



## Synthesis of novel tin complexes using functionalized oxime ligands



Eun Ae Jung<sup>a,b</sup>, Sheby Mary George<sup>a</sup>, Seong Ho Han<sup>a,b</sup>, Bo Keun Park<sup>a</sup>, Jeong Hwan Han<sup>a</sup>, Seung Uk Son<sup>b</sup>, Chang Gyoung Kim<sup>a,\*</sup>, Taek-Mo Chung<sup>a,\*</sup>

<sup>a</sup>Thin Film Materials Research Center, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong, Daejeon 34114, Republic of Korea

<sup>b</sup>Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 16419, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 10 November 2015  
Received in revised form 25 February 2016  
Accepted 27 February 2016  
Available online 4 March 2016

#### Keywords:

Tin  
Precursor  
Oxime  
Thin film

### ABSTRACT

Novel tin complexes stabilized by alkoxy-functionalized oxime ligands [Sn(L<sup>1</sup>)<sub>2</sub>]<sub>2</sub> (**1**) and [Sn(L<sup>2</sup>)<sub>2</sub>]<sub>2</sub> (**2**), were prepared and characterized. Single-crystal X-ray diffraction analysis revealed that the complexes were obtained as dimers in which the tin metal centers are bridged by a pair of μ<sub>2</sub>-oxygen atoms. Due to the ligand steric effects, the metal centers in these complexes adopted an unusual distorted square pyramidal geometry and displayed interesting structural features. The thermo-gravimetric analyses of the complexes showed major mass loss in the 175–380 °C region.

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## 1. Introduction

Tin oxide (SnO<sub>2</sub>) has attracted great attention in the field of semiconductor because of its wide band gap of ~3.62 eV [1,2]. Additional unique properties such as high transparency, infrared reflectivity, and conductivity make it a valuable material and have been applied to energy-conserving windows for buildings [3], gas sensors, [4] and transparent conductive electrodes in thin film solar cells [5–7]. For these applications tin oxide thin film deposition depends on the availability of suitable precursors. The use of oxime derivatives as ligands in organometallic chemistry is well known [8]. Generally oxime complexes involve an oximate N-metal bonding, which, based on the known geometrical configuration of the ligands, has been accepted as their most stable form. However, some complexes exhibit oximate O-metal bonding [9] and thus revealing the ambidentate character of the oxime ligands.

Tin-oxime complexes and their chemistry have not been well studied to date, except for a few examples [10] especially in the field of precursors. The ambidentate character and the tunability of the steric properties of the substituents on the oxygen atom make oximes attractive ligands in precursor chemistry. In this study, tertiary alkoxy functionalized oximes, 3-hydroxy-3-methylbutan-2-one-O-methyl oxime (L<sup>1</sup>H) and 3-hydroxy-3-methylbutan-2-one-O-tertbutyl oxime (L<sup>2</sup>H) were used as coordinating ligands for tin (II) complexes, where the oximate O

atom is bonded to the methyl group in L<sup>1</sup>H and to the tertiary butyl group in L<sup>2</sup>H. The resulting complexes [Sn(L<sup>1</sup>)<sub>2</sub>]<sub>2</sub> (**1**) and [Sn(L<sup>2</sup>)<sub>2</sub>]<sub>2</sub> (**2**) were obtained as dimers and were characterized using single-crystal X-ray diffraction analysis, FT-NMR, FT-IR, elemental analysis and thermo-gravimetric analysis (TGA).

## 2. Experimental

### 2.1. General

Tin bis(trimethylsilyl)amide [Sn{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] was prepared by the literature method [11]. All reactions were carried out under inert and dry conditions using standard Schlenk techniques or in an argon-filled glove box. Hexane and toluene were purified by Innovative technology PS-MD-4 solvent purification system. All other chemicals were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker 300 MHz spectrometer with C<sub>6</sub>D<sub>6</sub> as solvent and standard. IR spectra were collected on a Nicolet Nexus FT-IR spectrophotometer. Elemental analyses were carried out on a Thermo Scientific OEA Flash 2000 Analyzer. Thermogravimetric analyses were conducted on a SETARAM 92-18 TG-DTA instrument.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 3-hydroxy-3-methylbutan-2-one-O-methyl oxime (L<sup>1</sup>H)

O-Methylhydroxylamine hydrochloride (14.7 g, 0.18 mol), sodium acetate (19.3 g, 0.23 mol), and 3-hydroxy-3-methyl-2-

\* Corresponding authors. Fax: +82 42 861 4151.

