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Thermal studies of new precursors to indium–tin oxides for use as sensor materials in the detection of NO_x

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Abstract

Control of combustion product emissions in both sub- and super-sonic jet engines can be facilitated by measurement of NO_x levels with metal oxide sensors. In_2O_3, metal-doped SnO_2, and SnO_2 (as well as other materials) show resistivity changes in the presence of NO_x but often their sensitivity, stability, and selectivity are low. This study was designed to develop new synthetic pathways to precursors that produce high purity, two phase In_2O_3–SnO_2. The precursors were formed by complexation of tin(IV) with chelating aryloxide ligands to give the ammonium salt, $(NH_4)_2[Sn(ligand)_3]\cdot xH_2O$ or the neutral molecule, $[Sn(ligand)_2]\cdot xH_2O$, followed by reaction with In(III) to form the monomolecular precursors. Thermal studies of these precursors were carried out by thermal gravimetry (TG) and differential scanning calorimetry (DSC). Further studies by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) were also conducted.

Keywords: Sensors; NO_x; Indium–tin oxide; 2,3-dihydroxynaphthalene; Tiron™; Caffeic acid

1. Introduction

Control of combustion product emissions in both sub- and super-sonic jet engines can be facilitated by measurement of NO_x levels with metal oxide sensors [1–3] Previous studies [4] have found that In_2O_3, metal-doped SnO_2, and SnO_2 (as well as other materials) show resistivity changes in the presence of NO_x but often these materials were not evaluated for selectivity. The few tests conducted, showed that the materials exhibited low selectivity for NO_x in the presence of CO and hydrocarbons [5]. Further, the materials were tested at temperatures below those common in jet engine exhaust streams [6].

Indium tin oxides are suitable candidates for NO_x, sensors because both In_2O_3 and SnO_2 have melting points above 1500°C and are thus stable in the engine exhaust environment (up to 1200°C) [7]. Further, indium oxide–tin oxide is a two-phase material with known sensor capabilities in the detection of NO_x, CO, and hydrocarbons [1–7]. The present study was designed to pursue two goals: develop new synthetic pathways to precursors of In_2O_3–SnO_2, the work presented here, and develop pathways to metal-doped indium–tin oxide materials for sensors that preferentially detect NO_x in the presence of CO and hydrocarbons. Sensor materials must exhibit high purity and function at elevated temperatures while retaining

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microstructural integrity. In addition to the development of new synthetic pathways, thermal analysis of our precursors showed that variations in the formation temperature of the metal oxides (tin oxide, indium oxide, indium–tin oxide) are due in large part to the volatility of the specific oxyligand during the heating process and additionally, to the number of intermediates formed during ligand decomposition.

Our novel synthetic pathways give monomolecular precursors that assemble the atoms necessary for the formation of indium–tin oxide and, unlike available In_2O_3–SnO_2, contaminants such as organic species or metals present in the starting material are eliminated during synthesis of the precursors. Pathways 1 and 2 (Fig. 1) illustrate the formation of coordination complex precursors that precipitate from aqueous solution leaving behind resistivity-altering contaminants. Pathway 1 illustrates complexation of tin(IV) with chelating aryloxide ligands that form the ammonium salt, $(NH_4)_2[Sn(ligand)_3]\cdot xH_2O$. The neutral molecule, $[Sn(ligand)_2]\cdot xH_2O$, is the initial product in pathway 2. These precursors are unique powders generated from anions like, but not limited to, $[M^{m}(ligand)_n]^{m-2n}\cdot xH_2O$.

Transition and main group metals in high oxidation states ($M = Sn^{4+}$, In^{3+}, Mn^{4+}, etc.) complex with aryloxide, chelating ligands that are weak acids [5]. This complexation occurs in part because the chelating, deprotonated ligands become strong organic bases. For instance, 2,3-dihydroxynaphthalene ($pK_1 = 8.6$, $pK_2 = 12.5$) [8] complexes with tin(IV) from depolymerized SnO_2 in the presence of ammonium hydroxide (pathway 1) to form the ammonium salt of tris(2,3-dihydroxynaphthalato) tin(IV).

