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Inorganica Chimica Acta 333 (2002) 124–131

Inorganica Chimica Acta

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Synthesis and characterization of organotin Schiff base chelates

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Received 12 September 2001; accepted 16 January 2002

Abstract

The synthesis and characterization of five organotin compounds containing Salophen(^{t}Bu) [Salophen(^{t}Bu) = *N*,*N*′-phenylene-bis(3,5-di-*tert*-butylsalicylideneimine)], Salomphen(^{t}Bu) [Salomphen(^{t}Bu) = *N*,*N*′-(4,5-dimethyl)phenylene-bis(3,5-di-*tert*-butylsalicylideneimine)] and Phensal(^{t}Bu) [Phensal(^{t}Bu) = 3,5-di-*tert*-butylsalicylidene(1-aminophenylene-2-amine)] ligands is described. These compounds include the monomeric complexes $LSnCl_2$ (where L = Salophen(^{t}Bu), L = Salomphen(^{t}Bu)), L(^{n}Bu)SnCl (where L = Salophen(^{t}Bu), Salomphen(^{t}Bu)), L(^{n}Bu)$SnCl_2$ (where L = Phensal(^{t}Bu)). Spectroscopic techniques including ^{119}Sn NMR and X-ray crystallography were used in the characterization of the compounds. © 2002 Published by Elsevier Science B.V.

Keywords: Tin; Schiff base; Salen; Sn NMR; Tetradentate ligand

1. Introduction

The Salen [1] class of ligands has been used for some time to explore fundamental aspects of structure and bonding in transition metals [2]. For the main group metals the majority of the work has involved the Group 13 elements [3], although Group 14 compounds with these ligands have received increased attention recently [4]. For instance, the compounds, R_2Sn(Vanophen) [R = Ph, ^{n}Bu, Me; Vanophen = *N*,*N*′-1,2-phenylene-bis(3-methoxysalicylideneimine)], (^{n}Bu)Sn(Salophen) [Salophen = [*N*,*N*′-phenylene-bis(salicylideneimine)], [5] SalenGe, and SalenPb [Salen = *N*,*N*′-ethylene-bis(salicylideneimine)] have been reported [4a].

There are few cationic tin salen compounds. Most past work has focused on the isolation of lower-coordinate unsolvated derivatives [6]. More recently a series of higher coordinate derivatives, including some cations, have been reported [7,8]. These charged species may have important applications. For example, cations of the form, $[R_2SnOH(H_2O)]_2^{2+}$ $(OTf)^{2-}$ (R = ^{n}Bu and ^{t}Bu), have been shown to be catalysts in the acetylation of alcohols [9]. To date, however, there have been no structurally characterized organotin cations with the Salen class of ligands. Previous research in our lab has used Salen type ligands to produce cationic compounds with Group 13 metals. These compounds were shown to act as catalysts in the polymerization of propylene oxide [10]. We have extended our studies to the complexes formed between Group 14 metals and the Salen class of ligands, formation of cationic species, and their efficacy as catalysts for ring opening polymerizations. On our way to produce the cationic tin salen class of compounds, we report the synthesis and characterization of some intermediate compounds.

The present publication will entail a description of the syntheses and characterization of the monomeric complexes $LSnCl_2$ (where L = Salophen(^{t}Bu), [*N*,*N*′-phenylenebis(3,5-di-*tert*-butylsalicylideneimine)] (**1**), L = Salomphen(^{t}Bu) (**2**)), L(^{n}Bu)SnCl (where L = Salophen(^{t}Bu) (**3**), Salomphen(^{t}Bu) (**4**)), and L(^{n}Bu)$SnCl_2$ (where L = Phensal(^{t}Bu), [3,5-di-*tert*-butylsalicylidene(1-aminophenylene-2-amine)] (**5**)). Spectroscopic techniques including ^{119}Sn NMR were used in the characterization of the compounds and the structure of **1**, **2**, and **5** were determined by X-ray crystallography.

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PII: S0020-1693(02)00803-4

2. Experimental

2.1. General procedures

All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-200 and -400 instruments operating at 200.17 and 400.25 MHz (^{1}H) and are reported relative to $SiMe_4$ and are in ppm. ^{1}H-decoupled ^{119}Sn spectra were recorded on the JEOL-GSX-270 and are reported relative to Me_4Sn [11]. Elemental analyses were obtained on an Elementar III Analyzer. IR data were recorded as KBr and CsI pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. Mass spectral data were obtained on a Kratos CONCEPT 1H instrument at 70 eV.

