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Tin (II) ketoacidoxoimates: synthesis, X-ray structures and processing to tin (II) oxide

Jayaprakash Khanderi,a Bambar Davaasurena, Buthainah Ameen Alshankiti a and Alexander Rothenberger a,b*

Tin (II) ketoacidoxoimates of the type [HON=CRCOO]2Sn (R = Me 1, CH2Ph 2) and (MeON=CMeCOO)2Sn] NH2·2H2O 3 were synthesized by reacting pyruvate- and hydroxyl- or methoxylamine RONH2 (R = H, Me) with tin (II) chloride dihydrate SnCl2·2H2O. The single crystal X-ray structure reveals the geometry at Sn atom as trigonal bipyramidal in 1, 2 and trigonal pyramidal in 3. Inter- or intramolecular hydrogen bonding is observed in 1-3. Thermogravimetric (TG) analysis shows the decomposition of 1-3 to SnO occurs at ca. 160°C. The evolved gas analysis during TG indicates complete loss of the oximate ligand in one step for 1 whereas a small organic residue is additionally removed at temperature >400°C for 2. Above 140°C [HON=C(Me)COO]2Sn (1) decomposes in air to spherical SnO particles of size 10-500 nm. Spin coating of 1 on Si or glass substrate followed by heating at 200°C results in uniform film of SnO. The band gap of the produced SnO film and nanomaterial was determined by diffuse reflectance spectroscopy and found to be in the range of 3.0-3.3 eV. X-ray photoelectron spectroscopy indicates surface oxidation of the SnO film to SnO2 in ambient atmosphere.

Introduction

Semiconducting stannic oxide (SnO2) and stannous oxide (SnO) have attracted considerable research interest in the area of electronics and optoelectronics. SnO2 finds application in thin film transistors, sensors, heat reflecting filters as anode material in rechargeable Li ion battery. Tin (II) ketoacidoximates of the type [HON=CRCOO]2Sn (R = Me 1, CH2Ph 2) and (MeON=CMeCOO)2Sn] NH2·2H2O 3 were synthesized by reacting pyruvate- and hydroxyl- or methoxylamine RONH2 (R = H, Me) with tin (II) chloride dihydrate SnCl2·2H2O. The SnO thin films have shown a hole mobility of 2.4 cm2V⁻¹s⁻¹, largest amongst the p-type oxide semiconductors. Tin (II) ketoacidoximates of the type [HON=CRCOO]2Sn (R = Me 1, CH2Ph 2) and (MeON=CMeCOO)2Sn] NH2·2H2O 3 were synthesized by reacting pyruvate- and hydroxyl- or methoxylamine RONH2 (R = H, Me) with tin (II) chloride dihydrate SnCl2·2H2O. The SnO thin films have shown a hole mobility of 2.4 cm2V⁻¹s⁻¹, largest amongst the p-type oxide semiconductors. Tin (II) ketoacidoximates of the type [HON=CRCOO]2Sn (R = Me 1, CH2Ph 2) and (MeON=CMeCOO)2Sn] NH2·2H2O 3 were synthesized by reacting pyruvate- and hydroxyl- or methoxylamine RONH2 (R = H, Me) with tin (II) chloride dihydrate SnCl2·2H2O. The SnO thin films have shown a hole mobility of 2.4 cm2V⁻¹s⁻¹, largest amongst the p-type oxide semiconductors.
in the metal activated synthesis of α-amino acids, the oximate ligands are structurally analogous to 2-amino acids and the complexes have shown medical and biological functions and they are used in the synthesis of metal nanoparticles and thin films.

Here, we report the synthesis, crystal structures of tin (II) ketoacidoximate complexes 1-3, experimental condition for the synthesis and detailed characterization of SnO nanoparticles and thin films that were obtained by the decomposition of 1 and 2.