Similarly, the neutral molecule, bis(2,3-dihydroxynaphthalato) tin(IV), is formed with tin acetate (pathway 2):

$$\begin{aligned}&Sn(CH_3COO)_4 + 2C_{10}H_8O_2 + 4NH_4OH\\&\quad\rightarrow [Sn(C_{10}H_6O_2)_2]\cdot H_2O + 3H_2O\\&\quad + 4NH_4^{+}CH_3COO^{-}\end{aligned} \tag{1}$$

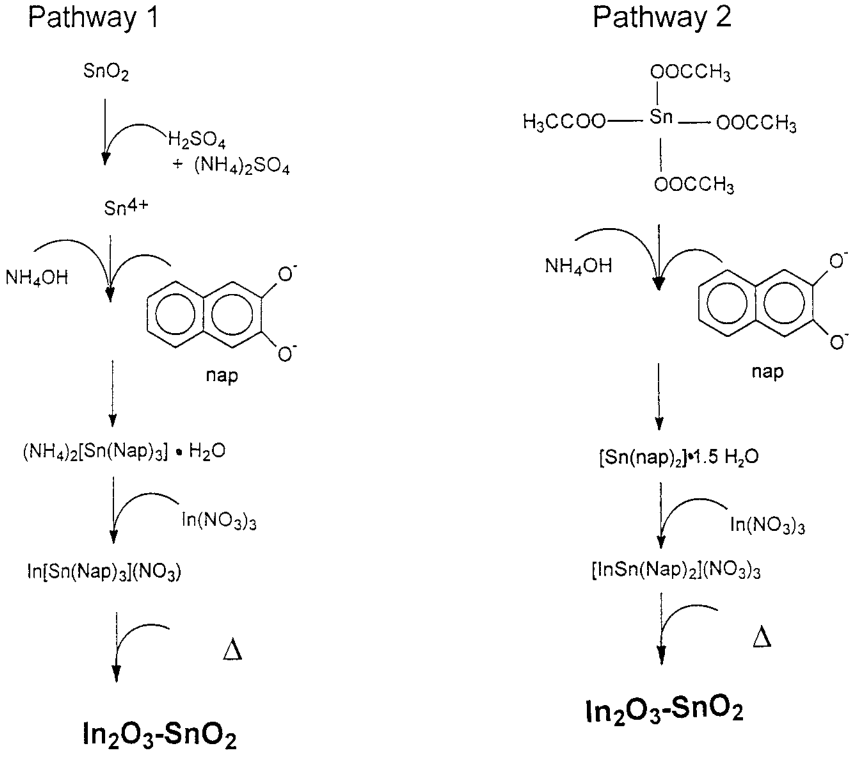

Fig. 1. Synthesis of indium–tin oxide by monomolecular precursor pathways 1 (formation of the ammonium salt) and 2 (formation of the neutral molecule).

Both tin-containing complexes are reacted with In(III) from nitrate to produce indium–tin monomolecular precursors that calcine in air to the two-phase material, In_2O_3–SnO_2 (monitored by X-ray powder diffraction). Three aryloxyligands were utilized in these reactions (2,3-dihydroxynaphthalene, Tiron^{TM}, and caffeic acid) to give multiple initial precursors so that studies of decomposition temperature, smooth transition to the oxide and full conversion to the oxide could be made. This paper presents the completed synthesis and characterization of the coordination compound precursors and their oxide residues. In subsequent studies the powders will be pressed into pellets and sintered at high temperatures to yield a well-compacted material to which resistivity-measuring electrodes are attached. Changes in resistivity will be measured during exposure to environments containing NO_x species.

2. Experimental

2.1. Preparation of the complexes

SnO_2 was depolymerized by placing 1.002 g of SnO_2 (6.64×10^{-3} mole, Aldrich) into a 100 ml round-bottom flask with 16.01 g (1.2×10^{-1} mole) of $(NH_4)_2SO_4$ (Mallinckrodt) and 41 ml of concentrated H_2SO_4 (Mallinckrodt). A reflux condenser was added to the flask although no cooling water was run through the condenser. The apparatus was placed in a sand bath and heated in a hood over a burner until a clear, colorless solution resulted and no undissolved material remained. Depolymerization was complete in 6–12 h. On cooling the solution volume was measured and three portions of deionized water were added before the Sn(IV) solution was reacted with the deprotonated aryloxy ligand solution.

