A Simple Synthesis and the Crystal Structure of a Novel Tetranuclear Diorganotin Compound

Dilip Kumar Dey,*[#] Manas Kumar Saha, Samiran Mitra, Raj Kumar Bansal,[†] and Lutz Dahlenburg[††]
Departmeut of Chemistry, Jadavpur University, Calcutta 700 032, India
[†]*Departmeut of Chemistry, University of Rajasthan, Jaipur 302004, India*
[††]*Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany*

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The tetranuclear dimethyltin(IV) complex (L)SnMe$_2$(μ_3-O)(SnMe$_2$)$_2$(μ_3-O)SnCl$_2$Me$_2$, which was obtained from Me$_2$SnCl$_2$ and the tetradentate Schiff base ligand *N*-2-[3'-(methoxysalicylideneimino)benzyl]-3"-methoxysalicylideneimine (H$_2$L) avoiding strictly moisture-free conditions, displays one seven and three five-coordinate dimethyltin moieties bridged by two μ_3-oxo groups as the basic structural features. Retention of solid state structure in solution is indicated by NMR spectra.

A good deal of recent research in organotin chemistry has been devoted to the structure and reactivity of oxo-bridged trinuclear tin salicylaldoximate complexes.[1–6] The great current interest in this family of compounds stems, inter alia, from the observation that these species (i) are inevitably obtained as the initial products of the condensation of diorganotin oxide, salicylaldoxime and derivatives thereof,[5] (ii) play an important role in the generation of other such trinuclear tin clusters,[5] and (iii) have been identified as intermediates of the formation of organotin oligomers featuring higher degrees of aggregation.[6] Furthermore, organotin oxo clusters have potential application in catalysis[7] and in the development of advanced materials.[8]

We have demonstrated recently that the symmetrical tetradentate Schiff base ligand *N,N'*-1,2-phenylene-bis(3'-methoxysalicylideneimine), H$_2$L', merely affords mononuclear chelated organotin complexes, R$_2$Sn(L') (R = Ph, *n*-Bu, Me), if combined with diaryl- or dialkyltin dichlorides.[9] Because of the presence of an additional benzylic methylene group, the unsymmetrical tetradentate *N*-2-[3'-(methoxysalicylideneimino)benzyl]-3"-methoxysalicylideneimine, 1,2-C$_6$H$_4$[N=CHC$_6$H$_3$(OMe-3')OH-2']CH$_2$N=CHC$_6$H$_3$(OMe-3")OH-2" (H$_2$L), is more flexible than its synunetrical ortho-phenylene-based analogue H$_2$L' and, hence, should be more prone to act as an oligonucleating ligand.[10]

In fact, the reaction of Me$_2$SnCl$_2$ with H$_2$L in 4:l stoichiometry in benzene containing added triethylamine, without the exclusion of air and moisture, fumished a 70% yield of tetranuclear (L)SnMe$_2$(μ_3-O)(SnMe$_2$)$_2$(μ_3-O)SnCl$_2$Me$_2$ (**1**) as a yellow air-stable solid.[11] The same product was obtained using the reactants in molar ratios varying between 3 : 1 and 1 : 1, the unreacted excess of the Schiff base ligand being recovered during work-up in these cases. Preliminary investigations suggest that substituting Ph$_2$SnCl$_2$ for Me$_2$SnCl$_2$ under similar conditions furnishes a tetranuclear product as well. On the other hand, we isolated mononuclear complexes employing rigorously anhydrous conditions, which points to the involvement of residual solvent water or atmospheric moisture in the formation of the oxo bridges. The formation of **1** is shown below.

$$4\mathrm{Me_2SnCl_2} + \mathrm{H_2L} + 2\mathrm{H_2O} + 6\mathrm{Et_3N} \xrightarrow[\text{reflux}]{\text{Benzene}}$$

$$\mathrm{(L)SnMe_2(\mu_3\text{-}O)(SnMe_2)_2(\mu_3\text{-}O)SnCl_2Me_2} + 6[\mathrm{Et_3NH}]\mathrm{Cl}$$

