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Synthesis and Characterization of Two Novel Tin(IV) Compounds Containing 12-Membered Metallarings

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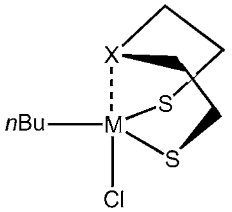
ABSTRACT: *12-Chloro-12-n-butyl-1,11-dioxa-4,8-dithia-12-stannacyclododecane (***3a***) and 12-chloro-12-n-butyl-1,4,8,11-tetrathia-12-stannacyclododecane (***3b***) have been prepared by reacting n-butyltin trichloride with 1,11-dioxa-4,8-dithiaundecane and 1,4,8,11-tetrathiaundecane, respectively. Complexes* **3a,b** *were characterized by elemental analyses, IR, electron impact mass spectrometry, and multinuclear NMR (^{1}H, ^{13}C, and ^{119}Sn). The spectroscopic data are consistent with bonding of the ligands through both sulfur and oxygen atoms in* **3a** *and through all sulfur atoms in* **3b** *to the Sn(IV) center. We suggest hexacoordination around the Sn atoms.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:451–453, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20040

INTRODUCTION

The coordination chemistry of polydentate thioether ligands has been studied in detail with elements from across the transition series, as detailed in several review articles which have appeared over the last decade [1–4]. In contrast, complexes of these ligands with main group elements have been much less studied. Similarly studies exist of the 1,11-dioxa-4,8-dithiaundecane (**1a**) and 1,4,8,11-tetrathiaundecano (**1b**) with transition metals [5–7] but their chemistry with main group elements have not been studied until now.

We have reported the preparation of stannocanes of the type **2** that show a 1,5-transannular interaction between the donor group X and Sn [8].



2a, X = O
2b, X = S

In this work we present the synthesis and structural characterization of two new organotin(IV) derivatives of the tetradentate (**1a**) and (**1b**) ligands, with the purpose of obtaining compounds in which the Sn atom presents a high coordination number in a flexible ring system, as well as studying the presence of transannular interactions inside a 12-membered ring and their possible use as starting material in the synthesis of new derivatives using the chlorine atom as a leaving group.

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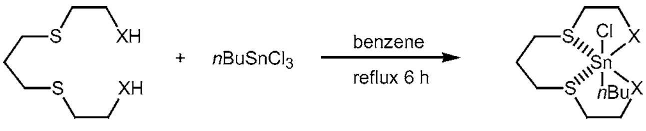
RESULTS AND DISCUSSION

The reaction between *n*-butyltin trichloride and **1a,b** in benzene gave 12-chloro-12-*n*-butyl-1,11-dioxa-4,8-dithia-12-stannacyclododecane (**3a**) and 12-chloro-12-*n*-butyl-1,4,8,11-tetrathia-12-stannacyclododecane (**3b**). Both compounds are air-stable, colorless, and thick liquids. They were characterized by IR, electron impact (EI) mass spectrometry, and multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy.



1a, X = O
1b, X = S

3a, X = O
3b, X = S

The absence of bands in the regions 3200–3400 cm^{-1} due to ν(O—H) in the IR spectrum of **3a** as well of in 2550–2600 cm^{-1} for ν(S—H) in the spectrum of **3b** indicates that the oxygen and sulfur atoms are bonded to the Sn(IV).

EI mass spectra for **3a** and **3b** do not show the molecular ion, but the data are easily related to the proposed structures. The base peak in both spectra corresponds to the ions $C_4H_9^+$, and the fragmentation patterns are similar to that of **2** with the loss of C_2H_4X (X = S,O) and C_3H_6S fragments to give $[S(CH_2)_3S(CH_2)_2X]SnCl^+$ and $[S(CH_2)_2X]SnCl^+$, respectively. Additionally, there are fragments arising from the ligands, that is, $C_5H_{11}S_3^+$(167 *m/z*), $C_5H_{11}S_2O^+$(151 *m/z*), and $C_3H_7S_2^+$(107 *m/z*).

The ^{1}H NMR spectra of compounds **3a** and **3b** confirm the identity of the compounds, showing the expected integration and multiplicities. With transition metals and a similar ligand, a mixture of *trans* and *cis* products was obtained and was observed because the ^{13}C NMR spectra show a double set of signals, one for each isomer [9]. This is confirmed with the X-ray diffraction studies. The ^{13}C NMR spectra of **3a** and **3b** exhibit only one set, however.