The ammonium salts [9] of the depolymerized tin source, $(NH_4)_2[Sn(nap)_3]\cdot H_2O$, $(NH_4)_2[Sn(tironato)_3]\cdot 2H_2O$, and $(NH_4)_2[Sn(caffeiato)_3]\cdot 4H_2O$, were prepared in a similar manner by dissolving three equivalents of the aryloxyligand (2,3-dihydroxynaphthalene, Aldrich; Tiron^{TM}, Aldrich; caffeic acid, Aldrich) in 50–100 ml of concentrated ammonium hydroxide (Aldrich, reagent grade) and slowly adding the Sn(IV) species prepared from depolymerized SnO_2. The solution was stirred for two hours and the precipitated product was vacuum filtered, washed with 2 ml portions of water and diethyl ether, and vacuum dried.

$[Sn(nap)_2]\cdot 1.5H_2O$ is prepared [10] by adding 0.71 g of tin(IV)acetate (2.00×10^{-3} mole, Alfa) as the powder to a solution of three equivalents of 2,3-dihydroxynaphthalene in 100 ml of NH_4OH. The solution is stirred overnight and gold-colored crystals are isolated the following day by gravity filtration.

To prepare [10] $In[Sn(nap)_2](NO_3)_3$ a slurry of two grams of $[Sn(nap)_2]\cdot 1.5H_2O$ (4.29×10^{-3} mole) in 100 ml of deionized water is added to one equivalent of indium(III) nitrate (1.68 g, 4.29×10^{-3} mole, Aldrich). The tan product is gravity filtered and washed several times with 2 ml portions of water after which it is air dried.

In_2O_3–SnO_2 was prepared from $In[Sn(lig)_3]NO_3$ (lig = nap, tironato, caffeiato) calcined for five hours at 900°C in an ambient air atmosphere or from $In[Sn(nap)_2](NO_3)_3$ calcined for five hours at 900°C. Formation of the indium–tin oxide was confirmed in each instance by an X-ray powder pattern analysis from the bulk sample.

2.2. Instrumentation

FTIR spectra were obtained from a Perkin-Elmer 1760X FTIR with a Harrick split pea, horizontal, attenuated total reflectance accessory utilizing a single bounce, silicon crystal.

NMR ^1H spectra were obtained from a Bruker AM-300, 300 MHz NMR spectrometer controlled by a TECMAG data system running MACNMR 5.4 software with DMSO-d_6 as the sample solvent. Spectra were gathered at room temperature with TMS as the internal standard.

TG/DSC analyses were obtained with a: (a) Netzsch simultaneous thermal analyzer STA 409C employing alumina powder as reference, in a temperature range from 20°C to 800°C with an increase in temperature of 10 K/min in an air atmosphere (or nitrogen atmosphere as noted) flowing at 140 cc/min in an Al_2O_3 pan with lid; samples ranged in size from 14.8 to 30.2 mg; (b) Dupont (TA Instruments) thermogravimetric analyzer (1090 controller) in a temperature range from 20°C to 800°C with an increase in temperature of 10 K/min in a flowing air atmosphere (or nitrogen atmosphere as noted) in a platinum pan with samples that ranged in size from 5.0 to 20.0 mg; (c) Perkin-Elmer 7 Series Thermogravimetric Analyzer in a temperature range from 50°C to 550°C with a temperature ramp of 40 K/min in an air atmosphere in a platinum pan with samples that ranged in size from 12.0 to 20.0 mg.

X-ray powder diffraction patterns were collected on a Philips X'pert Multi-Purpose Powder Diffraction system employing Cu K_α radiation. Powder patterns were compared with the database of the International Centre for Diffraction Data for purposes of identification. Powder patterns that could not be identified in this manner were considered to represent complexes for which powder patterns have not been catalogued.

3. Results and discussion

3.1. Thermal gravimetry

$(NH_4)_2[Sn(nap)_3]\cdot H_2O$ calcines to SnO_2 (confirmed by X-ray powder diffraction) in an air atmosphere (Fig. 2). The molecule is typical of coordination compounds that form an inorganic metal oxide on heating. Between 120°C and 250°C dehydration and loss of ammonium cations occur. Between 278°C to 344°C, the first decomposition and pyrolysis of the 2,3-dihydroxynaphthalene ligands occur. This initial loss of ligands is followed by two additional regions of decomposition: in the temperature range 345–418°C and 418–498°C. At 500°C oxygen present in the 2,3-dihydroxynaphthalene ligands and additional oxygen from the air environment react with the tin(IV) cations to form tin oxides (Sn_xO_y). Above 500°C further reorganization of the inorganic material occurs to form the final product, SnO_2. Heating to temperatures above 800°C results in no additional mass change. Formation of the SnO_2 oxide was confirmed by X-ray powder diffraction analysis of tin precursor residue and comparison with the X-ray powder pattern of SnO_2.

