

Preliminary communication

Tetradentate $-N_2O_2$ ligand complexes of Tin(II). X-ray crystal structure of [N,N' -(1,2-ethylene) bis(salicylaldamine)]tin(II), (SaleanH₂Sn)

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Abstract

The tetradentate $-N_2O_2$ ligands, [N,N' -(1,2-ethylene)bis(salicylaldamine)] (SaleanH₄) (1), [N,N' -(1,3-propylene)bis(salicylaldamine)] (SalpanH₄) (2) and [N,N' -(1,2-phenylene)bis(salicylaldamine)] (SalophanH₄) (3), were used to prepare Sn(II) complexes that are monomeric (SaleanH₂Sn (7), SalpanH₂Sn (8)) and dimeric ([SalophanH₂Sn]₂) (9). The structure of 7 was determined by single-crystal X-ray crystallography: orthorhombic, space group pbcn with $a = 19.849(4)$, $b = 10.791(3)$, $c = 18.559(5)$ Å and $Z = 8$. Compounds 8 and 9 undergo transmetallation reactions with three equivalents of AlMe₃ to produce the trimetallic derivatives, SalpanAlMe(AlMe₂)₂ (10) and SalophanAlMe(AlMe₂)₂ (11).

Keywords: Tin; Aluminium; Transmetallation

Multidentate Schiff base chelates, made from the condensation of a diamine with salicylaldehyde (SalenH₂), have been used extensively in the preparation of unimolecular Sn(IV) [1,2], and to a lesser extent, Sn(II) complexes [2,3]. Based upon spectroscopic data, and in rare cases, X-ray analysis, these complexes have been demonstrated to adopt octahedral (SalenSnR₂) and square pyramidal (SalenSn) geometries, respectively. In each case the ligand occupies the equatorial coordination sites around the central tin atom. A similar type of bonding arrangement may be available with the reduced version of these Schiff base ligands (SalanH₄), shown in Scheme 1. However, these molecules will be more flexible owing to the absence of the imine bond, and thereby, may accommodate a wider range of metal geometries. Additionally, these can act as 2- ligands as for the Schiff bases, but may also act as 3- and 4- ligands by forming sigma bonds through the amine functionalities.

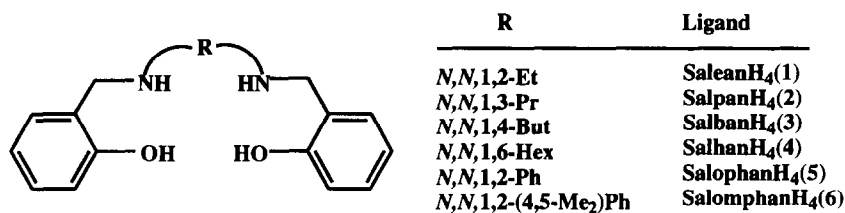
We have been actively examining the unique and unusual complexes that form from the use of these ligands with the s and p block elements. For example, we have shown that Zn(II) complexes of 2, 5 and 6

adopt dimeric structures in the solid and solution state [4]. Additionally, we have prepared a series of complexes between 2 and AlMe₃ in stoichiometries of 1:1 (SalpanH₂AlMe), 1:2 (SalpanAlMe(AlMe₂)) and 1:3 (SalpanAlMe(AlMe₂)₂) [5]. The trimetallic gallium complexes, SalanGaMe(GaMe₂)₂ where Salan = 1, 2, 5 and 6 have also been reported [6].

In the present work we continue this study to include complexes of Sn(II). Thus, the synthesis and characterization of SaleanH₂Sn (7), SalpanH₂Sn (8) and SalophanH₂Sn (9) are reported. Monomeric structures for 7 and 8 have been determined by single-crystal X-ray analysis and spectroscopic data, respectively. The data, however, suggests a dimeric structure for 9. These are the first reported complexes of Sn(II) with the SalanH₄ class of ligand.