2.2. Structure determinations

X-ray diffraction data for **1**, **2**, and **5** were collected at 173 K (**2** and **5**) and at 144 K (**1**) on a Nonius kappa CCD diffractometer from an irregular-shaped crystal, mounted in oil on a glass fiber. Initial cell parameters were obtained from ten 1° frames (DENZO-SMN) and were refined via a least-squares scheme based on all frames (SCALEPACK, DENZO-SMN) [12]. Lorentz/polarisation corrections were applied during data reduction. The structures were solved by direct methods (SHELXS-97) [13] and difference Fourier maps (SHELXL-97). Refinement was carried out against F^2 by weighted full-matrix least-squares (SHELXL-97). Empirical absorption corrections (XABS2) [14] were applied for **2**. Hydrogen atoms were either found in difference maps or placed at calculated positions, and refined using a riding model with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the amine for compound **5** were found in difference Fourier maps. Atomic scattering factors were taken from the International Tables for Crystallography [15]. Crystal data and relevant details of the structure determinations are summarized in Table 1 and selected geometrical parameters are given in Table 2. Figs. 1–3 show the molecular structures of **1**, **2**, and **5**.

Table 1
Crystallographic data for **1**, **2** (**a** and **b**), and **5**

	1	**2**	**5**
Empirical formula	$C_{36}H_{46}Cl_2N_2O_2Sn$	$C_{90}H_{114}Cl_4N_4O_4Sn_2$	$C_{25}H_{36}Cl_2N_2OSn$
Formula weight	728.34	1695.03	570.15
λ (Å)	0.71073	0.71073	0.71073
Temperature (K)	144(1)	173(1)	173(1)
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	11.369(2)	25.4290(10)	13.068(2)
b (Å)	13.087(2)	28.232(2)	12.185(2)
c (Å)	13.101(2)	12.0860(10)	16.553(3)
α (°)	74.716(10)	90	90.00(2)
β (°)	75.828(10)	97.159(10)	100.53(2)
γ (°)	87.217(10)	90	90.00(2)
V (Å^3)	1822.8(5)	8609.0(10)	2591.4(7)
Z	2	4	4
δ (g cm^{-3})	1.327	1.308	1.461
μ (mm^{-1})	0.879	0.755	1.211
R_1 (%)	3.32	3.37	5.94
wR_2 (%)	5.82	8.26	6.70
Goodness-of-fit	1.042	1.058	1.135

Table 2
Selected bond lengths (Å) and angles (°) for **1**, **2**, and **5**

	1	**2(a)**	**2(b)**	**5**
Bond lengths				
Sn–O1	1.9969(14)	1.9998(14)	1.9913(13)	2.040(3)
Sn–O2	1.9965(14)	1.9985(13)	1.9949(14)	
Sn–N1	2.1501(17)	2.1390(16)	2.1487(16)	2.196(3)
Sn–N2	2.1455(17)	2.1522(16)	2.1433(16)	2.270(3)
Sn–Cl1	2.4250(6)	2.4107(6)	2.4263(6)	2.4675(13)
Sn–Cl2	2.4241(6)	2.4276(6)	2.4123(6)	2.4781(12)
Sn–C				2.136(4)
Bond angles				
O1–Sn–O2	103.23(6)	101.34(6)	100.78(6)	
O1–Sn–N1	89.36(6)	90.87(6)	90.44(6)	85.23(12)
O2–Sn–N2	90.01(6)	90.22(6)	91.02(6)	
O1–Sn–N2	166.35(6)	168.39(6)	168.16(6)	160.74(11)
O2–Sn–N1	167.10(6)	167.71(6)	168.73(6)	
N1–Sn–N2	77.61(6)	77.56(6)	77.74(6)	75.52(12)
O1–Sn–Cl2	89.54(4)	89.47(5)	89.95(4)	91.05(8)
O2–Sn–Cl2	90.66(5)	91.63(4)	91.10(5)	
N1–Sn–Cl2	92.26(5)	87.11(5)	89.98(5)	82.36(9)
N2–Sn–Cl2	86.96(5)	89.22(5)	90.82(5)	86.98(9)
O1–Sn–Cl1	90.35(4)	90.73(5)	91.46(4)	92.45(8)
O2–Sn–Cl1	89.63(5)	90.37(4)	89.54(5)	
N1–Sn–Cl1	87.46(5)	90.81(5)	89.09(4)	83.36(9)
N2–Sn–Cl1	93.08(5)	90.17(5)	87.62(5)	84.90(9)
Cl1–Sn–Cl2	179.70(2)	177.91(2)	178.32(2)	164.96(4)

2.3. Syntheses

The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature [16]. Triethylamine, n-butyltin trichloride, and tin tetrachloride were purchased (Aldrich) and used as received.