Calcination of the molecular precursors results in the formation of tin oxides by abstraction of oxygen atoms from the oxyligands supplemented with oxygen

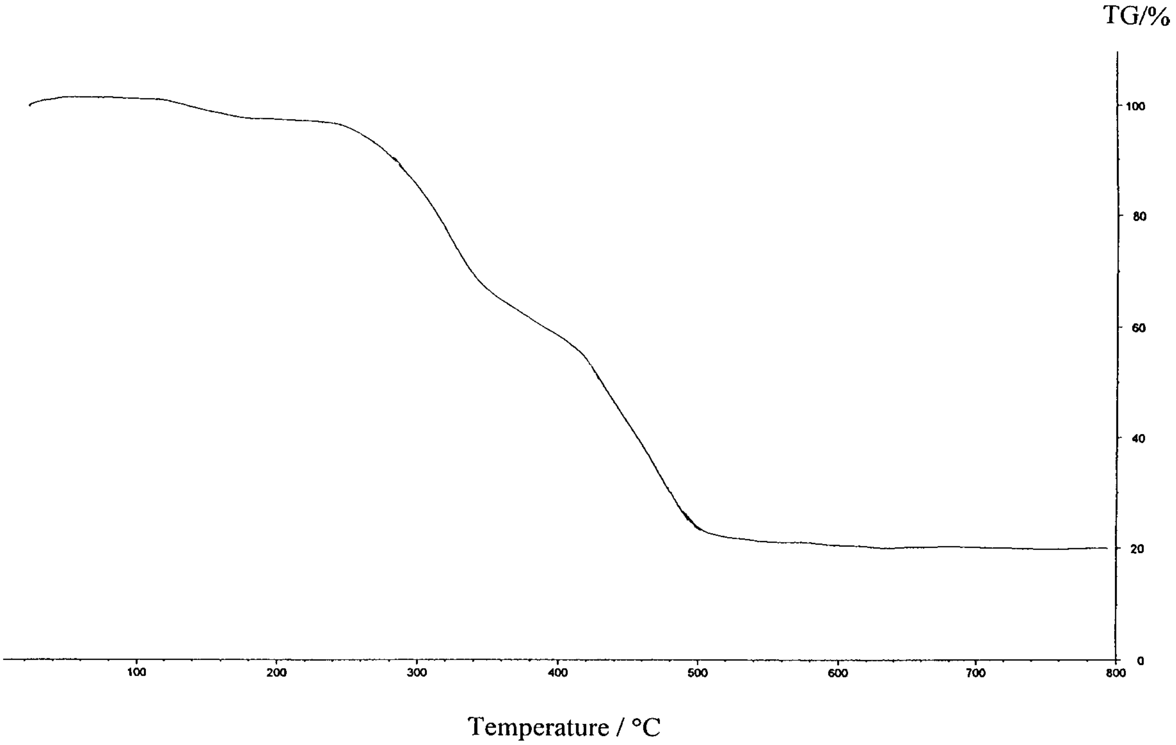

Fig. 2. Calcination of the salt, $(NH_4)_2[Sn(nap)_3]\cdot H_2O$, in air atmosphere with a temperature ramp of 10 K/min over the range 20–800°C.