Compounds 7–9 were prepared by the following general method. To a stirring solution of the ligand (7.34 mmol) in refluxing methanol (50 ml) was added NEt₃ (14.69 mmol). After stirring for 5 min a solution of SnCl₂ (7.34 mmol) in refluxing methanol (15 ml) was added over a period of 5 min. The nearly colorless ligand solution turned yellow upon addition of the SnCl₂ solution. The solution was allowed to reflux for 35 min at which point it was filtered while hot to remove a small amount of insoluble material which had formed. After cooling to 25 °C the solution was stored at –30°C for 15 h during which time the product

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Scheme 1. A listing of the SalanH₄ ligands used in this study and mentioned in the text.

appeared as pale yellow needles (for **7**) or as a pale microcrystalline solid (for **8** and **9**). The products were isolated by filtration, washed with three portions of cold MeOH (5 ml), and dried at 25°C for 3 h to give **7**, **8** and **9** in 71%, 50% and 63% yield, respectively. Compounds **7** and **8** were soluble in a wide range of solvents including benzene, toluene, MeOH, DMSO and THF. However, **9** proved to be completely insoluble in these and other solvents. As such, solution state data were unavailable.

Previously reported zinc [4] and aluminum [5] complexes of **1**, **2**, **5** and **6** indicated that the ligands maintained a rigid solution state geometry. This was evidenced by methylene groups that possessed inequivalent protons (PhCH_aH_b) and were thus manifested as doublets of doublets. A similar type of solution-state behavior was not seen for **7** and **8**. Rather, the ¹H NMR data [7] for these complexes exhibited broad resonances

with no resolved coupling. Collection of the NMR data at –80 °C did not appreciably affect the spectra. For **7** there are two broad singlets at 3.58 and 3.81 ppm which can be attributed to the PhCH₂ groups and two broad singlets for the NCH₂ groups at 2.75 and 2.95 ppm. The inequivalence of the O and N atoms that this data implies is also evident in the solid state structure (vide infra). For **8**, the proton NMR did not reveal this type of inequivalence, and the methylene groups appeared as a broad singlet at 4.00 ppm while the propyl hydrogens appeared as two broad multiplets at 2.25 and 3.19 ppm. This may be indicative of a more fluxional ligand environment for **8** compared with **7**. The NH groups were confirmed by the presence of broad singlets at 4.42 and 4.35 ppm for **7** and **8**, respectively.

The ¹¹⁹Sn NMR of **7** and **8** demonstrated singlets at –523.6 and –521.3 ppm, respectively, which fall in the range of shift values corresponding to 4-coordinate