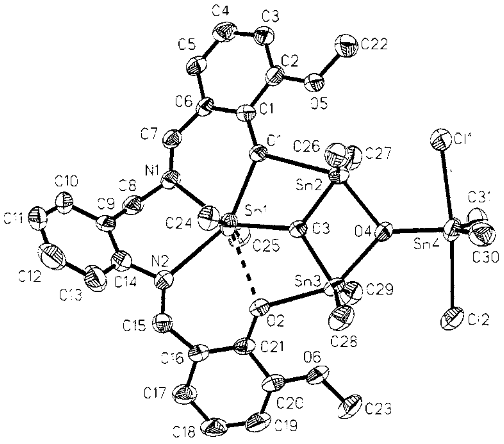

Figure 1 Molecular structure of **1** without hydrogen atoms. Selected bond lengths (Å) and angles (°): Sn1–O1, 2.295(5), Sn1–O2 2.601(5), Sn1–O3 2.082(5), Sn1–N1 2.389(6), Sn2–O1, 2.490(5), Sn2–O3 2.007(5), Sn2–O4 2.111(5), Sn3–O2, 2.298(5), Sn3–O3 2.005(4), Sn3–O4 2.193(5), Sn4–Cl2 2.589(3), Sn4–O4 1.970(5), O1–Sn1–O2 136.5(2), O1–Sn1–O3 71.1(2), O1–Sn1–N1 77.0(2), O1–Sn1–N2 152.6(2), O2–Sn1–O3 65.5(2), C24-Sn1-C25 171.5(3), O2–Sn1–N1 144.6(2), O2–Sn1–N2 69.8(2), N1–Sn1–N2 79.7(2), O1–Sn2–O3 68.1(2), O1–Sn2–O4 143.1(2), C26-Sn2-C27 149.3(4), O3–Sn2–O4 75.3(2), O2–Sn3–O3 73.2(2), O2–Sn3–O4 146.6(2), Cl1–Sn4–Cl2 173.20(8), C30–Sn4–C31 135.3(4), Sn1–O1–Sn2 97.5(2), Sn1–O2–Sn3 95.2(2), Sn1–O3–Sn2 123.3(2), Sn1–O3–Sn3 125.3(2), Sn2–O3–Sn3 110.7(2), Sn2–O4–Sn3 100.2(2), Sn2–O4–Sn4 126.7(3), Sn3–O4–Sn4 133.0(3).

The solid-state structure of **1** was established by X-ray crystallography (Figure 1).[12] The tetranuclear structure features four near coplanar tin atoms connected by two triply bridging oxo groups. Tin atom Snl adopts a distorted pentagonal bipyramidal coordination geometry with bonds to one tri-coordinate oxo ligand, O3, and to the Schiff base nitrogen and oxygen donor atoms, Nl/N2 and Ol/O2, in the equatorial plane, the axial positions being occupied by methyl groups. The distortion arises both from the asymmetric framework of tetradentate ligand and from its bite angles which vary between 69.8(2)° for O2–Sn1–N2 and 79.7(2)' for N1–Sn1–N2. Distortion from ideal pentagonal bipyramidal geometry is also evident from the length of the Sn1–O2 bond, 2.601(5) Å, which by far exceeds the distances between the metal atom and oxygen atoms O3 [Snl–O3 = 2.082(5) Å] and, respectively, O1 [Sn1–Ol = 2.295(5) Å]. The six-membered chelate rings formed by the tetradentate Schiff base about Snl deviate significantly from planarity. This applies especially to the diimine-bonded chelate system which adopts a skew-boat form with Sn1–N1–C8–C9 and Sn1–N2–C14–C9 torsion angles of 70.6° and 56.1°, respectively. The pentacoordinate metal centers Sn2 and Sn3 are in distorted tetragonal pyramidal environments with the pairs of methyl groups, the two phenolate oxygen atoms O1 and O2 and the oxo bridge O4 residing in basal positions. The oxo bridge O3 occupy the axial positions of both Sn2 and Sn3. The indices of trigonality, τ, within the structural continuum between tetragonal pyramidal ($\tau = 0$) and trigonal bipyramidal ($\tau = 1$), as defined by Addison and Reedijk,[13] are $\tau = 0.10$ for Sn2 and and $\tau = 0.03$ for Sn3. The pentacoordinate geometry found for tin atom Sn4, on the other hand, deviates only slightly from that of an undistorted trigonal bipyramid. Thus, the equatorial interligand angles add up to 359.9° and the axial chlorine substituents are only slightly bent towards O4 [angle C11–Sn4–C12, 173.20(8)°]. The triply bridging oxo groups show planar coordination environments as evidenced from the sum of the three Sn–O–Sn angles, which amounts to 359.3° for O3 and 359.9° for O4.