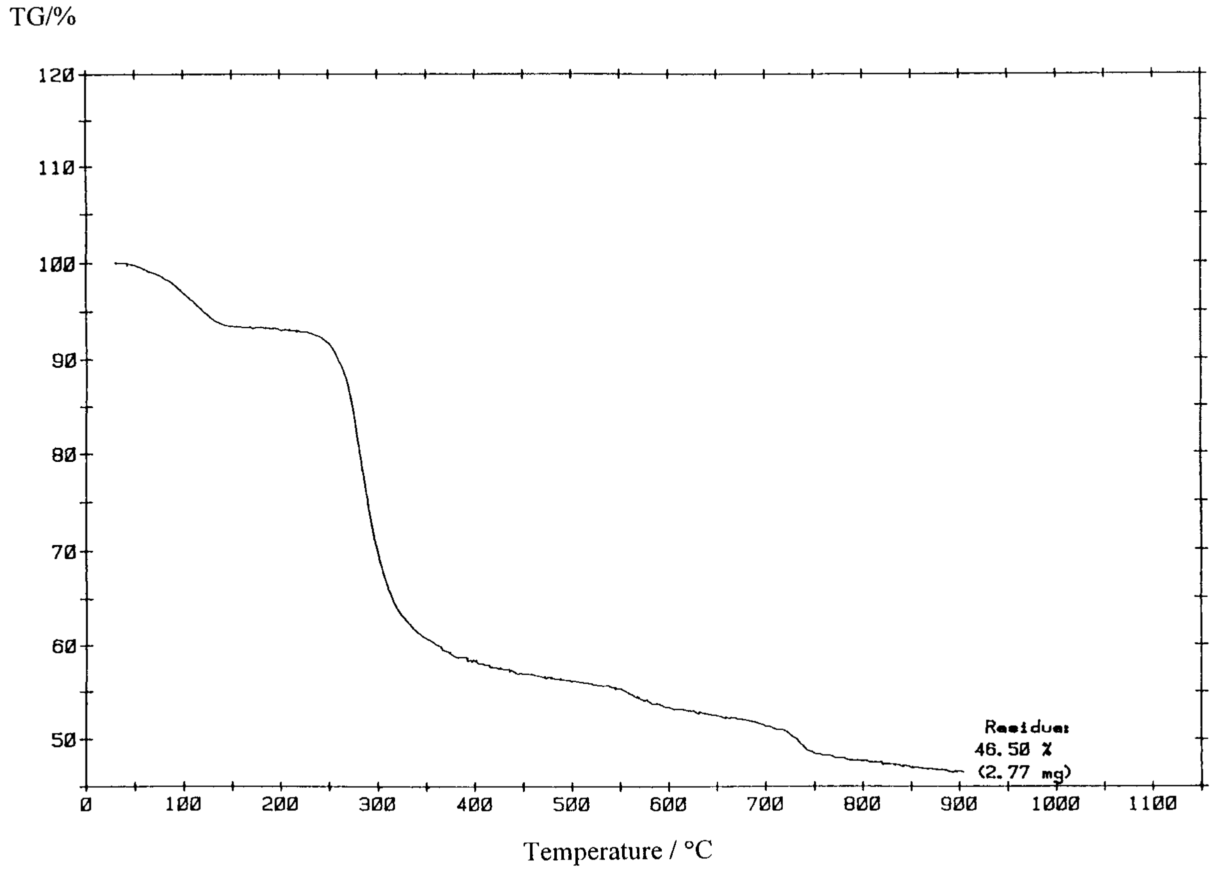

Fig. 3. TGA of $(NH_4)_2[Sn(nap)_3]\cdot H_2O$ in nitrogen atmosphere with a temperature ramp of 10 K/min over the range 20–900°C.

from the flowing air atmosphere [11]. Comparison of the TG plots for tin precursors heated in air with those heated in nitrogen supports this idea.[1] In nitrogen (Fig. 3) decomposition of $(NH_4)_2[Sn(nap)_3]\cdot H_2O$ proceeds as in air to 340°C (i.e. with the loss of ammonium cations and water). A 30% mass loss occurs over the temperature range from 250°C to 330°C similar to the loss for samples heated in air. However, above 300°C there is loss of mass that appears almost continuous with the exception of two small steps at 550°C and 740°C until the temperature limit of the analysis (900°C) is reached. At that point the total remaining mass is 46.5% compared to 20.0% for the samples heated in air. X-ray powder diffraction analysis of the residue from the sample heated under nitrogen atmosphere gives a powder pattern that is not consistent with any pattern in the database.

Results similar to those of the ammonium salt of tris-2,3-dihydroxynaphthalato tin(IV) were obtained for the TGA of the ammonium salt of tris-tironato tin(IV) (Tiron^{TM}, $H_2C_6H_4O_8S_2$). In an air atmosphere the water of hydration and ammonium cations (8% of the sample mass) are lost between 50° and 200°C while ligand decomposition and oxide formation occur at higher temperatures. Between 227°C and 343°C almost 24% of the sample's mass is lost. This mass change results from the decomposition and loss of the tironato ligands. Between 353°C and 459°C 41% of the remaining mass is lost so that 27% of the original mass remains. Tin oxide formation occurs

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[1] The tin complex was analyzed with both a Perkin-Elmer 7 Series Thermal Analysis System with a DuPont 1090 controller in nitrogen atmosphere and with a Netzsch Simultaneous Thermal Analyzer 409C in a bottled air atmosphere.

over that range because at temperatures above 460°C no further mass loss is detectable. The X-ray powder diffraction of the residue was consistent with that of SnO_2.