2.3.1. Synthesis of Salophen(^{t}Bu)$SnCl_2$ (**1**) and Salophen(^{t}Bu)(^{n}Bu)SnCl (**3**)

Triethylamine (1.03 ml, 7.4 mmol) was added to a solution of Salophen(^{t}Bu)H_2 (2.0 g, 3.70 mmol) dissolved in 40 ml of $C_6H_5CH_3$. The reaction mixture was stirred, and n-butyltin trichloride (0.62 ml, 3.70 mmol)

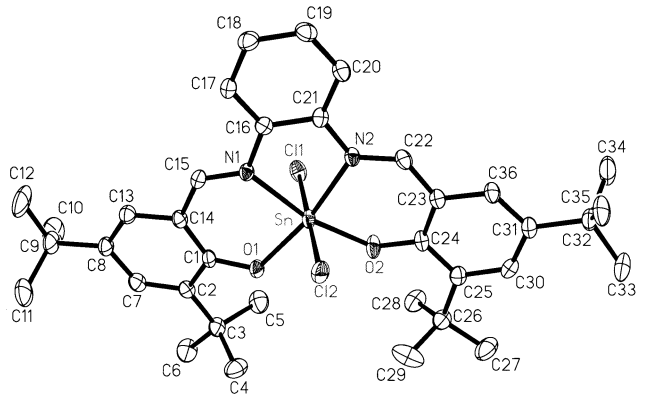


Fig. 1. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **1**. Hydrogens atoms are omitted for clarity.

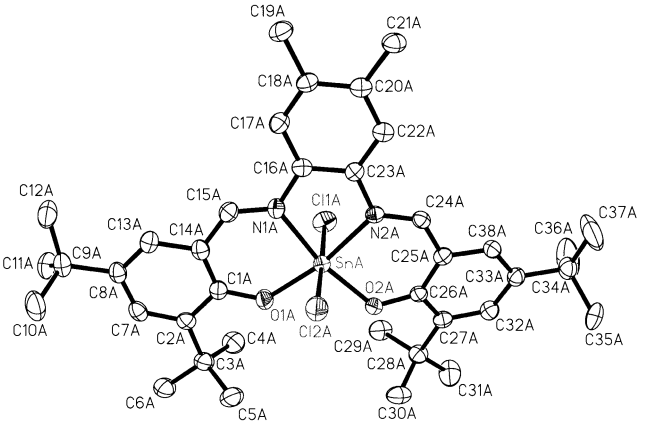


Fig. 2. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **2**. Hydrogens atoms are omitted for clarity.

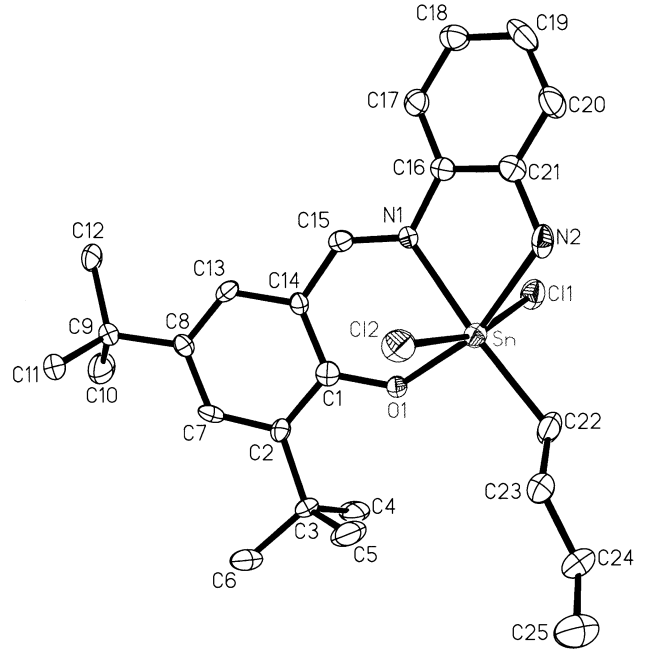


Fig. 3. Thermal ellipsoid plot (50% probability ellipsoids) showing the molecular structure of **5**. Hydrogens atoms are omitted for clarity.

added. The orange solution turned red during the course of the addition, and a precipitate formed. The mixture was refluxed for 1 h, and then allowed to cool to room temperature (r.t.) The solvent layer was filtered by cannula into another Schlenk flask. The solvent layer was divided into two equal portions. The solvent was removed from one portion via vacuum to leave behind an orange solid. NMR, IR and MS characterized this solid as **3** (yield: 1.530 g, 55%, based on ligand). Yellow X-ray quality crystals (yield: 0.809 g, 30%, based on ligand) were obtained from the other solvent layer portion, after being stored at r.t. for 3 days. These crystals were identified as **1** by NMR, IR and single crystal X-ray analysis.

