Journal of Organometallic Chemistry 733 (2013) 36–43

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and structural studies of diorganotin(IV) compounds derived from (*E*)-3-hydroxy-2-((2-hydroxybenzylidene)amino)propanoate and (*E*)-3-hydroxy-2-((1-(2-hydroxyphenyl)ethylidene)amino)propanoate

Tushar S. Basu Baul [a,*], Pelesakuo Kehie [a], Oinam Bijeta Chanu [a], Andrew Duthie [b], Herbert Höpfl [c,**]

[a] Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793022, India
[b] School of Life & Environmental Science, Deakin University, Geelong Victoria 3217, Australia
[c] Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca 62209, Mexico

ARTICLE INFO

Article history:
Received 29 January 2013
Received in revised form
14 February 2013
Accepted 14 February 2013

Keywords:
Tin
Organotin compounds
Amino acids
Carboxylate ligands
Schiff bases
X-ray diffraction analysis

ABSTRACT

Five new diorganotin(IV) compounds were prepared by reacting diorganotin dichlorides R_2SnCl_2 (R = Me, *n*Bu and Ph) with sodium salts of the tridentate NO_2 ligands (*E*)-3-hydroxy-2-((2-hydroxybenzylidene)amino)propanoic acid (L^1H_2Na) and (*E*)-3-hydroxy-2-((1-(2-hydroxyphenyl)ethylidene)amino)propanoic acid (L^2H_2Na). The molecular structures of the resulting diorganotin (IV) compounds have been established by elemental analysis and a combination of IR and NMR (^1H, ^{13}C, ^{119}Sn) spectroscopy. In all cases, the ^{119}Sn NMR chemical shifts were indicative of five-coordinate tin atoms in solution. However, investigation of compounds $[Me_2SnL^1H]\cdot H_2O$ (**1**), $[Ph_2SnL^1H]\cdot 2C_6H_6$ (**3**), $[Me_2SnL^2H]\cdot CHCl_3$ (**4**) and $[Ph_2SnL^2H]$ (**5**) by single-crystal X-ray diffraction revealed that only compound **3** has a distorted trigonal–bipyramidal geometry in the solid state. For compounds **1**, **4** and **5** the coordination geometries are distorted octahedral, either due to intermolecular association through Sn···O interactions (**1**) or coordination through the oxygen atom from the pendant CH_2OH group (**4** and **5**). At the supramolecular level, the molecular structures are linked through O–H···O hydrogen bonds to give discrete dimeric assemblies (**4**), 1D chains (**3**, **5**) and 2D hydrogen bonded layers (**1**).

1. Introduction

Organotin compounds are an important family of organometallic compounds and their use in a large variety of applications, particularly, in the chemical industry as PVC stabilizers, polyurethane foam formers and antifungal agents, is well known [1]. A recent review provides an account of the use of organotin compounds in the preparation of diverse polysiloxane-containing materials via cross-linking with either organic or inorganic polymers [2]. Besides varied applications of organotin(IV) compounds, their pharmaceutical potential remains at the forefront of their continued research [1,3]. While macrocyclic tin compounds, *e.g.* tin ethyl etiopurpurin, are used clinically for the treatment of age-related macular disease [4], a noteworthy research effort has been and is directed toward the development of organotin-based anti-tumor drugs [5]; the latter motivated research in this area [6–8]. Recently, the chemistry of organotin(IV) complexes of Schiff bases has also stemmed from their antitumor, antimicrobial, antinematicidal, anti-insecticidal and anti-inflammatory activities [9]. Among these, the organotin(IV) derivatives of Schiff bases prepared from amino acids and amino-alcohols have also exhibited various structural possibilities and cytotoxic potential [10–22]. During the past few years, we have reported on a series of organotin(IV) compounds derived from NO_2 ligands such as 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}acetates [10–16], 2-{[(2*Z*)-3-hydroxy-1-methyl-2-butenylidene]amino}acetate [17], [((*E*)-1-{2-hydroxy-5-[(*E*)-2-(aryl)-1-diazenyl]phenyl}methylidene)amino]acetate [18], *β*-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}propionate [19], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}phenylpropionate and 2-{[(*E*)-1-(2-hydroxyaryl)alkylidene]amino}phenylpropionate [20], 2-{[(2*Z*)-(3-hydroxy-1-methyl-2-butenylidene)]amino}-4-methylpentanoate, and 2-{[(*E*)-1-(2-hydroxyphenyl)alkylidene]amino}-4-methylpentanoates [21]. Single-crystal X-ray diffraction analysis of several such organotin(IV) compounds revealed that Schiff bases derived from amino acids are versatile ligands with conformational flexibility, thereby