In a nitrogen atmosphere the tin–tironato complex, $(NH_4)_2[Sn(tironato)_3]\cdot 2H_2O$, loses water and ammonium cations in a manner similar to that of $(NH_4)_2[Sn(nap)_3]\cdot H_2O$. The mass decreases by 7.5% over the temperature range from 60°C to 221°C. Between 221°C and 545°C, the second mass loss occurs (39% of the sample) and no formation of tin oxides (Sn_xO_y) is detected after X-ray powder diffraction analysis of the sample residue. Further, the 39% mass loss occurs continually over the temperature range rather than sharply as did the losses for samples heated in an air atmosphere. The total mass loss for the sample under nitrogen is 46% so that 54% of the sample mass remains as residue compared to 27% for the air-heated samples (Table 1).

Caffeic acid (3,4-dihydroxycinnamic acid, $H_2C_9H_6O_4$) is a weak acid but a useful base after deprotonation ($pK_1 = 4.5$, $pK_2 = 8.9$) [8]. It complexes readily with Sn(IV) to form the ammonium salt complex of tris-caffeiato tin(IV), $(NH_4)_2[Sn(caffeiato)_3]\cdot 4H_2O$. The results of thermal gravimetry of this complex demonstrate that within a group of similar aryloxy ligands, some ligands are lost more quickly than others. For instance, the formation of SnO_2 as the final oxide product from $(NH_4)_2[Sn(caffeiato)_3]\cdot 4H_2O$ occurs at 570°C, while the onset of the same final product from $(NH_4)_2[Sn(tironato)_3]\cdot 2H_2O$ occurs between 425°C and 430°C. Variations in the temperature of formation of the tin oxide are due to the volatility of the specific ligand during the heating process and, additionally, to the number of intermediates formed during ligand decomposition.

The Sn(IV) caffeiato complex loses water and ammonium cations from 180°C to 200°C. Ligands are lost in two stages between 200°C and 350°C and between 350°C and 570°C. The mass of the sample remaining at 570°C is 13% of the initial mass with the loss of water and ammonium cations representing 15% of the original mass and the two-stage loss of the ligands accounting for 72% of the original mass. Between 570°C and 800°C no further change in mass occurs and the only material present is the final oxide, SnO_2, (confirmed by X-ray powder diffraction).

The bis(2,3-dihydroxynaphthalato) tin(IV) complex does not decompose as readily or at the lower temperatures common with the ammonium salt complexes prepared by pathway 1. The initial loss of loosely held water occurs between 100°C and 201°C. Between 202°C and 727°C decomposition of the ligands and formation of SnO_2 takes place. These changes occur in a slow, steady realignment of atoms (Fig. 4). Unlike the decomposition of ligands for the ammonium salt tin complexes which tend to lose ligands rather quickly at lower temperatures, stoichiometric formation of the SnO_2 residue does not occur until more than 500°C after the onset of ligand decomposition.

3.2. Differential scanning calorimetry

The DSC trace for the ammonium salt, $(NH_4)[Sn(nap)_3]\cdot H_2O$, exhibits a small endothermic peak with an onset temperature of 113°C followed by two exothermic peaks corresponding to the decomposition and pyrolysis of the ligands. The exothermic peak with an onset temperature of 246°C is the point at which ligand decomposition first occurs. This smaller peak is followed by a large exothermic peak with an

Table 1
Percentage initial and total mass loss in air or nitrogen atmospheres during thermal gravimetry

Precursor sample	Initial mass loss[a] (%)		Total mass loss (%)	
	Air	Nitrogen	Air	Nitrogen
$(NH_4)_2[Sn(nap)_3]\cdot H_2O$	3	7	80	47
$(NH_4)_2[Sn(tironato)_3]\cdot 2H_2O$	8	8	73	46
$(NH_4)_2[Sn(caffeiato)_3]\cdot 4H_2O$	15	–	87	–
$[Sn(nap)_2]\cdot 1.5H_2O$	6	–	77	–
$In[Sn(nap)_2]\cdot (NO_3)_3$	9	–	66	–

[a] Initial mass loss is the mass lost between 30°C and 221°C.