The ^{1}H, ^{13}C, and ^{119}Sn solution NMR spectra of **1** show all the peaks that can be expected from its solid state structure.[11] In particular, the ^{119}Sn spectrum in $CDCl_3$ exhibits four singlets whose shifts values, δ ca. –405 (Sn1), –192 and –206 (Sn2 and Sn3), and –105 (Sn4), closely correspond to the ^{119}Sn chemical shifts reported by others[6,14] for tin(IV) in the respective hepta- or pentacoordinate environment and, hence, indicate that the solid-state structure is retained in solution.

Compound **1** is the first example of a fully characterized tetranuclear organotin(IV) complex derived from a tetradentate Schiff base ligand, which possesses both chelated and adducted organotin moieties and is prepared in very straightforward way. Obviously, the facile formation of **1** from Me_2SnCl_2 and Schiff base ligand H_2L is assisted to a high degree by the flexibility of the benzylidene-based asymmetric framework of this particular tetradentate, since analogous condensation reactions of diorganotin(IV) dichlorides with the symmetric and more rigid phenylene-based *N,O* donor ligand H_2L' resulted only in the formation of mononuclear chelate complexes.[9] Detailed studies on the interaction of this ligand and nature of products formed with other organotin(IV) halides under moist and rigorously dry conditions are in progress.

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References and Notes

Present address: Department of Chemistry, Chandidas Mahavidyalaya, Khujutipara - 731 215, District - Birbhum, West Bengal, India.

1 F. Kayser, M. Biesemans, M. Bouâlam, E. R. Z. Tiekink, A. El Khloufi, J. Meunier-Piret, A. Bouhdid, K. Jurkschat, M. Gielen, and R. Willem, *Organometallics*, **13**, 1098 (1994).

2 R. Willem, A. Bouhdid, F. Kayser, A. Delmotte, M. Gielen, J. C. Martins, M. Biesemans, B. Mahieu, and E. R. T. Tiekink, *Organometallics*, **15**, 1920 (1996).

3 R. Willem, A. Bouhdid, A. Meddour, C. Camacho-Camacho, F. A. G. Mercier, M. Gielen, M. Biesemans, F. Ribot, C. Sanchez, and E. R. T. Tiekink, *Organometallics*, **16**, 4377 (1997).

4 A. Meddour, F. A. G. Mercier, J. C. Martins, M. Gielen, M. Biesemans and R. Willem, *Inorg. Chem.*, **36**, 5712 (1997).

5 F. A. G. Mercier, A. Meddour, M. Gielen, M. Biesemans, R. Willem, and E. R. T. Tiekink, *Organometallics*, **17**, 5933 (1998).

6 A. Meddour, A. Bouhdid, M. Gielen, M. Biesemans, F. A. G. Mercier E. R. T. Tiekink, and R. Willem, *Eur. J. Inorg. Chem.*, **1998**, 1467.