* Corresponding author. Tel.: +91 364 272 2626; fax: +91 364 2550486, +91 364 2721000.
** Corresponding author. Tel./fax: +52 777 3297997.
E-mail addresses: basubaul@nehu.ac.in, basubaulchem@gmail.com (T.S. Basu Baul), hhopfl@uaem.mx (H. Höpfl).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.02.021

creating mono-, di-, tri-, tetra- or polymeric assemblies with a variety of coordination modes [10–21]. The molecular structures of the compounds are strongly influenced by the nature of the ligand, although in some cases the structure can be modulated by varying the reaction conditions. An overview of the structural versatility resulting by the coordination of such Schiff bases toward organotin(IV) is given in Scheme 1. Some structures related to those described in Scheme 1 are also documented [23]. A number of these organotin(IV) compounds were tested *in vitro* as antitumor agents and the results showed promising cytotoxic activity [12,19–21].

In continuation of our studies with Schiff base ligands derived from amino acids and encouraged by the finding of *in vitro* antitumor activity, we prepared a new series of five diorganotin(IV) compounds using sodium (*E*)-3-hydroxy-2-((2-hydroxybenzylidene)amino)propanoate and sodium (*E*)-3-hydroxy-2-((1-(2-hydroxyphenyl)ethylidene)amino)propanoate. The molecular structures of the compounds were established from a combined study of elemental analysis, ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy, IR spectroscopy and X-ray diffraction analysis.

2. Experimental

2.1. Materials

Me_2SnCl_2 (Merck), nBu_2SnCl_2, Ph_2SnCl_2, 2′-hydroxyacetophenone (Aldrich), 2-hydroxybenzaldehyde, L-serine (Sisco) were used as received. Solvents used in the reactions were of AR grade and dried using standard procedures. Benzene was distilled from sodium benzophenone ketyl.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range of 4000–400 cm^{-1} were obtained on a Perkin Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr discs. ^{1}H and ^{13}C NMR spectra of the compounds were recorded on a Bruker AMX 400 spectrometer and measured at 400.13 and 100.62 MHz, respectively. ^{119}Sn NMR spectra were measured on a Jeol GX 270 spectrometer at 100.75 MHz. The ^{1}H, ^{13}C and ^{119}Sn chemical shifts were referred to Me_4Si (δ 0.00 ppm), $CDCl_3$ (δ 77.00 ppm), and Me_4Sn (δ 0.00 ppm), respectively.

2.3. Synthesis of the ligand salts

2.3.1. Sodium (E)-3-hydroxy-2-((2-hydroxybenzylidene)amino) propanoate (L^1H_2Na)

L^1H_2Na was prepared by stirring a methanolic solution (30 mL) of 2-hydroxybenzaldehyde (1.15 g, 9.49 mmol) and sodium 2-amino-3-hydroxypropanoate that was generated *in situ* from a hot aqueous solution (10 mL) of $NaHCO_3$ (0.79 g, 9.40 mmol) and 2-amino-3-hydroxypropanoic acid (L-serine) (1.00 g, 9.51 mmol). A yellow color developed almost immediately, and stirring was continued for 1 h, followed by reflux for 4 h. After removal of the volatile components, the residue was washed thoroughly with hot hexane, filtered and dried *in vacuo*. After extraction into anhydrous methanol followed by filtration, the resulting solution was concentrated to a minimum and allowed to cool to room temperature, affording the crude product. Repeated recrystallization from methanol yielded pure L^1H_2Na (1.35 g, 62% yield). M.p.: >250 °C. IR (cm^{-1}): 1653 $\nu(OCO)_{asym}$.