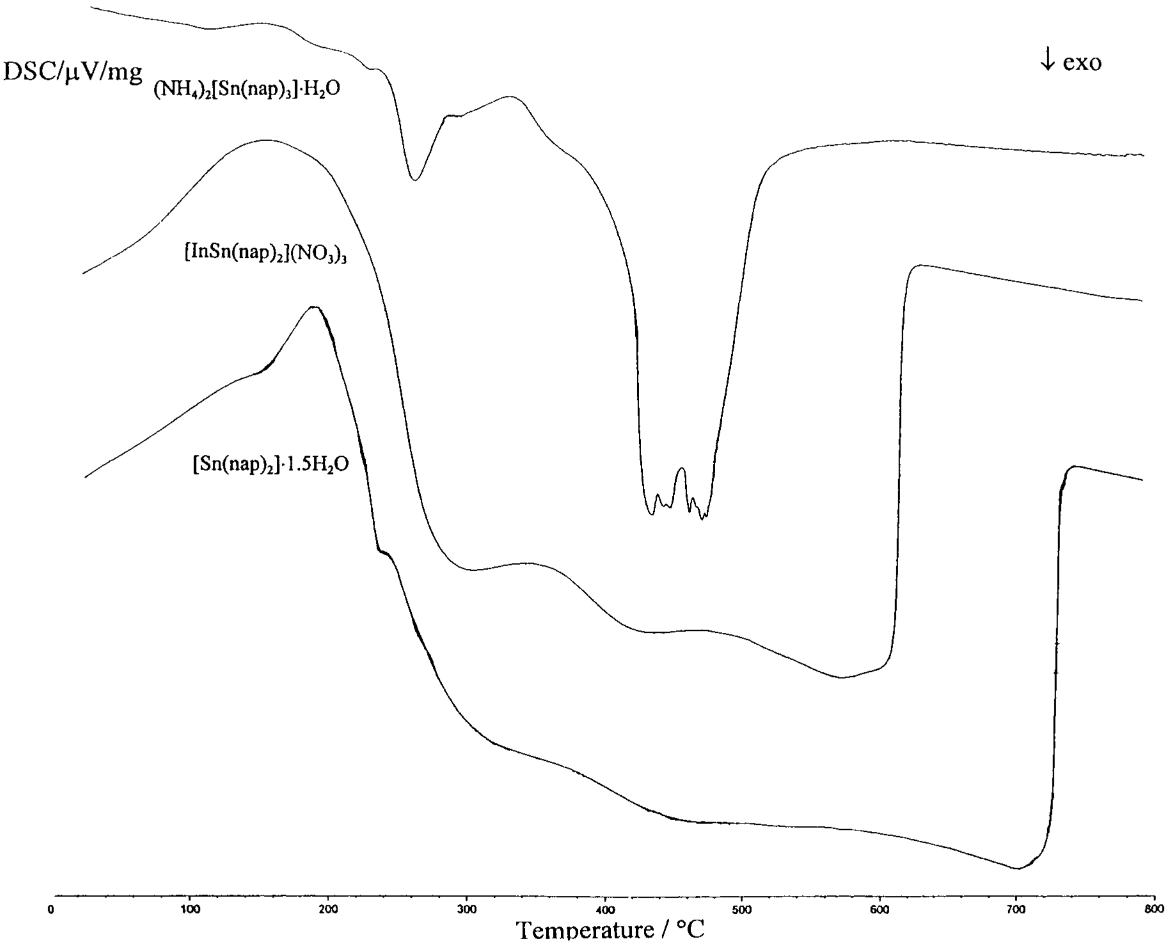

Fig. 4. DSC traces of $(NH_4)_2[Sn(nap)_3]{\cdot}H_2O$, $In[Sn(nap)_3](NO_3)_3$, and $[Sn(nap)_2]{\cdot}1.5H_2O$ over the temperature range 20–800°C.

onset temperature of 422°C. The large peak is the most conspicuous pyrolysis peak exhibited by the three precursors examined with DSC. Further, the 422°C temperature is a higher temperature than the ligand decomposition temperatures of the other two precursors indicating that the ligand–metal anion of the complex, $[Sn(nap)_3]^{-2}$, decomposes rapidly but at a higher temperature than the ligand–metal moities of the other precursors. Its stability appears to be the highest of the three precursors.