Result and discussion

The tin (II) ketoacidoximate complexes 1-3 were synthesized by the condensation reaction of α-ketocarboxylate and hydroxyl- or methoxyl amine with tin (II) chloride dihydrate in water (Scheme 1). 1 and 2 are isolated as crystalline solids with good yield (67-78%) whereas 3 was isolated in poor yield (~10%). All the complexes are soluble in N,N-dimethyl formamide and dimethyl sulfoxide and sparingly soluble in methanol and ethanol. The IR spectra of 1-3 shows characteristic absorptions between 1650-550 cm⁻¹ (ESI Fig. S1). The absorption bands at 1620 cm⁻¹ (C=N), 1590 cm⁻¹ (asymmetric vibrations of COO⁻), 1350 cm⁻¹ (-C=O symmetric or CH₃), 1050 cm⁻¹ (N-O), 850 cm⁻¹ (-OCO- in plane) could be assigned unambiguously. The appearance of ν(sym) and ν(asym) COO band indicate possible π-delocalization of C–O bond. The absorption bands at 3280-3290 cm⁻¹ for 3 could be assigned to NH stretching vibrations of the ammonium ion. The NMR chemical shifts observed for 1, 2 and 3 are in agreement with the previously reported transition metal complexes.

Scheme 1. Synthesis of Sn (II) ketoacidoximates, where R = Me 1, CH₂Ph 2.

Description of molecular structures of 1-3

The crystal structure of 1, 2 and 3 are determined from single crystal X-ray diffraction data. Fig. 1a-c shows the molecular geometry, bonding and atom labelling of 1, 2 and 3. The details on data collection and refinement are summarized in Table 1. The crystal structure of 1 and 2 contains two bidentate 2-oxyiminopropionato anions, which are bonded to the Sn core through the oxime nitrogen atom and one of the carboxylic oxygen atoms forming a trans complex with butterfly configuration (Fig. 1a and b). The Sn (II) atom lies on an inversion centre. A distorted trigonal bipyramidal geometry around Sn atom is enforced by the stereochemically active lone pair on tin (II) atom in 1 and 2, as observed previously and confirmed by τ-test. The Sn–O distances of 2.178(2)-2.204(2) Å in 1, 2.167(5)-2.175(6) Å in 2 and Sn–N distances 2.508(2)-
as Sn (II) complexes containing poly-functional ligands.\textsuperscript{64-66} The extensive donor type intermolecular hydrogen bonding exists between –NOH and COO groups in both the molecules.

### Table 1. Details of the X-Ray data collection and refinement for 1, 2 and 3.

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<td>0.69/-0.71</td>
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\(^a R1 = \Sigma|F_o|-|F_c|)/\Sigma|F_o|,\)

\(^b wR2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)]^2/\Sigma[w(|F_o|^2)]\}^{1/2}\) and \(w = 1/[σ(|F_o|^2)]^2 + (mP/\alpha)^2\)

\(^c GooF = \Sigma[w(|F_o|^2 - |F_c|^2)]^2/(n_{obs} - n_{par})\)\(^{1/2}\)

Short C–O bonding distances of \(d(C1-O1) = 1.272(3)\) Å and \(d(C1-O2) = 1.240(3)\) Å (I) and \(d(C1-O4) = 1.2774(4)\) Å and \(d(C1-O6) = 1.239(5)\) Å (2) in carboxylic groups suggests π-delocalization, which is probably caused by H-bonding and intermolecular Sn–O dative interactions. Similar π-delocalization of C–O bond is also observed in Co (III), Ni (II) and Zn (II) 2-oximinopropionate complexes.\textsuperscript{48, 51, 53} The atomic coordinates, anisotropic atomic displacement parameters, bond lengths and angles are listed in table S1-S8 (ESI) respectively.

The first structural difference between 1, 2 and the previously reported Ni (II), Co (III), Zn (II), Cu (II) and Cd (II) complexes is the long Sn-N bond distance. This bond length ranges between 2.391(2)-2.526(8) Å for 1, 2 while it is 2.111(1), 1.875(1), 2.334(2), 2.049(2), 2.461(15) Å for Ni-N, Co-N, Zn-N, Cu-N, Cd-N respectively.\textsuperscript{48, 51, 53} The long metal-N bond distance is also observed in sodium oximate complex as well.\textsuperscript{54}