Compound **1** can also be prepared by the reaction of $SnCl_4$ and Salophen(^{t}Bu)H_2 in the presence of Et_3N. Triethylamine (0.26 ml, 1.86 mmol) was added to a solution of Salophen(^{t}Bu)H_2 (0.50 g, 0.93 mmol) dissolved in 40 ml of $C_6H_5CH_3$. The reaction mixture was stirred, and tin tetrachloride (0.11 ml, 0.93 mmol) added. The orange solution turned red during the course of the addition. The mixture was refluxed overnight, and then the solvent layer was cannula filtered into another Schlenk flask. A small portion of the solvent layer was removed for recrystallisation. The solvent was removed from the major portion of the solvent layer under vacuum to leave behind a red solid. This solid, and the red crystals formed from the solvent layer, were show to be **1** by NMR, IR, m.p. and single crystal X-ray analysis. Yield: 0.610 g, 90%, based on ligand. Salophen(^{t}Bu)$SnCl_2$ (**1**): M.p. 165–170 °C, gel formed. At 180–182 °C the gel melted to a red/orange liquid. ^{1}H NMR ($CDCl_3$): δ 1.35 [s, 18H, $C(CH_3)_3$], 1.55 [s, 18H, $C(CH_3)_3$], 2.36 [s, 3H, $C_6H_5CH_3$], 7.16 [d, 2H, Ar–H], 7.50–7.81 [m, 11H, Ar–H + $C_6H_5CH_3$], 8.60 [s, 2H, N=CH]. $^3J(^{119}Sn–H)$ 37 Hz. IR cm^{-1}: ν 1620 (C=N), 560 (Sn–O), 499 (Sn–N), 305 (Sn–Cl). *Anal*. Calc. (found) for $C_{36}H_{46}Cl_2N_2O_2Sn$: C, 59.32 (59.42); H, 6.37 (6.32%).

Salophen(^{t}Bu)(^{n}Bu)SnCl (**3**): M.p. 184–186 °C. ^{1}H NMR ($CDCl_3$): δ 0.73 [t, 3H, CH_3 of ^{n}Bu], 0.95 [m, 2H, CH_2 of ^{n}Bu], 1.16–1.30 [m, 4H, CH_2+CH_2 of ^{n}Bu], 1.31 [s, 18H, $C(CH_3)_3$], 1.50 [s, 18H, $C(CH_3)_3$], 7.12 [d, 2H, Ar–H], 7.10–7.61 [m, 11H, Ar–H + $C_6H_5CH_3$], 8.58 [s, 2H, N=CH]. ^{119}Sn NMR (Me_4Sn): δ −501. $^3J(^{119}Sn–H)$ 12.7 Hz. IR cm^{-1}: ν 1615 (C=N), 540 (Sn–C), 552 (Sn–O), 490 (Sn–N), 300 (Sn–Cl). *Anal*. Calc. (found) for $C_{40}H_{55}ClN_2O_2Sn$: C, 63.97 (64.01); H, 7.39 (7.47%).

2.3.2. Synthesis of Salomphen(^{t}Bu)$SnCl_2$ (2) and Salomphen(^{t}Bu)(^{n}Bu)SnCl (4)

These compounds were synthesized utilizing a similar procedure to that for **1** and **3**, using 3.0 g (5.28 mmol) of Salomphen(^{t}Bu)H_2, 1.47 ml (10.56 mmol) of Et_3N, and 0.88 ml (5.28 mmol) of ^{n}BuSnCl_3. Crystals of **2** suitable for X-ray analysis were formed from the solvent layer after 2 weeks. Yield: 1.343 g, 30% (based on li-

gand).Compound **4** was obtained as an orange/red solid when the solvent was removed in vacuo from the solvent layer. Yield: 2.465 g, 60% (based on ligand).

Compound **2** can also be prepared by the reaction of $SnCl_4$, Salomphen(^{t}Bu)H_2, and Et_3N. Triethylamine (0.25 ml, 1.76 mmol) was added to a solution of Salomphen(^{t}Bu)H_2 (0.45 g, 0.79 mmol) dissolved in 40 ml of $C_6H_5CH_3$. The reaction mixture was stirred, and tin tetrachloride (0.09 ml, 0.79 mmol) added. The orange solution turned red and was refluxed overnight. The solvent layer was filtered by cannula into another Schlenk flask. A small portion of the solvent layer was removed for recrystallisation. The solvent was removed under vacuum to leave behind an orange solid. Yield: 0.589 g, 88% (based on ligand). This solid and the crystals formed from the solvent layer was shown to be **2** by NMR, IR, m.p. and single crystal X-ray analysis. Salomphen(^{t}Bu)$SnCl_2$ (**2**): M.p. 128–130 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.33 [s, 18H, $C(CH_3)_3$], 1.54 [s, 18H, $C(CH_3)_3$], 2.35 [s, 3H, $C_6H_5CH_3$], 2.41 [s, 6H, Ar–CH_3], 7.15–7.25 [m, 5H, $C_6H_5CH_3$], 7.18 [d, 2H, Ar–H], 7.52 [s, 2H, N–Ar–H–N], 7.68 [d, 2H, Ar–H], 8.70 [s, 2H, N=CH]. $^3J(^{119}Sn–H)$ 39 Hz. IR cm^{-1}: ν 1616 (C=N), 557 (Sn–O), 491 (Sn–N), 300 (Sn–Cl). *Anal*. Calc. (found) for $C_{45}H_{57}Cl_2N_2O_2Sn$ (one molecule of $C_6H_5CH_3$ included): C, 63.73 (63.69); H, 6.78 (6.89%).