E-mail addresses: [cgkim@kRICT.re.kr](mailto:cgkim@kRICT.re.kr) (C.G. Kim), [tmchung@kRICT.re.kr](mailto:tmchung@kRICT.re.kr) (T.-M. Chung).

butanone (12.0 g, 0.12 mol) were added to 100 mL of ethanol at room temperature. After stirring for 2 h, the reaction mixture was concentrated and extracted with ethyl acetate. The organic layer was washed with water and dried over magnesium sulfate. The solvent was evaporated to give the crude product, which was purified by distillation (72 °C/30 Torr) to afford L<sup>1</sup>H as a colorless liquid. Yield 10.0 g (72%). FT-IR ( $\nu_{\max}$ , cm<sup>-1</sup>): 3434 (s), 2980 (s), 2939 (s), 2901 (s), 2818 (m), 1754 (w), 1716 (m), 1635 (w), 1464 (s), 1441 (m), 1367 (s), 1264 (m), 1173 (s), 1142 (s), 1053 (s), 948 (s), 914 (w), 894 (s), 855 (s), 754 (w) 595 (w), 519 (w). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta_{\text{H}}$  1.24 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>COH), 1.69 (s, 3H, CH<sub>3</sub>CNO), 3.69 (br, s, 4H, CNOCH<sub>3</sub> & -OH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta_{\text{C}}$  10.1 (CH<sub>3</sub>CNO), 27.9 ((CH<sub>3</sub>)<sub>2</sub>COH), 61.3 (CH<sub>3</sub>CNOCH<sub>3</sub>), 72.2 ((CH<sub>3</sub>)<sub>2</sub>COH), 160.9 (CH<sub>3</sub>CNOCH<sub>3</sub>). Anal. Calc. for C<sub>6</sub>H<sub>13</sub>NO<sub>2</sub>: C, 54.9; H, 10.0; N, 10.7. Found: C, 54.3; H, 10.0; N, 9.9%.

### 2.2.2. Synthesis of 3-hydroxy-3-methylbutan-2-one-O-tertbutyl oxime (L<sup>2</sup>H)

O-tert-Butylhydroxylamine hydrochloride (16.0 g, 0.13 mol), sodium acetate (19.3 g, 0.23 mol) and 3-hydroxy-3-methyl-2-butanone (12.0 g, 0.12 mol) were added to 100 mL of ethanol at room temperature. After stirring for 4 h, the reaction mixture was concentrated and extracted with ethyl acetate. The organic layer was washed with water and dried over magnesium sulfate. The solvent was evaporated to give the crude product which was purified by distillation (86 °C/30 Torr) to afford L<sup>2</sup>H as a colorless liquid. Yield 16.0 g (77%). FT-IR ( $\nu_{\max}$ , cm<sup>-1</sup>): 3428 (s), 2978 (s), 2932 (s), 1639 (w), 1457 (m), 1364 (s), 1241 (m), 1195 (s), 1174 (s), 1145 (s), 1013 (s), 988 (m), 952 (s), 858 (s), 788 (w), 721 (w), 591 (w), 565 (w), 541 (w), 476 (w), 441 (w). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta_{\text{H}}$  1.26 (s, 9H, CNOCH<sub>3</sub>), 1.26 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>COH), 1.66 (s, 1H, -OH), 1.72 (s, 3H, CH<sub>3</sub>CNO). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta_{\text{C}}$  10.2 (CH<sub>3</sub>CNO), 27.6 (CH<sub>3</sub>CNOCH<sub>3</sub>), 28.2 ((CH<sub>3</sub>)<sub>2</sub>COH), 72.6 ((CH<sub>3</sub>)<sub>2</sub>COH), 78.2 (CH<sub>3</sub>CNOCH<sub>3</sub>), 159.9 (CH<sub>3</sub>CNOCH<sub>3</sub>). Anal. Calc. for C<sub>9</sub>H<sub>19</sub>NO<sub>2</sub>: C, 62.3; H, 11.1; N, 8.1. Found: C, 61.4; H, 11.1; N, 7.6%.

### 2.2.3. Synthesis of [Sn(L<sup>1</sup>)<sub>2</sub>]<sub>2</sub> (1)

To a solution of [Sn{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (1.00 g, 2.27 mmol) in 50 mL of hexane was added L<sup>1</sup>H (0.60 g, 4.55 mmol) at room temperature. The reaction mixture was allowed to stir for 15 h, during which, the color changed from orange to colorless. The resulting reaction mixture was then filtered and the volatiles were removed in vacuo to obtain the product as a white crystalline solid. The product was further purified by recrystallization from the concentrated hexane solution. Yield: 0.49 g (57%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta_{\text{H}}$  1.50 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>CO), 1.69 (s, 3H, CH<sub>3</sub>CNO), 3.98 (s, 3H, CNOCH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta_{\text{C}}$  12.3 (CH<sub>3</sub>CNO), 31.5 ((CH<sub>3</sub>)<sub>2</sub>CO), 62.6 (CH<sub>3</sub>CNOCH<sub>3</sub>), 78.5 ((CH<sub>3</sub>)<sub>2</sub>CO), 169.0 (CH<sub>3</sub>CNOCH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 2962 (s), 2932 (w), 2814 (w), 1634 (w), 1460 (m), 1375 (m), 1354 (m), 1170 (m), 1130 (s), 1048 (s), 965 (s), 908 (m), 864 (m), 757 (w) 596 (s), 528 (s), 418 (w). Anal. Calc. for C<sub>24</sub>H<sub>48</sub>N<sub>4</sub>O<sub>8</sub>-Sn<sub>2</sub>: C, 38.0; H, 6.4; N, 7.4. Found: C, 38.5; H, 6.0; N, 7.0%. EI-MS: m/z calc. for [Sn(L<sup>1</sup>)<sub>2</sub>]<sub>2</sub>: 758 [M]<sup>+</sup>; found 380 [Sn(L<sup>1</sup>)<sub>2</sub>]<sup>+</sup>, 250 [Sn(L<sup>1</sup>)]<sup>+</sup>.