The other interatomic distance in both 1 and 2 are in same range as found in the literature.\textsuperscript{45, 67, 68} The second difference is the O-Sn-N bite angle of the ligand to the metal ion. The bite angles in 1 are 67.29\(^\circ\) (7), 66.86\(^\circ\) (8) and 70.0\(^\circ\) (8) 77.7\(^\circ\) (2) in 2. In the similar Cu(II)\textsuperscript{69} complex it is 80.69\(^\circ\) and it decreases in Zn(II)\textsuperscript{69} 77.69\(^\circ\) and Cd(II)\textsuperscript{69} 68.78\(^\circ\) and 65.77\(^\circ\). The smaller bite angle of the ligand in 1 and 2 as well as in Cd (II) complex is related to the larger ionic radii of Sn (II) and Cd (II) ions.

The Sn atom, in the crystal structure of 3, is coordinated by three monodentate 2-methoxyiminopropionato- ligands forming perfect trigonal pyramidal geometry with the \(\tau\)-value of unity.\textsuperscript{65, 69} The three-fold coordination of the Sn (II) ion by COO- groups results in the accumulation of negative charge on Sn atom, which is balanced by \(\text{NH}_4^+\) counter ion. The H2O molecules form H-bonding with oxygen atoms of the carboxyl groups (ESI Fig. S2). The Sn-O distances \((d(2.178(2) - 2.199(1))\) Å are in good agreement with the distances reported in the literature.\textsuperscript{69} Similar to 1, 2 short C-O distances, \(d(C3-O5) = 1.237(6)\) Å and \(d(C3-O4) = 1.287(6)\) Å, are found in carboxylic group of the 2-methoxyiminopropionato- ligands. However, Sn1...N3 distance is 2.862(1)Å, longest among reported oximate- complex. The atomic coordinates, interatomic distances and angles are listed in table S9-S12 (ESI). The interatomic distances in this structure are close to the distances found in similar tin coordination complexes and tin oxides.\textsuperscript{45, 67, 68}

**Thermal decomposition of 1, 2 and 3**

Thermal behaviour of 1-3 were studied under nitrogen and air atmosphere by thermogravimetry, TG coupled IR and mass spectrometry. Fig. 2a is the TG curve for 1 under N\textsubscript{2}. The decomposition is not affected by the reaction atmosphere (air or nitrogen) and takes place between 155 – 160 °C. The residual mass observed in N\textsubscript{2} (36.9%) and air (43.4%) agrees well with the theoretical value for the formation of SnO (41.5%) for 1 implying complete decomposition of the ligand. This is supported by the Gram-Schmidt curve showing one maximum for the IR signal, indicating simultaneous removal of all
gaseous fragments (ESI Fig. S3). The IR spectra and mass spectrometry of the gases evolved during the decomposition of 1 could be assigned to water, CO, CO₂, and acetonitrile (ESI Fig. S4 and S5). The fragments observed in the TG-MS of 2 are H₂O, CO, CH₃CN, CO₂, benzene, toluene and benzyl cyanide (Fig. 2b: fragments with higher m/z are only shown). Decomposition of similar Zn and alkali metal complexes indicate a second order Beckmann rearrangement with elimination of CH₃CN, H₂O and CO₂. The metal complex with monoalkylcarbonate ligand is suggested as intermediate, which finally forms the metal oxide.⁴¹, ⁵⁴ Similar decomposition pathway could be responsible for formation of SnO from 1 and 2 (Scheme 2).

The CHN analysis of the residue obtained after heating of 1 in air shows average carbon of 1.65% for decomposition temperature between 140-180 °C, whereas carbon value of 0.86% for temperature of 200 °C (ESI, table 13). Carbon content of <1% has been reported for ZnO films from similar Zn oximate complex at 150 °C and those have been used for FET devices⁷⁰. The decomposition of 2 and 3 in nitrogen follows the same trend as that of complex 1 (ESI Fig. S6). In air 2 and 3 undergo additional weight loss at higher temperature, attributed to the removal of surface organic carbon.

**Tin (II) oxide synthesis**

SnO was synthesized by decomposing 1 and 2, whereas 3 has not been used for the decomposition study due to its low yield during synthesis.