Salomphen(^{t}Bu)(^{n}Bu)SnCl (**4**): M.p. 240–242 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 0.72 [t, 3H, CH_3 of ^{n}Bu], 0.94 [m, 2H, CH_2 of ^{n}Bu], 1.16–1.30 [m, 4H, CH_2+CH_2 of ^{n}Bu], 1.31 [s, 18H, $C(CH_3)_3$], 1.50 [s, 18H, $C(CH_3)_3$], 2.35 [s, 3H, $C_6H_5CH_3$], 2.39 [s, 6H, Ar–CH_3], 7.12 [d, 2H, Ar–H], 7.15–7.25 [m, 5H, $C_6H_5CH_3$], 7.34 [s, 2H, N–Ar–H–N], 7.60 [d, 2H, Ar–H], 8.53 [s, 2H, N=CH]. ^{119}Sn NMR (Me_4Sn): δ −450. $^3J(^{119}Sn–H)$ 39 Hz. IR cm^{-1}: ν 1601 (C=N), 549 (Sn–C), 542 (Sn–O), 453 (Sn–N), 301 (Sn–Cl). MS (EI$^+$): 743 [M^+ −Cl], 721 [M^+ −Bu]. *Anal*. Calc. (found) for $C_{42}H_{59}ClN_2O_2Sn$: C, 64.75 (64.70); H, 7.64 (7.71%).

2.3.3. Synthesis of Phensal(^{t}Bu)(^{n}Bu)$SnCl_2$ (**5**)

To a solution of Phensal(^{t}Bu)H_3 (2.0 g, 6.16 mmol) dissolved in 30 ml of $C_6H_5CH_3$ was added 1.03 ml (6.16 mmol) of ^{n}BuSnCl_3. The resulting orange solution was stirred at r.t. for 5 h. The solvent was removed to leave behind an orange solid. Yield: 2.810 g, 80% (based on ligand). The solid was recrystallized from $C_6H_5CH_3$, affording crystals suitable for X-ray analysis. M.p. 134–136 °C. ^{1}H NMR ($CDCl_3$): δ 0.74 [t, 3H, CH_3 of ^{n}Bu], 0.9–1.0 [m, 2H, CH_2 of ^{n}Bu], 1.2–1.3 [m, 2H, CH_2 of ^{n}Bu], 1.32 [s, 18H, $C(CH_3)_3$], 1.4–1.42 [m, 2H, CH_2 of ^{n}Bu], 1.52 [s, 18H, $C(CH_3)_3$], 2.35 [s, 3H, $C_6H_5CH_3$], 2.91 [s, 2H, Ar–NH_2], 7.1–7.7 [m, C_6H_2+C_6H_4+$C_6H_5CH_3$], 8.60 [s, 2H, N=CH]. $^3J(^{119}Sn–H)$ 13.4 Hz. IR cm^{-1}: ν 1617 (C=N), 552 (Sn–C), 560 (Sn–O), 497 (Sn–N), 310 (Sn–Cl). *Anal*. Calc. (found) for $C_{25}H_{36}Cl_2N_2OSn$: C, 51.18 (50.97); H, 6.19 (6.30%).

3. Results and discussion

3.1. Synthesis

The Schiff base ligands, LH_2 (L = Salophen(^{t}Bu), Salomphen(^{t}Bu)) and LH_3 (Phensal(^{t}Bu)), were prepared by the condensation of 3,5-di-*tert*-butylsalicylaldhyde with the corresponding phenylenediamine in a 2:1 or 1:1 stoichiometry, respectively. Compounds **1** and **2** were prepared by combining $SnCl_4$ with LH_2 in the presence of triethylamine. Synthesis of compounds **1** and **2**, along with **3** and **4**, can also be achieved by combining (^{n}Bu)$SnCl_3$ with LH_2 in the presence of triethylamine (Scheme 1a). This reaction leads to a mixture of L(^{n}Bu)SnCl and $LSnCl_2$. The formation of $LSnCl_2$ may be due to a disproportionation reaction (Eq. (1)) or a redistribution (Eq. (2)) occurring in solution.