For the indium–tin precursor, $[InSn(nap)_2](NO_3)_3$, a broad endothermic peak appears concurrent with the loss of three nitrate anions. At 170°C a sharp exothermic peak coincides with the initial decomposition of the ligands. This exothermic peak is followed by two smaller exothermic peaks in the temperature range between 350°C and 605°C during which pyrolysis of the ligands is completed and formation of the final oxides occurs. Above 620°C the two oxide phases, In_2O_3–SnO_2, are the only materials present (confirmed by X-ray powder diffraction).

The DSC trace for $[Sn(nap)_2]{\cdot}1.5H_2O$ shows a sharp endothermic peak at 160°C (dehydration) followed by an exothermic curve that continues during ligand decomposition and pyrolysis until the temperature reaches 726°C. Above 733°C the only species present is stoichiometric SnO_2 (confirmed by X-ray powder diffraction).

Although the same ligands are present in each of the three monomolecular precursors examined by DSC, the differences in the DSC traces are the result of the individual molecules present: an ammonium salt containing Sn(IV), a neutral molecule containing Sn(IV), and a nitrate salt containing both Sn(IV) and In(III). Pyrolysis completion occurs at 733°C for the neutral molecule indicating that its reorganization of atoms and formation of intermediates is the most complex of the three precursors. The ammonium salt sample quickly loses water, ammonium cations and ligands at a much lower temperature than the neutral molecule. Further, the final oxide forms in the pyrolysis of the ammonium salt at a temperature over 100°C lower than that of the other two precursors.

4. Conclusions

Monomolecular precursors to In_2O_3–SnO_2 have been synthesized by two novel pathways. The precursors have been examined by TG and DSC and show the loss of water molecules and nitrate anions followed by the decomposition and loss of aryloxy ligands that were complexed with tin(IV). At higher temperatures rearrangement leads to the formation of the oxide product after which there is no further loss of mass detected in the TG or DSC traces. Of the three precursors it appears that the neutral molecule, $[Sn(nap)_2]\cdot 1.5H_2O$, has the largest decomposition/rearrangement temperature range and the ammonium salt, $(NH_4)_2[Sn(nap)_3]\cdot H_2O$, has the smallest decomposition/rearrangement temperature range so it reaches the tin oxide at the lowest temperature.

Acknowledgements

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[9] (a) $(NH_4)_2[Sn(nap)_3]\cdot H_2O$ FTIR: (Galaxy Series FTIR 3000, cm^{-1}) 3610, 3147, 1627, 1619, 1500, 1462, 1400 (ν, $NH_4{}^+$), 1255, 1173, 1111, 853, 748, 630, 579, 480; NMR: (Bruker, ^1H, ppm, solvent DMSO-d_6, TMS as internal standard) 2.60 (m, DMSO-d_6), 3.72 (H_2O), 6.85 (t), 7.08 (m), 7.48 (m); (b) $(NH_4)_2[Sn(tironato)_3]\cdot 2H_2O$ FTIR: (Perkin-Elmer 1760X, cm^{-1}) 3033, 1571, 1499, 1461, 1400, 1337, 1253, 1172, 1149, 1110, 864, 851, 748, 716, 652, 629, 580, 481; (c) $(NH_4)_2[Sn(caffeiato)_3]\cdot 4H_2O$ FTIR:(Galaxy Series FTIR 3000, cm^{-1}) 3437, 3411, 3305, 3041, 2852, 1649, 1618, 1610, 1596, 1512, 1493, 1437, 1381, 1352, 1329, 1277, 1227, 1198, 1163, 1119, 976, 900, 858, 800, 781, 694, 656, 615, 577.

[10] (a) $[Sn(nap)_2]\cdot 1.5H_2O$ FTIR: (Galaxy Series FTIR 3000, cm^{-1}) 3605, 1618, 1610, 1575, 1484, 1452, 1260, 122, 1172, 865, 750, 710; NMR: (Bruker, ^1H, ppm, solvent DMSO-d_6, TMS as internal standard) 2.60 (m, DMSO-d_6), 3.75 (H_2O), 7.52 (s), 7.57 (m), 7.97 (m); (b) $In[Sn(nap)_2](NO_3)_3$ FTIR: (Perkin-Elmer 1760X, cm^{-1}) 3433, 1626, 1460, 1382 (ν $NO_3{}^-$), 1250, 1167, 1099, 859, 744, 626, 478; NMR: (Bruker, ^1H, ppm, solvent DMSO-d_6, TMS as internal standard) 2.60 (m, DMSO-d_6), 3.50 (H_2O), 6.85 (t), 6.90 (d), 7.05 (m), 7.23 (s), 7.45 (m).

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