**SnO powder formation from 1 and 2**

1 and 2 are heated from 140-200 °C for one hour in air. SnO formation is observed at 140 °C itself for 1 (Fig. 2c). The crystallinity of the formed SnO independent of decomposition...
temperature (140-200 °C). Amorphous SnO was obtained from Sn even at 200 °C (ESI Fig. S7). The formation of amorphous SnO from Sn could be attributed to incomplete removal of the benzene fragment during the decomposition at 163 °C. This is supported by the appearance of signal for benzene (m/z 78) and toluene (m/z 92) fragment at above 400 °C during the decomposition of Sn (Fig. 2b). Hence, Sn was chosen for making nanoparticle and thin films of SnO. The average crystallite size of SnO from Sn is in the range of 47-50 nm for temperatures between 140-200 °C, determined by Scherrer equation. Raman spectra of SnO from Sn recorded from 100-500 cm⁻¹ show two vibrational absorptions at 109 and 209 cm⁻¹ corresponding to characteristic B₃g and A₁g modes of SnO. The similarity of the Raman spectra for both 140 °C and 200 °C shows similar decomposition at these temperatures (ESI Fig. S8).

Scanning and transmission electron microscope images of SnO particle formed at 200 °C is shown in Fig. 3a and b respectively. At 200 °C SnO particles appear spherical in shape and have rough surface morphology. The particle size is between 50-250 nm. At 140 °C they are lumped together, with fewer non-agglomerated particles. The particle size is between 100-150 nm at 140 °C (ESI Fig. S9). Transmission electron microscope images (Fig. 3b) of the SnO particles at 200 °C indicate the presence of hollow and dense SnO particles. The high resolution TEM image (inset: Fig. 3b) show lattice fringes of 0.30 nm spacing corresponding to (101) plane of SnO.

Comparison with spherical SnO particles from Sn with those prepared by aqueous route using Sn₃O₅(OH)₄ derived from tin halides and amides or by vapour deposition and carbothermal reaction of SnO reveal various hierarchical morphologies such as nanoribbons, nanobelts, dendrimers and meshes. In addition, some level of control on oxidation state in the final tin oxide has been achieved through the use of well-defined Sn (II) centres precursors. However, rapid precipitation in aqueous route and formation of sub-stoichiometric tin oxide in vapour based methods are not suitable for thin film preparation. The tin oximate thus provides process flexibility for thin film preparation.

SnO thin film from Sn

Thin films of SnO are prepared by spin-coating a saturated solution of Sn in methanol or ethylene glycol/methanol mixture (1:9 v/v). The SEM micrograph of the single and 16 layers of SnO film on Si substrate, from ethylene glycol/methanol mixture, after heating the substrate to 200 °C is shown in Fig. 4a and b respectively. The energy-dispersive X-ray spectroscopy (EDX) analysis confirmed the presence of tin in the film for single layer SnO deposition (ESI Fig. S10). The 16 layer spin coated sample show a film thickness of 268 nm. Thus, the average thickness per layer is estimated to be 16-20 nm on silicon substrate. Comparing the morphology of SnO thin films from reported metalorganic precursors showed platelets and cubes with several grain boundaries, whereas with Sn smooth films could be obtained over larger area.

UV-Vis spectra of the SnO film measured in the diffuse reflection setup shows a band gap in the range of 3.0-3.3 eV (ESI Fig. S11) and is comparable to the reported data. X-ray photoelectron spectroscopy (XPS) for sample spin coated to 10 layers of SnO is shown in Fig. S12a-c (ESI). XPS survey spectrum of the SnO layer indicates incorporation of carbon and small amount of nitrogen (ESI, Fig. S13 and S14). The occlusion of these elements could be due to the residual solvent remaining or incomplete removal of the decomposition product of Sn during several heating cycle. The binding energies at 487.0 and 495.4 eV can be assigned to Sn 3d₅/₂ and 3d₃/₂ electrons of tin. The Os spectral lines show binding energies at 530.8 eV and 532.4 eV. The binding energy of 530.8 can be correlated to lattice oxygen in the tin oxide film and 532.4 for adsorbed OH on the surface. The valence band spectral peaks at 9 eV and below 2 eV due to the formation of antibonding and bonding Sn(II) 5s-6O₂p states were not observed, indicating surface of the SnO film has oxidised to Sn(V) (Fig. S12c ESI). Thus it can be concluded that the SnO film reacts with adsorbed/atmospheric oxygen to convert to SnO₂ as observed in the XPS analysis. Similar surface oxidation was observed for SnO film deposited from Sn(II) bis(ureide) during its exposure to ambient atmosphere.