$$2L(^nBu)SnCl \rightarrow LSnCl_2 + (^nBu)_2SnL \quad (1)$$

$$L(^nBu)SnCl + (^nBu)SnCl_3 \rightarrow LSnCl_2 + (^nBu)_2SnCl_2 \quad (2)$$

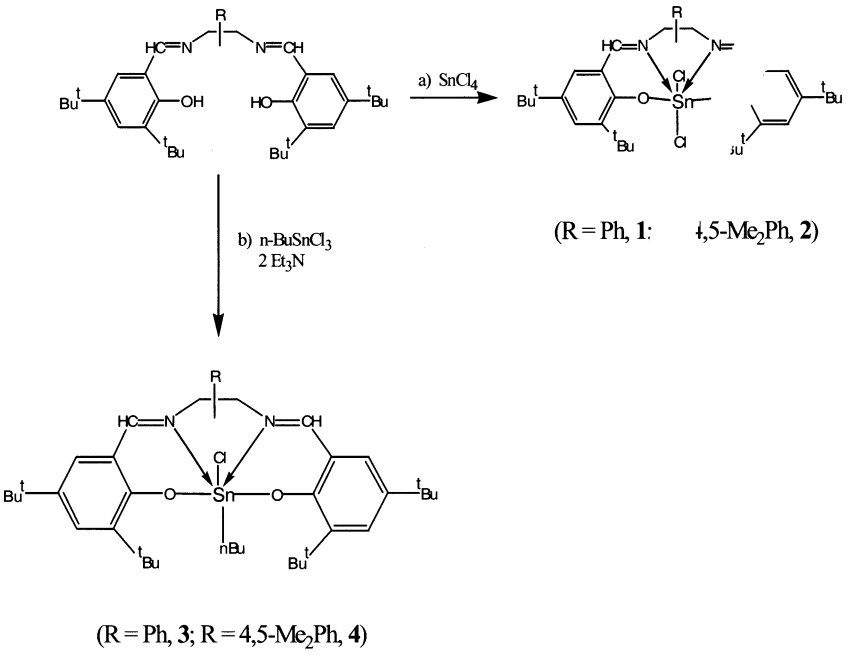
Aliquots of the reaction mixture were removed, and tested by NMR. However, formation of the dialkyl tin species was not detected. ^{119}Sn NMR did not detect the presence of a four-coordinate species (as would be expected in Eq. (2)). We cannot be certain of the reaction path for the formation of the $LSnCl_2$ products, however further investigations are being carried out in our labs to determine the mechanism of this reaction.

The L(^{n}Bu)SnCl and $LSnCl_2$ products can be observed in solution by measurement of the tin coupling constants, and may be separated by fractional crystallization. The $LSnCl_2$ products crystallize out of solution prior to the L(^{n}Bu)SnCl product when cooled to −30 °C. The solubility in organic solvents is expected to decrease in the order (^{n}Bu)$_2$SnL > L(^{n}Bu)SnCl > $LSnCl_2$. The L(^{n}Bu)SnCl species is observed in solution by NMR after $LSnCl_2$ is crystallized out. Integration of the methyl peak (approximately δ 0.7 ppm) of the ^{n}Bu group indicates the presence of only one ^{n}Bu group (as opposed to two, as would be expected if L(^{n}Bu)$_2$Sn were formed). It is possible that the presence of only one ^{n}Bu group per ligand could indicate the presence of the products from the disproportionation reaction (Eq. (1)). However, the signals due to the ligand indicate the presence of only one type of ligand (for example, only one imine proton is observed). If both products were present, two types of ligand peaks would be expected.

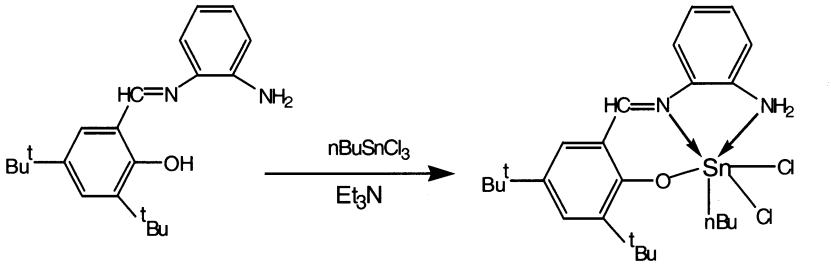
Compound **5** was prepared by the reaction of the tridentate ligand, Phensal(^{t}Bu)H_3, with ^{n}BuSnCl_3 (Scheme 1b).

Compounds **1**–**5** are soluble in polar and non-polar solvents. Interestingly, **1**–**5** produces a yellow/orange solution when dissolved in THF, toluene, benzene, or acetonitrile, but a red solution when dissolved in

(a)



(b)



Scheme 1. (a) General syntheses of compounds **1**–**4**. (b) General syntheses of compound **5**.

dimethylsulfoxide. These compounds are relatively air stable, producing the same melting points and NMRs even after being left in air for a few days. Other Sn–Salen chelates have also been shown to be air stable [5,17,18].

3.2. Spectroscopy

3.2.1. NMR spectra

Compounds **1**–**4** retain their monomeric solid state structures in solution. The ^{t}Bu resonances of the ligands are seen as a pair of singlets in the region δ 1.3–1.5. Dimeric derivatives would show more complexity for these resonances, as observed in [Salen(^{t}Bu)Al]$_2$O [19]. Further confirming the monomeric nature of **2** and **4** is the presence of only one peak for the Me–Ph group (approximately δ 2.4) of the ligand. For **3**, **4**, and **5**, the CH_3 protons of the ^{n}Bu groups appear as a triplet at δ 0.6–0.8 ppm and the γ-CH_2 protons appear as a multiplet at approximately δ 1.0 ppm. The α- and β-CH_2 protons of the n-butyl groups also appear as multiplets, but overlap with the signals from the *tert*-butyl groups. The aromatic protons on the rings of the ligand of **2** and **4** can be distinguished from each other. The ^{t}Bu–Ph protons occur at 7.1, 7.6 ppm, and the N–Ph–N aromatic protons occur at 7.3–7.4 ppm.