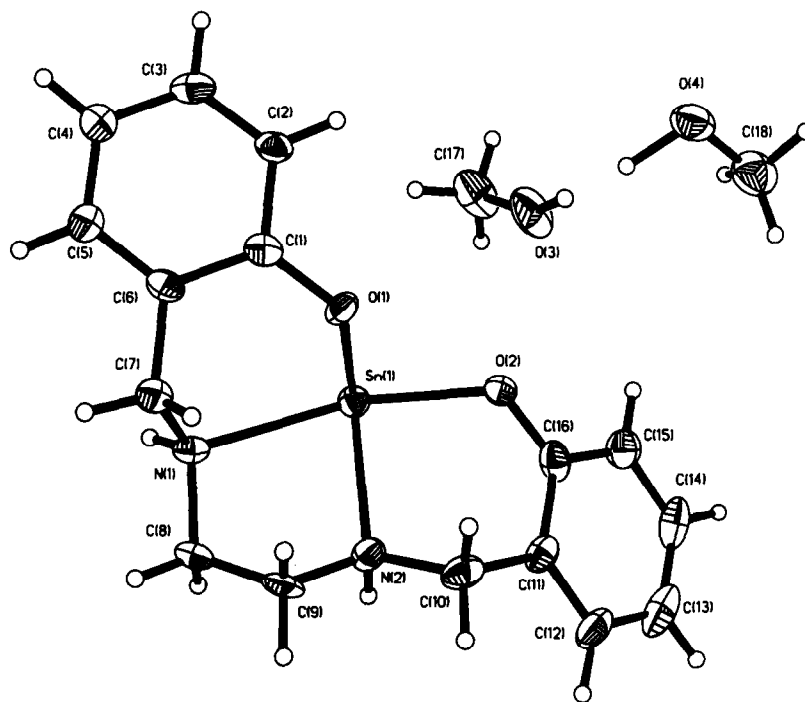


Fig. 1. Molecular structure and atom numbering scheme for **7**. Selected bond lengths (Å) and angles (°): Sn(1)–O(1) 2.095, Sn(1)–O(2) 2.202(6), Sn(1)–N(1) 2.535(9), Sn(1)–N(2) 2.369(8), O(1)–C(1) 1.348(12), O(2)–C(16) 1.328(14), N(1)–C(7) 1.482(14), N(1)–C(8) 1.477(13), N(2)–C(9) 1.468(15), N(2)–C(10) 1.500(14); O(1)–Sn(1)–O(2) 78.7(3), O(1)–Sn(1)–N(1) 80.0(3), O(2)–Sn(1)–N(1) 141.9(3), O(1)–Sn(1)–N(2) 101.7(3), O(2)–Sn(1)–N(2) 81.9(3), N(1)–Sn(1)–N(2) 72.0(3), Sn(1)–O(1)–C(1) 115.5(6), Sn(1)–O(2)–C(16) 117.9(6), Sn(1)–N(1)–C(7) 113.1(6), Sn(1)–N(1)–C(8) 106.4(7), Sn(1)–N(2)–C(9) 113.1(6), Sn(1)–N(2)–C(10) 113.8(6).

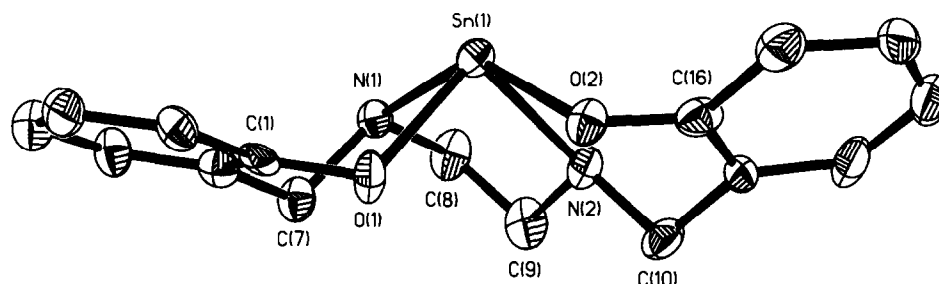


Fig. 2. A structural view of **7** emphasizing the position of the Sn(II) lone pair of electrons.

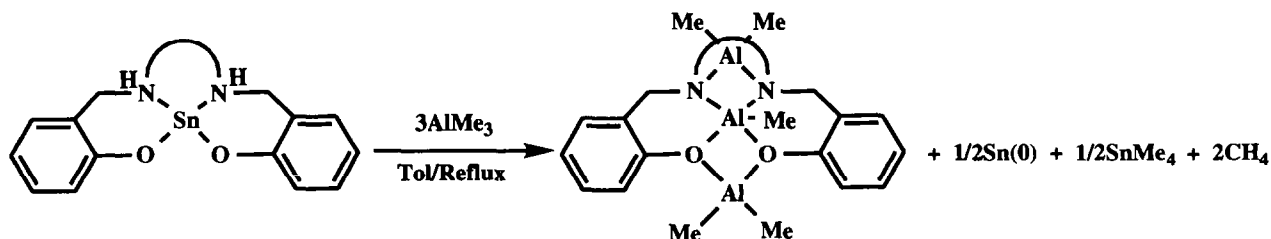
Sn(II). These values compare closely with that seen for the 4-coordinate complexes Sn(Salen) (-564.04 ppm) and Sn(Salophen) (-543.3 ppm) [3].