To understand the oxidation of deposited SnO thin film, a drop-cast film from Sn in DMF solution on Si substrate is analysed by IR before heating and by Raman spectroscopy after heating to 200°C. IR of the precursor film on Si and Sn as powder show
same absorption bands (ESI, Fig. S15) indicating that I remain in Sn (II) state on the substrate. Raman spectra of the SnO film formed after heating to 200°C shows both the characteristic B₁g and A₁g vibrational modes (Fig. 2d) in agreement with the SnO powder produced from I at 200°C. This result clearly indicates the observed Sn (IV) state in the XPS analysis is due to the surface oxidation.

The SnO thin films formed from the reported metalorganic precursor e.g. Sn₈O₆(OSiMe₃)₄, [Sn₂(OSiMe₃)₄]₋₂, Sn₂bis(ureide) (ureide = BuNCONMe₂), [Snµ-O(Nep)₆]₄ (ONep = OCH₂CMe₃)³¹ ³² ³⁴ indicate stringent control of oxygen environment, higher deposition temperature (>300°C) and formation of metallic Sn along with the desired tin (IV) oxide phase. The air/moisture sensitivity of these precursors and the disproportionation of SnO to Sn and SnO₂ at higher temperature make the process complicated. The air/moisture stability, low decomposition temperature and solubility of I in common organic solvent makes it suitable for large area processing such as spin coating and printing.

Thin films of SnO of thickness 30 - 50 nm and 300 – 400 nm were prepared on the interdigitated substrate at 200 °C. The I-V characteristics of these films in the forward bias indicate the semiconducting property of the film (ESI Fig. S16 and S17) with a breakdown voltage at 8.9 V in the forward bias. Further studies to understand the thin film behaviour for transistor application is currently underway.

Conclusions

Tin (II) ketoacidoximate complexes were successfully synthesized and characterized. The Sn atom is four-fold coordinated and is donor stabilised by the oxime nitrogen of the ligand in all the complexes. The bis[2-(hydroxyimino) propionato] tin (II) decompose above 140 °C both in air and nitrogen with complete elimination of ligand to form SnO. The SnO particles of average size 50 nm were synthesized below 200°C by heating I. SnO thin films of 16-20 nm thickness were prepared by spin-coating. The films slowly convert to Sn (IV) oxide at the surface on exposure to air. The bulk of the film remain in Sn(II) state. The ambient atmosphere synthesis and processing makes Sn(II) oximate attractive for solution processable application.

Experimental section

Reagents and General Procedures

All the syntheses were performed in ambient atmosphere and with deionized water. SnCl₂·2H₂O (98%, Alfa Aesar), pyruvic acid (98%, Alfa Aesar), sodium phenyl pyruvate (98%, Sigma-Aldrich), hydroxylamine hydrochloride (99%, Sigma-Aldrich), methoxylamine hydrochloride (98%, Sigma-Aldrich), ammonium bicarbonate (≥ 99%, Sigma-Aldrich), methanol and N,N-dimethylformamide HPLC grade are used as-received. The melting point/decomposition of 1-3 were determined from the DTA (ESI Fig. S18)

Precursor synthesis

Syntheses of Sn ketoacidoximate complexes were an adaptation of method described previously.³³ ³⁷ ³⁰ The in-situ generation of the α-ketoacid oxime ligand in water was carried according to the procedure described by Spenser et al.⁴⁰

Synthesis of bis[2-(hydroxyimino) propionato] tin (II) (I)