The methine proton for **1**–**5** were located at δ 8.5–8.7 as a single peak. This suggests that the two CH=N protons are equivalent, and further supports the idea of a monomeric solution state structure. It also suggests planarity of the ligand. The equivalence of the methine and ^{t}Bu protons, and the CH_3 protons of the Me–Ph group in **2** and **4** indicate a *trans* arrangement of the two alkyl groups on tin. The symmetrical arrangement of the

ligand, and *trans* arrangement of the alkyl groups on tin, suggest an octahedral environment around the central tin atom (as shown in Scheme 1a). The NH_2 protons for **5** were located at 2.91 ppm.

Coupling (^3J) of the methine proton to the tin atom was observed. The magnitude of the coupling constant was used to determine the tin species present in solution. For the dichloro compounds, **1** and **2**, a coupling constant of $^3J(^{119}Sn–H)$ 37 and 39 Hz, respectively, was observed. This compares well to the value calculated for $SalenSnCl_2$, $^3J(^{119}Sn–H)$ 36 Hz [20]. For the alkyl chloro Sn derivatives, **3** and **4**, coupling constants of $^3J(^{119}Sn–H)$ 12.6 and 13.2 Hz, respectively, were calculated. No coupling was observed between the protons on the ^{n}Bu group and the Sn atom. For Sn compounds ^3J is larger than ^2J [21]. When the triethylammonium chloride precipitate from **2** and **4** was washed with hexane, and the hexane extract evacuated to dryness, the NMR of the resulting yellow/orange solid showed it to contain both $LSnCl_2$ and L(^{n}Bu)SnCl. There were two pairs of peaks in the ^{t}Bu region (1.31, 1.33, 1.49, 1.54 ppm), two peaks (2.39, 2.41 ppm) in the L–CH_3 region, two sets of peaks in the aromatic region (7.12–7.34, 7.51–7.68 ppm), and two peaks due to the imine protons (8.52, 8.70 ppm). There was only one triplet (0.73 ppm) in the region of the spectra assigned to the methyl of the ^{n}Bu group. The coupling of the imine protons to the Sn atom was 13.1 (due to the signal at 8.53 ppm) and 39.2 Hz (due to the signal at 8.70 ppm).

^{119}Sn NMR was carried out on **3** (δ −501 ppm) and **4** (δ −450 ppm). The chemical shifts are in the range for six-coordinate tin compounds [22]. This further supports the structure shown in Fig. 2. The values for **3** and **4** also compare well with other six-coordinate Salen–Sn complexes. For example, R_2Sn(Vanophen) (R = Ph (−543); R = ^{n}Bu (−414); R = Me (−398); Vanophen = *N*,*N*′-1,2-phenylene-bis(3-methoxysalicylideneimine)), and R_2Sn(Salophen) (R = ^{n}Bu (−415)) [5]. These chemical shifts also show that substituents on the phenyl ring of the ligand (^{t}Bu for **3** and **4**, methoxy for Vanophen) have no significant effect on the shielding or deshielding of the tin nucleus.

3.2.2. IR spectra

The IR spectra of **1**–**5** showed strong absorption bands at 1600–1620 cm^{-1}, which can be attributed to the $\nu_{C=N}$ stretching frequency. The shift to lower frequencies (compared to the free ligand) indicates donation of the nitrogen lone pair of the azomethine group to the Sn atom. In contrast, adduct formation results in a $\nu_{C=N}$ shift to higher frequencies [5]. For **3** and **4**, the presence of ν(Sn–C) bands in the IR further confirm the structure proposed in Fig. 2. The (Sn–C) band for **3** is at 540 cm^{-1}, and at 549 cm^{-1} for **4**. This compares well with the ν(Sn–C) band (534 cm^{-1}) observed for (^{n}Bu)$_2$SnVanophen. The bands at 550–560 cm^{-1} can be assigned to the Sn–O bond. The bands at 450–500 cm^{-1} can be assigned to the Sn–N bond [5]. For **1** and **2**, the bands at 299–305 cm^{-1} can be assigned to the Sn–Cl bond [20].

3.2.3. Structural characterization

Compound **2** crystallizes with two independent molecules in the asymmetric unit that do not differ significantly from each other. The bond lengths and angles from molecule **2a** will be used in the discussion below. Two molecules of toluene, each disordered over two sites, are also present. Spectroscopic data and X-ray analysis have shown Salen–Sn complexes to have octahedral ($SalenSnR_2$), square pyramidal, and tetrahedral (SalenSn) geometries [4]. In each case the ligand occupies the equatorial coordination sites around the central tin atom. For the new Sn–Salen complexes presented here, the structures consist of a central six-coordinate tin atom in a distorted O_h geometry. For **1** (Fig. 1) and **2** (Fig. 2), the Salen(^{t}Bu) ligand occupies the four equatorial positions, with the chlorine atoms in the axial positions. For **5** (Fig. 3), the tridentate Phensal(^{t}Bu) ligand occupies three of the equatorial sites. The fourth is occupied by the n-butyl group. As in **1** and **2**, the axial positions are occupied by chlorine atoms.