7 J. Otera, *Chem. Rev.*, **93**, 1449 (1993).

8 F. Banse, F. Ribot, P. Tolédano, J. Maquet, and C. Sanchez, *Inorg, Chem.*, **34**, 6371 (1995).

9 D. K. Dey, M. K. Das, and H. Nöth, *Z. Naturforsch.*, **54b**, 145 (1999).

10 D. E. Fenton, and H. Okawa, *Chem. Ber./Recueil*, **130**, 433 (1997).

11 Synthesis of $(L)SnMe_2(\mu_3\text{–}O)(SnMe_2)_2(\mu_3\text{–}O)SnCl_2Me_2$ (1): To a stirred solution of *N*-2-[3'-(methoxysalicylideneimino)benzyl]-3"-methoxysalicylidenimine, H_2L (0.21 g, 54 mmol) and triethylamine (0.22 g, 2.17 mmol) in 30 mL benzene, a solution of Me_2SnCl_2 (0.473 g, 2.15 mmol) in 10 mL of benzene was added slowly at room temperature. After the addition of the Me_2SnCl_2 solution was complete, the mixture which turned turbid due to the precipitation of $[Et_3NH]$ Cl was allowed to gentle reflux with stirring for 2 h to ensure complete reaction. After cooling to room temperature, the precipitated triethylammonium chloride was filtered off and the filtrate was evaporated in vacuo. The crude product thus obtained was washed with petroleum ether (bp 40–60 °C). Recrystallization from chloroform/petroleum ether/n-hexanc (1:1:1) at ~10 °C (3 d) afforded the product as yellow crystals (0.41 g, 70%); mp 148–149 °C. Anal. Calcd. for $C_{31}H_{44}Cl_2N_2O_6Sn_4$: C, 34.27: H, 4.08; N, 2.58; Sn, 43.70 %. Found: C, 34.45; H, 4.02; N, 2.45; Sn, 43.61 %. δ_H(300 MHz, $CDCl_3$) 8.15 (s, 1H, CH=N), 8.13 (s, 1H, CH=N), 7.39–7.27 (m, 3H, ArH), 6.97–6.81 (m, 4H, ArH), 6.70–6.62 (m, 3H, ArH), 3.94 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 1.25–0.56 (m, 26H, CH_2 and $SnCH_3$); δ_C(75.47 MHz, $CDCl_3$) 168.09 (s, CH=N), 167.35 (s, CH=N), 156.01, 155.18, 152.39, 149.98, 149.92, 130.79, 130.64, 129.76, 129.17, 128.08, 127.38, 123.28, 121.06, 119.22, 115.60, 115.24, 114.20, 114.16 (all s, all aryl C), 64.12 (s, CH_2), 55.36 (s, OCH_3), 55.17 (s, OCH_3), 14.12 (s, $SnCH_3$), 13.02 (s, $SnCH_3$): δ_{Sn}(33.35 MHz, $CDCl_3$) –105.09 (Sn4), –191.62 and –205.80 (Sn2 and Sn3), –405.32 (Sn1).

12 Crystal data for **1**: $C_{31}H_{44}Cl_2N_2O_6Sn_4$; FW = 1086.34; T = 293(2) K; Mo Kα 0.7107Å; Monoclinic; Space group $P2_1/c$ (No. 14); a = 11.496(2) Å; b = 16.708(1) Å; c = 21.071(3) Å; β = 103.04(1)°; V= 3942.8(9) Å; Z = 4; D_c = 1.83 g/cm^3; μ(Mo Kα) = 2.68 mm^{-1}; F(000) = 2104; (0.55 × 0.38 × 0.18 mm); $2.19 \le \theta \le 25.97$; Independent reflections: 7708 (R_{int} = 0.0341); Full-matrix least-squares on F^2; Data/restraint/parameters: 7708/0/416; Goodness-of-fit on F^2: 1.022; Final R [$I \ge 2\sigma(I)$]: R_1 = 0.050, wR_2 = 0.1122 for 5230 data; R(all data): R_1 = 0.0886, wR_2 = 0.1292; Largest difference peak and hole: 1.661 and –0.153 eÅ^{-3}.

13 A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.

14 J. Otera, *J. Organomet. Chem.*, **221**, 57 (1981).