The mass spectral data [8] for **7** and **8** correspond to monomeric species in the gas phase. For **9**, however, the highest mass peak corresponded to a dimeric formulation. This would presumably give rise to a structure in which an oxygen of each ligand bridges the two Sn atoms. This would be the same type of structure seen for such zinc(II) complexes as [SalophanH₂Zn]₂ [4] and for Sn(II) complexes such as [Sn(Salop)]₂ (Salop = *N*-(2-oxidophenyl)salicylideneiminato) [3]. Crystals of **7** suitable for X-ray analysis were grown from MeOH which had been kept at -30 °C for 1 day. The molecular structure and atom numbering scheme is shown in Fig. 1. Selected bond distances and angles comprise the figure caption. In the crystal structure there are two molecules of MeOH which are hydrogen bonded to each other at a distance of 1.54 Å. The shortest contact between one of these molecules and the SalcanH₂Sn unit is 2.86 Å. The Sn atom adopts a square pyramidal geometry with the Salcan ligand forming the basal plane and the Sn lone pair in the axial position. The Sn atom is displaced 1.08 Å from the N₂O₂ plane. A structural view emphasizing this geometry is shown in Fig. 2. There are significant variations in the Sn–O (Sn–O(1) 2.095(7) and Sn–O(2) 2.202(6) Å) and Sn–N (Sn–N(1) 2.535(9) and Sn–N(2) 2.369(8) Å) bond lengths. The longest of these distances (to O(2) and N(1)) also include the atoms forming the most obtuse bond angle (O(2)–Sn–N(1) 141.9(3)°). This is indicative of a trigonal bipyramidal distortion in the square pyramidal coordination geometry around Sn. In this configuration the

O(2) and N(1) atoms occupy the axial positions and O(1), N(2) and the Sn lone pair of electrons occupy the equatorial sites. This structure may be compared with a related Sn(II) Schiff base complex, SalomphenSn(II) (Salomphen = *N,N'*-(4,5 dimethyl-1,2-phenylene)bis(salicylideneiminato) [3]. In this structure the Sn atom is in a square–pyramidal geometry with equivalent Sn–O (2.137 (8)Å) and Sn–N (2.376 (10)Å) bonds and the Sn atom 1.126 Å above the N₂O₂ plane. The widest bond angle in this structure is 119.4 (5)°.

The accessibility of Ge(II) and Sn(II) lone pairs of electrons is well established [9]. One notable example is the reaction of tmtaaM(II) (M = Ge, Sn, tmtaa = dibenzotetramethyltetraaza [14]–annulene) with Cr(CO)₅THF to yield the donor complexes tmtaaM → Cr(CO)₅ [10]. Thus, we were curious to see if traditional Lewis acid/base complexes could form for **7**–**9**. Reactions between **7**–**9** and AlMe₃ in a 1:1, 1:2, and 1:3 stoichiometry at 25 °C led to product mixtures that were difficult to characterize. However, when **8** and **9** (1.24 mmol) were each combined with 3 equivalents (3.72 mmol) of AlMe₃ in refluxing toluene, a clean transmetalation reaction occurred. The main products of this reaction were the trimetallic complexes, SalpanAlMe(AlMe₂)₂ (**10**) and SalophanAlMe(AlMe₂)₂ (**11**) [5]; the by-products were Sn(0) and SnMe₄, which were characterized qualitatively and by ¹¹⁹Sn NMR, respectively (Scheme 2).

The trimetallic derivatives can also be formed by the direct reaction of AlMe₃ with **1**, **2** and **5** in a 3:1 stoichiometry. Structurally characterized examples of this reaction include SalpanAlMe(AlMe₂)₂, SalcanAlMe(AlMe₂)₂ and SalophanAlMe(AlMe₂)₂ [5]. Anal-



Scheme 2. Transmetalation of **8** and **9** to yield the trimetallic aluminum derivatives, **10** and **11**.

gous reactions can also be used to prepare trimetallic gallium derivatives, for which a transmetallation-type synthesis has yet to be established.

In conclusion, we have shown that a new and interesting chemistry is available for the SalanH_4 class of ligands. There is a significant trigonal bipyramidal distortion for Sn(II) on going from SalenH_2 to SaleanH_4 . Additionally, the Sn complexes undergo unusual transmetallation reactions with AlMe_3 to form trimetallic Al derivatives. Future research will be focused on determining the solid state coordination geometry of Sn(II) with ligands 2–6 and on determining the mechanism by which the trimetallic derivatives are formed from these tin complexes.

Supplementary Material

Tables of bond lengths and angles, positional parameters, anisotropic thermal parameters, observed and calculated structure factors and a unit cell view of **7** are available from the authors on request.