Ammonium bicarbonate (0.49 g, 120 mmol) was added portion wise to a stirred solution of hydroxylamine hydrochloride (4.17 g, 60 mmol) and pyruvic acid (5.28 g, 60 mmol) in water (50 mL) at room temperature and the mixture was stirred until all gas evolution had ceased. SnCl₂·2H₂O (6.77 g, 30 mmol) was then added, and the mixture was stirred for 4 h, after which a white powder of I was filtered off and washed with ice cold water. The single crystals were obtained from concentrated ethanol solution of the compound at -35°C, Yield (6.5 g, 67%), mp 161°C (TG) (decomp.), Found: C 22.3; H, 2.5; N, 8.6, Calc. for C₃₇H₅₄N₂O₁₂Sn: C, 45.5; H, 3.4; N, 5.9, IR (νmax/cm⁻¹) ATR, powder: 3170 (w), 3050 (w), 2797 (w), 2725 (w), 1584 (s), 1487 (ms), 1366 (s), 1345 (s), 1195 (s), 1049 (s), 851(s), 759 (ms), 732 (s).¹ H NMR (400 MHz; (CD₃)₂SO, 25 oC), δ 1.95 (s, 6H, CH₂-C=N); ¹³C NMR (100 MHz; (CD₃)₂SO, 25 °C) δ 11.5 (CH₂-C=N), 151.1 (C=N), 167.2 (C=O).

Synthesis of bis[2-(hydroxyimino)3-phenyl-propionato] tin (II) (2)

Ammonium bicarbonate (0.395 g, 5 mmol) was added portion wise to a solution of hydroxylamine hydrochloride (0.347 g, 5 mmol) in 10 mL water and the mixture was stirred until all gas evolution had ceased. To the above solution sodium phenyl pyruvate (0.931 g, 5 mmol) in water (10 mL) was added at room temperature. The reaction was allowed to continue for 2 h. Then the mixture was filtered off and wash with ice cold water. The single crystals were obtained from concentrated methanol solution by slow evaporation method. Yield (1 g, 78%) mp 163°C (TG) (decomp.) Found: C 44.1; H, 3.4; N, 6.1, Calc. for C₃₅H₅₁N₂O₁₂Sn: C, 45.5; H, 3.4; N, 5.9, IR (νmax/cm⁻¹) ATR, powder: 3175 (w), 3062 (w), 2846 (w), 1600 (s), 1493 (m), 1453 (w), 1426 (w), 1373 (ms), 1337 (w), 1298 (w), 1230 (ms), 1158 (ms), 1137 (ms), 1055 (s), 1026 (s), 931 (w), 862 (s), 774 (ms), 754 (m), 715 (s), 695 (s), 552 (w).¹ H NMR (400 MHz; (CD₃)₂SO, 25 °C), δ: 3.83 (s, 4H, -CH₂-Ph), 7.24 (s, 10H, Ph) 12.4 (s, -N-O), 129.1 (s), 128.3 (s), 114.9 (s), 113.7 (s), 108.4 (s), 106.9 (s), 95.8 (s), 95.0 (s).¹³C NMR (100 MHz; (CD₃)₂SO, 25 °C) δ: 30.7(–CH₂), 126.6 (Ph), 128.7 (Ph), 129.2 (Ph), 137.1(Ph) 152.2 (C=N), 167.1 (C=O).

Synthesis of Diaqua[2-(methoxyimino) propionato] tin(II) ammonium salt (3)
Ammonium bicarbonate (9.49 g, 120 mmol) was added portionwise to a stirred solution of methoxylamine hydrochloride (5.01 g, 60 mmol) and pyruvic acid (5.28 g, 60 mmol) in water (30 mL) at room temperature, and the mixture was stirred until all gas evolution had ceased and stirred further for 3h. SnCl2·2H2O (6.77 g, 30 mmol) was then added; at the start reaction is slow. As the time progresses a white precipitate is seen. The precipitate is dissolved in ethanol, reduced in volume and kept at -35°C for recrystallization. Yield (0.8 g, 10%) mp 151°C (TG) (decomp.) Found: C: 27.9, H: 4.2, N: 10%. IR (νmax/cm–1), ATR, powder: 3284 (w), 3144 (w), 3052 (w), 2988 (w), 2943 (w), 2827 (w) 1649 (ms), 1533 (s), 1593(s), 1536 (m), 1442 (m), 1418 (ms), 1371 (s), 1349 (s), 1249(s), 1172 (s), 1043, (s) 927 (ms), 855 (s), 768 (m), 723 (s), 579(m); 1H NMR (400 MHz; (CD3)2SO, 25 °C), δ 1.91 (s, 9H, N=C–H3), 3.93 (s, 9H, N-OC3H7), 13C NMR (100 MHz; (CD3)2SO, 25 °C) δ 12.3(N=C-CH3), 62.4(N-OCH3), 152.7(C=N), 168.0(C=O).