The distorted octahedral geometry around the tin atom is a result of the strain imposed by the tetradentate ligand, and from the constraints imposed by the six-membered ring Sn–N–C–C–C–O. This is reflected in the equatorial plane for **1** and **2** with the large O1–Sn–O2 angle (103.23(6) and 101.34(6)°, respectively), and the correspondingly more acute N1–Sn–N2 angle [77.61(6) and 77.56(6)°, respectively]. The distorted geometry can also be seen in the deviation from 180° of the angles O1–Sn–N2 and O2–Sn–N2 [**1** 166.35(6) and 167.10(6)°, **2** 168.39(6) and 167.71(6)°).

The distorted octahedral geometry is not reflected in the axial plane. The Cl–Sn–Cl bond angle for **1** and **2** is close to the ideal value of 180° [179.70(2) and 177.91(2)°, respectively]. With the slightly more flexible tridentate Phensal(^{t}Bu) ligand, the Cl–Sn–Cl angle of 164.96(4)° in **5** is less than the idealized 180°. However, the geometry around the tin atom is not as distorted as reported for other six-coordinate organotin tetradentate ligand complexes [4]. The bite angles O1–Sn–N1 and O2–Sn–N2 are similar for **1**, **2**, and **5** (approximately 90°), but larger than those reported for other six-coordinate tin Schiff base compounds. For example, the bite angles for ^{n}Bu$_2$SnVanophen are 80.19(6)° and 78.98(7)°, respectively [23,24]. The four-coordinating atoms of the (N_2O_2) plane in **1** and **2** are coplanar, implying that the Salen(^{t}Bu) ligands are flat. This is reflected in the nearly identical $(O–Sn–N)_{trans}$ angles in **1** and **2** of 166 and 168°. SalomphenSn also possesses identical $(O–Sn–N)_{trans}$ angles (119.4°) and a planar

(N_2O_2) core [25]. For **1**, **2**, and **5**, the equatorial angles are more obtuse for the oxygens around tin (101.34(6)–103.23(6)°) and more acute for the nitrogens (75.52(12)–77.61(6)°).

The Sn–O bond lengths for **1**, **2**, and **5** (Table 2) are similar to other tin compounds, a typical Sn–O bond distance in the SnO_4N_2 system being around 2.02 Å [26]. The Sn–N distances for **1**, **2**, and **5** (average—2.148, 2.146, 2.233 Å, respectively) are much shorter than those observed in Sn(IV) systems with Sn←N donor acceptor bonds (> 2.37 Å) [27]. The Sn–N bond lengths for **5** are significantly larger than the Sn–N bond lengths for **1** and **2**. In compound **5** the Sn–N2 bond, 2.270(3) Å, is longer than the Sn–N1 bond, 2.196(3) Å. This is due to N1 being an imine and N2 being bound to a hydrogen. The Sn–C bond lengths of **5** compare well with the range found in other hexa-coordinate diorganotin(IV) compounds, for example 2.100(3) and 2.115(3) Å in Me_2SnVanophen, 2.17(1) Å in Ph_2SnVanophen, [5] and 2.16(4) and 2.07(3) Å in Me_2SnSalen [28]. The Sn–C bond in **5**, 2.136(4) Å, is slightly longer than in other organotin complexes derived from ONO donor tridentate Schiff bases, for example 2.102(7) and 2.103(6) Å in [*N*-(2-carboxyphenyl)salicylideneiminato]-dimethyltin(IV) [24]. In Ph_2SnSalAp (where SalAp = salicylideneamino-*o*-hydroxybenzene), the Sn–C bonds are 2.118(5) and 2.111(5) Å [29].

The tin atom is slightly displaced from the N_2O_2 plane by 0.056 Å in **1**. However, in **2** (which possess a dimethylphenyl backbone instead of a phenyl backbone), the Sn atom is significantly more out of the N_2O_2 plane. The tin atom is 0.719 Å above the plane for one of the molecules in the asymmetric unit of **2**, and 0.897 Å above the plane for the other molecule in the asymmetric unit of **2**. The displacement of the Sn atom from the N_2O_2 plane has also been observed in SalenSn (1.08 Å) [30], and SalomphenSn (1.13 Å) [25].

4. Supplementary material

Crystallographic data for compounds **1**, **2** and **5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176737, 176762, and 176738. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Science Foundation NSF-CAREER award (CHE 9816155). NMR instruments used in this research were obtained with funds from the CRIF program of the National Science Foundation (CHE 997841) and from the Research Challenge Trust Fund of the University of Kentucky.

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