The ^{119}Sn chemical shift is influenced by the coordination number and bond angles at tin and by electronegative substituents [10–12]. When the tin coordination number increases, the ^{119}Sn signal moves to higher field. Thus, for five-coordinate tin, δ ^{119}Sn has values from -90 to -330 ppm, for six-coordinate tin from -125 to -515 ppm [13]. Although δ ^{119}Sn of **3a**, **b** are not in the range reported, it is suggested that both the sulfur and oxygen atoms in **3a** and all the sulfur atoms in **3b** participate in the bonding to Sn. This suggestion is made on basis of the studies with stannocanes [8], in which our group had reported the ^{119}Sn chemical shifts for **2a** as -10.93 ppm and as -8.83 ppm for **2b**. In comparison the shifts of compounds **3a** and **3b**, -74.44 and -42.8 ppm, respectively, are at higher field, from which we suggest the coordination number for the tin atom as six.

EXPERIMENTAL

General Comments

Reagents were commercial grade and used as received. **1a** and **1b** were prepared by the known procedures [7]. IR spectra were recorded in the region 4000–400 cm^{-1} as KBr pellets using a Bruker-Vector spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity Inova System 400 MHz operating at 399.747, 100.515 MHz, ^{119}Sn NMR spectra were obtained on a Bruker 300 MHz operating at 111.853 MHz using $CDCl_3$ as solvent. The chemical shifts are relative to internal Me_4Si (^{1}H, ^{13}C) and external Me_4Sn (^{119}Sn) for the indicated nuclei. Mass spectra determinations were performed on a Hewlett–Packard MS/GS 598 instrument by electron impact at 70 eV.

Synthesis of **3a**

1a (4.9 g, 0.025 mol) was dissolved in benzene (25 mL), and *n*-butyltin trichloride (4.16 mL, 0.025 mol) was added to the mixture and refluxed for 6 h. After that, the benzene was evaporated and the resulting thick liquid was dried under vacuum, yield 9.11 g (92%). Anal. Calc. for $C_{11}H_{23}ClO_2S_2Sn$: C, 32.57; H, 5.72. Found: C, 32.73; H, 5.55%. EI MS (70 eV) 305 (<10%, $C_5H_{10}S_2OSnCl$), 253 ($C_5H_9SO_2Sn^+$, <10%), 225 ($C_3H_5SO_2Sn^+$, <10%), 151 ($C_5H_{11}S_2O^+$, 64%), 107 ($C_3H_6S_2^+$,22%), 57 ($C_4H_9^+$,100%). IR (KBr) 2964.3s, 2879.4s (νC—H), 1466s (δCH_2), 1406s (δCH_3), 693.3m (νC—S), 1051.4m (νC—O). ^{1}H NMR ($CDCl_3$) δ 0.98 (t, $J = 7.2$, 3H), 1.5 (sext, $J = 7.2$, 2H), 1.89 (q, $J = 7.2$, 4H), 2.33 (t, $J = 7.2$, 2H), 2.67 (t, $J = 7.2$, 4H), 2.75 (t, $J = 5.6$, 4H), 3.76 (t, $J = 5.6$, 4H). ^{13}C NMR ($CDCl_3$) δ 13.54, 27.11, 29.53 (*n*-Bu), 35.53 (CH_2), 25.86, 30.65 (CH_2—S), 60.61 (CH_2—O). ^{119}Sn NMR ($CDCl_3$) δ -74.44.

Synthesis of **3b**

1b (5.7 g, 0.025 mol) was dissolved in benzene (25 mL), and *n*-butyltin trichloride (4.16 mL, 0.025 mol) was added to the mixture and refluxed for 6 h. After that, the benzene was evaporated and the resulting thick liquid was dried under vacuum, yield 9.11 g (92%). Anal. Calc. for $C_{11}H_{23}ClS_4Sn$: C, 30.18; H, 5.30. Found: C, 30.38; H, 5.38%. EI MS (70 eV) 381

($C_7H_{14}S_4ClSn^+$, 28%), 321 ($C_5H_{10}S_3ClSn^+$, <10%), 247 ($C_2H_4S_2ClSn^+$, 12%), 225 ($C_3H_5S_2Sn^+$, 17%), 155 ($SnCl^+$, 20%), 57 ($C_4H_9^+$,100%). IR (KBr) 2959.4s, 2868.9s (νC H), 1421.3s (δCH_2), 1377.9s (δCH_3), 685.8m (νC—S). ^{1}H NMR ($CDCl_3$) δ 0.97 (t, $J = 7.2$, 3H), 1.49 (sext, $J = 7.2$, 2H), 1.9 (m, 4H), 2.25 (t, $J = 7.2$, 2H), 2.9 (m, 12H) CH_2—S. ^{13}C NMR ($CDCl_3$) δ 25.83, 27.90, 31.62 (CH_2—S), 37.90 (CH_2), 13.77, 24.85, 28.81, 36,34 (*n*-Bu).^{119}Sn NMR ($CDCl_3$) δ −42.80.

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