**Synthesis of SnO**

**Heating I**

150 mg of the complex 1 is heated in a nickel crucible to 140 – 200°C in air for one hour in a general purpose laboratory furnace. 52 mg (yield 100% based on Sn content)

**Thin film deposition-spin coating**

Saturated solution of 1 in methanol or ethylene glycol mixture (9:1) is used to spin-coat a thin layer of precursor on Si substrate. A filtered, 50 mL of the solution is dropped on the substrate with coating programme 1000 rpm/30 seconds/5000 rpm/20 seconds. The relative humidity during spin coating was between 57-60 %.

**Thin film deposition-drop coating**

100 μL of saturated solution of 1 in DMF is drop-cast on Si substrate. The solvent is allowed to evaporate in a well-ventilated chemical hood.

**Characterization**

IR spectroscopic measurements were carried out using Nicolet iS10 FTIR spectrometer with ATR setup. The scans were performed from 4000 – 525 cm–1. 1H NMR and 13C NMR spectra were recorded on a Bruker AC300F spectrometer at 400 MHz. Elemental analysis (C,H,N) was performed in Flash 2000 instrument from thermo scientific. Thermogravimetry measurements were carried out using a Netzsch STA 449 F3 Jupiter instrument equipped with a TG/DSC sample carrier. Thermogravimetry coupled infra-red (TG-IR) measurements were performed on a Netzsch TGA 209 F1 Iris instrument coupled to a Tensor 27 TGA-IR. Thermogravimetry coupled mass spectrometry (TG-MS) measurements were carried out on a Netzsch TG 209 F1 Iris coupled with QMS 403 C Aeros mass spectrometer. Micro Raman measurements were performed on LabRAM HR high resolution microscope from Horiba Jobin Yvon model HR 800. The excitation wavelength was 532.2 nm. The spectrum was recorded in the range of 50 – 1000 cm–1. X-ray powder diffraction patterns (XRD) of the samples at room temperature were recorded using a STOE Stadi MP instrument equipped with Cu-Kα source and Mythen detector. SEM investigations were performed with Quanta 600 FEG microscope typically at low keV (3 – 5 keV), TEM analysis was conducted on a Titan Super Twin instrument at 300 kV. Single-crystal X-ray diffraction experiments for 1–3 were carried out on IPDS2 (STOE) image plate diffractometer with graphite monochromatized Mo-Kα (λ = 0.71069 Å) radiation, at 150 K with a detector distance of 100 mm. Single crystals of 1–3 were mounted on a glass capillary using perfluoroalkylether (viscosity 1800cSt., ABCR GmbH & Co. KG Karlsruhe. For data collection, determination, and refinement of the lattice parameters as well as for data reduction including LP correction, the STOE X-Area27 software package was used. The intensity data were corrected for absorption numerically using the crystal habit and the program X-Shape.76 The crystal structure was solved by direct methods and refined using the program packages SHELXS97 and SHELXL97.77

**Acknowledgements**

This work was supported by the King Abdullah University of Science & Technology (KAUST) baseline (BAS/1/1302-01-01) and AEA funding. J. K. thanks, Dr. Rachid Sougrat and Ms. Nini Wei for TEM imaging, Dr. Mohamed Nejib Hedhili for XPS analysis.

**Notes and references**

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†Electronic Supplementary Information (ESI) available: [IR, gas phase IR, mass of decomposition products, UV-Vis spectrum of SnO thin film. Details on data collections, refinements, atomic coordinates, anisotropic atomic displacement parameters, bond lengths and angles for the reported complexes, XRD and SEM of decomposition product of 2, XPS, I-V characteristics of the film]. See DOI: 10.1039/b000000x/

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