### 2.2.4. Synthesis of [Sn(L<sup>2</sup>)<sub>2</sub>]<sub>2</sub> (2)

To a solution of [Sn{N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (1.00 g, 2.27 mmol) in 50 mL of hexane was added L<sup>2</sup>H (0.79 g, 4.55 mmol) at room temperature. The reaction mixture was allowed to stir for 15 h, during which time, the color changed from orange to colorless. The resulting reaction mixture was then filtered and the volatiles were removed in vacuo to obtain the product as white crystalline solid. The product was further purified by recrystallization from the concentrated hexane solution. Yield: 0.84 g (80%) <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta_{\text{H}}$  1.39 (s, 9H, CNOCH<sub>3</sub>), 1.62 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>CO),

1.93 (s, 3H, CH<sub>3</sub>CNO). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta_{\text{C}}$  12.2 (CH<sub>3</sub>), 28.3 (CH<sub>3</sub>CNOCH<sub>3</sub>), 31.4((CH<sub>3</sub>)<sub>2</sub>CO), 77.1 ((CH<sub>3</sub>)<sub>2</sub>CO), 77.9 (CH<sub>3</sub>-CNOCH<sub>3</sub>), 165.7 (CH<sub>3</sub>CNOCH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 2974 (s), 2927 (m), 2875 (w), 1627 (w), 1453(m), 1379 (s), 1363 (s), 1286 (w), 1258 (w), 1239 (w), 1195 (s), 1163 (s), 1131 (m), 1012 (m), 950 (s), 933 (s), 917 (m), 895 (w), 870 (m), 789 (w), 722 (w), 618 (m), 595 (w), 521 (w), 488 (w), 412 (w). Anal. Calc. for C<sub>36</sub>H<sub>72</sub>N<sub>4</sub>O<sub>8</sub>Sn<sub>2</sub>: C, 46.7; H, 7.8; N, 6.1. Found: C, 46.7; H, 8.0; N, 5.9%. EI-MS: m/z calc. for [Sn(L<sup>2</sup>)<sub>2</sub>]<sub>2</sub>: 926 [M]<sup>+</sup>; found 464 [Sn(L<sup>2</sup>)<sub>2</sub>]<sup>+</sup>, 292 [Sn(L<sup>2</sup>)]<sup>+</sup>.

### 2.3. Crystallographic data collection and refinement of the structure

Crystals of **1** and **2** suitable for an X-ray diffraction analysis were obtained from a saturated hexane solution at -30 °C. A specimen of suitable size and quality was coated with Paratone oil and mounted onto a glass capillary. Reflection data for **1** and **2** were collected on a Bruker Apex II CCD-area detector diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The hemisphere of reflection data was collected as  $\omega$ -scan frames with 0.3°/frame and an exposure time of 10 s/frame. The SAINT [12] software was used for cell refinement and data deduction. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [13]. The structure was solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares cycles on  $F^2$  using the SHELXTL/PC package [14]. Hydrogen atoms were placed at their geometrically calculated positions and refined as riding on the corresponding carbon atoms with isotropic thermal parameters. Details of experimental crystallographic data for **1** and **2** are summarized in Tables 1 and 2.

**Table 1**  
Crystallographic data and data collection parameters for **1** and **2**.

	<b>1</b>	<b>2</b>
Formula	C <sub>24</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub> Sn <sub>2</sub>	C <sub>36</sub> H <sub>72</sub> N <sub>4</sub> O <sub>8</sub> Sn <sub>2</sub>
Formula weight	758.04	926.36
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.9625(1)	8.6169(4)
<i>b</i> (Å)	9.6419(1)	11.6486(6)
<i>c</i> (Å)	10.6078(1)	11.7129(6)
$\alpha$ (°)	90.665(1)	99.946(2)
$\beta$ (°)	102.771(1)	100.917(2)
$\gamma$ (°)	112.575(1)	92.989(2)
<i>V</i> (Å <sup>3</sup> )	805.42(2)	1132.67(10)
<i>Z</i>	1	1
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.563	1.358
$\mu$ (mm <sup>-1</sup> )	1.597	1.149
<i>F</i> (000)	384	480
<i>T</i> (K)	100(1)	100(1)
<i>hkl</i> range	-11 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -14 ≤ <i>l</i> ≤ 14	-11 ≤ <i>h</i> ≤ 11, -15 ≤ <i>k</i> ≤ 15, -13 ≤ <i>l</i> ≤ 15
Total reflections	14600	19350
Independent reflections	3972	5654
Parameters	172	226
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0184	0.0328
<i>wR</i> <sub>2</sub> <sup>b</sup> all data	0.0529	0.0923
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.160	1.191

<sup>a</sup>  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = [\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega(F_o^2)^2]^{1/2}$ .

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