, K. C. K.; Holmes, J. M. In *Inorganic and Organometallic Polymers*; Zeldin, M., WynnE, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. Swamy, K. C. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 7543.

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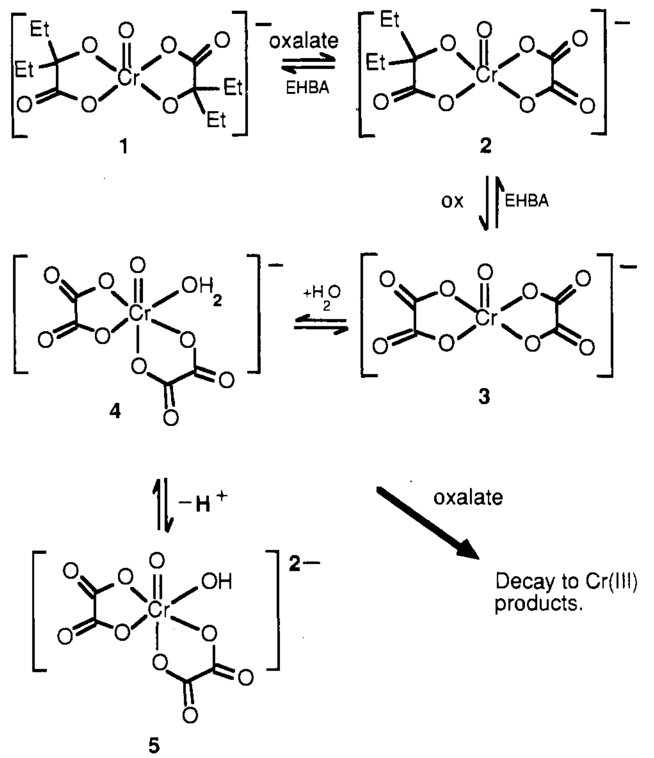
Ligand Exchange and Reduction Reactions of Oxochromate(V) Complexes: Characterization of the Common Chromium(V) Intermediates in the Reductions of Chromium(VI) and of *trans*-Bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V) by Oxalic Acid

Chromium(V) intermediates play an important role in the mechanisms of Cr(VI) oxidations commonly used in organic chemistry[1-5] and are implicated as the active carcinogens in Cr(VI)-induced cancers.[6-8] However, Cr(V) chemistry is poorly characterized, and only a few Cr(V) complexes have been isolated (e.g. *trans*-bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V), **1**).[1,2,9] Despite detailed studies on the mechanisms of Cr(VI) oxidations of organic substrates, we report here that even the mechanism which has been studied in most detail (the oxidation of oxalic acid)[2,4,5] is incorrect. This arose because the structures of the Cr(V) intermediates were wrongly assigned as monooxalato complexes, on the basis of EPR and kinetic analyses.[5] The more detailed studies we report here have enabled the structures of these complexes to be reassigned as bis(oxalato(2−))oxochromate(V) (**3**) and *cis*-aquabis(oxalato(2−))oxochromate(V) (**4**). A crucial part of the determination of these structures is that these intermediates are also common to the reduction of **1** by oxalic acid. This also establishes, for the first time, the importance of a ligand exchange preequilibrium (Scheme I) as the first step in the oxidation of organic substrates by **1**. While this had previously been suggested on the basis of kinetic data,[2] such ligand exchange chemistry in these reactions has not been characterized previously. The combination of electrochemical and EPR spectroscopic techniques that are used in this study is likely to enable the characterizations of the intermediates in many other oxidation reactions of high-valent chromium and thus aid in the elucidation of the mechanisms of these complex redox reactions. In addition, these results indicate that common Cr(V) intermediates are responsible for the mutagenicity of either Cr compound toward *Salmonella typhimurium* TA100, and are important in delineating the mechanism(s) of the rapid in vitro cleavage of DNA by Cr(V).[6]

Scheme I



Our EPR spectroscopic studies on the oxidation of oxalic acid by CrO_3[10] confirm that two Cr(V) complexes (g = 1.9766 (2), A_{iso} = 18.1$_5$ ± 0.2 G; g = 1.9714 (2), A_{iso} = 21.9 (2) G) form and decay with the same rate constants. The g values reported here are more accurate than those in the literature,[5] and the isotropic hyperfine parameters have not been reported previously. Under the same conditions, the reaction of **1** with oxalic acid results in two signals identical with those reported above,[11] but a third Cr(V) signal assigned to (2-ethyl-2-hydroxybutanoato-(2−))(oxalato(2−))oxochromate(V) (**2**, g = 1.9783 (2), Figure 1) is observed at a g value similar to that of **1** (g = 1.9785 (2) in the absence of oxalic acid). At concentrations of oxalic acid ≥100 mM, the ratio of this third signal to the other two signals is dependent linearly on the concentration ratio oxalic acid:EHBA released,[12] showing that the equilibrium involves the exchange of only one EHBA ligand for an oxalate ligand.[13] All three

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(10) Experimental conditions: 50% aqueous acetic acid; 25 °C.

(11) The apparent difference in the ratio of the two peaks of **3** and **4** in the two reactions arises from the overlap of the signals due to **2** and **3**.

(12) EHBA = 2-ethyl-2-hydroxybutanoate(2−).