Acknowledgments

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References and notes

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- [7] Spectroscopic and physical data for **7**: Mp. 135–140 °C (dec); ^1H NMR (270 MHz, D_6 -DMSO, 25 °C): δ 2.75 (s(br), 2H, NHCH_aH_b), 2.95 (s(br), 2H, NHCH_aH_b), 3.58 (m(br), 2H, PhCH_aH_b), 3.81 (m(br), 2H, PhCH_aH_b), 4.42 (s(br), NH), 6.48(t, 2H, PhH), 6.62 (d, 2H, PhH), 7.02 (m, 4H, PhH). ^{13}C NMR (67.94 MHz, D_6 -DMSO, 25 °C): δ 47.1 (NHCH_2), 50.6 (PhCH_2), 115.7 (PhH), 118.3 (PhCH_2), 120.4 (PhH), 126.4 (PhO), 129.6 (PhH), 130.4 (PhH). ^{119}Sn NMR (D_6 -DMSO): δ -523.55 (s). IR (KBr, cm^{-1}): 3281 (m), 2922 (m), 1596 (s), 1568(s), 1478(s), 1454(s), 1262(s), 1191(w), 1147(w), 1108 (m), 1037(m), 879(m), 780(s), 730(s). MS (EI, 70eV): m/e 280 (M^+ -O PhCH_2 -2H), 236 (M^+ -SnO $_2$ -2H). Analysis: calcd (found); C 47.72 (47.71), H 5.78 (5.83), N 6.44 (6.18). **8**: Mp. 193–197 °C; ^1H NMR (270 MHz, D_6 -DMSO, 25 °C) δ 2.25 (br s, 2H, CH_2CH_2), 3.19 (br s, 4H, NCH_2), 4.00 (br s, 4H, PhCH_2), 4.35 (br s, 2H, NH), 6.78–6.93 (m, 4H, Ph-H), 7.30–7.43 (m, 4H, Ph-H); ^{13}C NMR (67.94 MHz, DMSO-d_6 , 25 °C) δ 22.8 (CH_2CH_2), 49.5 (NCH_2), 51.5 (PhCH_2), 114.9 (Ph), 115.1 (Ph), 120.3 (Ph), 129.0 (Ph), 129.6 (Ph), 163.0 (Ph); IR (KBr, cm^{-1}) 3258 (m), 2916 (s), 1596(m), 1475(m), 1445(s), 1267(m), 871(m), 761(s) cm^{-1} ; MS (EI) m/e 403 (M^+), 297 (M^+ - CH_2PhO), 240 ($\text{NCH}_2\text{PhOSn}^+$), 120 (NCH_2PhO^+), 106 (CH_2PhO^+). Analysis: calcd (found); C 50.67 (50.28), H 4.97 (5.20), N 6.95 (6.58). **9**: (Mp. 141–143 °C (dec)). IR (KBr, cm^{-1}): 3287(m, br), 2907(m, br), 2795(m), 2365(w, br), 1593(w), 1447(w), 1400(w), 1258(w, br), 1103(w, br), 1024(s), 939(w), 756(w, br), 542 (s, br) MS (EI, 70eV, m/e) 871 (M^+ , dimer), 690 (dimer-2 PhCH_2), 388 (dimer-2 PhCH_2 + 2 PhN_2 + PhCH_2), 285 (Sn_2O_3), 151 (SnO_2). Analysis: calcd (found); C 54.96 (54.58), H 4.15 (4.46), N 6.41(6.18)
- [8] Crystal data: $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_4\text{Sn}$, colorless, 0.9 mm \times 0.2 mm \times 0.15 mm, orthorhombic, Pbcn; $a = 19.849(4)$, $b = 10.791(3)$, $c = 18.559(5)$, $Z = 8$; $V = 3975(2)$ \AA^3 ; $T = 25$ °C; $FW = 453.1$; $D_c = 1.514$ g cm^{-3} ; Mo $K\alpha$ radiation, 3318 data collected $2.0^\circ \leq 2\theta \leq 45^\circ$; 2592 unique reflections with $I \geq 4.0\sigma(I)$, no absorption correction applied; refinement by full-matrix least squares, all non-hydrogen atoms anisotropic; 226 parameters, data-to-parameter ratio = 6.9; final $R = 0.0418$; $R_w = 0.0448$; error of fit = 4.37; largest residual density = 0.53 $\text{e}\text{\AA}^{-3}$.
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