2.3.2. Sodium (E)-3-hydroxy-2-((1-(2-hydroxyphenyl)ethylidene) amino)propanoate (L^2H_2Na)

L^2H_2Na was prepared by dissolving $NaHCO_3$ (0.79 g, 9.40 mmol) in water (5 mL) and adding this solution to a stirred hot aqueous solution (5 mL) containing 2-amino-3-hydroxypropanoic acid (L-serine) (1.00 g, 9.51 mmol). The reaction mixture was refluxed for 1 h and then evaporated to dryness. The residue was extracted into hot anhydrous methanol and filtered while hot. To the hot filtrate, an anhydrous methanolic solution (5 mL) of 2′-hydroxyacetophenone (1.29 g, 9.47 mmol) was added under stirring. A yellow color developed almost immediately and stirring was continued for 1 h, followed by reflux for 4 h. After removal of the volatile components, the residue was washed thoroughly with hexane, filtered and dried *in vacuo*. The product was extracted into hot anhydrous methanol and removal of the volatile components under vacuum yielded pure L^2H_2Na (0.90 g, 39% yield). M.p.: >250 °C. IR (cm^{-1}): 1635 $\nu(OCO)_{asym}$.

2.4. Preparation of the diorganotin(IV) compounds

2.4.1. $[Me_2SnL^1H]\cdot H_2O$ (**1**)

Me_2SnCl_2 (0.47 g, 2.13 mmol) dissolved in anhydrous methanol (30 mL) was added dropwise under stirring to an anhydrous methanolic solution (30 mL) containing L^1H_2Na (0.50 g, 2.16 mmol). The reaction mixture was refluxed for 6 h, whereupon the solvent was removed under vacuum. The residue was washed thoroughly with hexane, filtered, dried *in vacuo* and then extracted into chloroform. After filtration, the chloroform solution was concentrated and slow evaporation at room temperature yielded yellow crystals of **1** in 68% (0.52 g) yield. M.p.: 158–160 °C. Anal. calcd. for $C_{12}H_{17}NO_5Sn$ (%): C, 38.52; H, 4.58; N, 3.75. Found: C, 38.43; H, 4.62; N, 3.80. IR (cm^{-1}): 1645 $\nu(OCO)_{asym}$; 1617 ν(C(H)=N). ^{1}H NMR ($CDCl_3$) δ: 8.45 [s, 1H, C(H)N]; $^{3}J(^{119/117}SnN{=}C^{1}H) = 58$ Hz], 7.43 [dd, 1H, H7], 7.23 [d, 1H, H9], 6.77 [m, 2H, H6 & H8], 4.17 [m, 2H, H10], 4.08 [d, 1H, H2], 3.97 [br, 1H, OH (D_2O exchangeable)], 0.94, 0.69 [s, 6H, Sn–Me, $^{2}J(^{119}Sn,^{1}H = 75$ Hz)] ppm. ^{13}C NMR ($CDCl_3$) δ: 172.6 [C3], 171.8 [C1], 167.6 [C5], 137.0 [C7], 134.9 [C9], 121.6 [C8], 116.6 [C6], 116.3 [C4], 69.0 [C2], 64.5 [C10], 0.60, −0.18 [Sn–Me] ppm. ^{119}Sn NMR ($CDCl_3$) δ: −155.8 ppm.

2.4.2. $[nBu_2SnL^1H]$ (**2**)

A similar synthetic procedure to that for **1** was used, except that Me_2SnCl_2 was replaced by nBu_2SnCl_2. In the work-up, the chloroform extract was concentrated to give a pasty material that was thoroughly washed with hexane and kept in the refrigerator overnight. Trituration with hexane in an ice bath afforded **2** as an amorphous powder in 44% yield. M.p.: 78–80 °C. Anal. calcd. for $C_{18}H_{27}NO_4Sn$ (%): C, 49.10; H, 6.19; N, 3.18. Found: C, 48.90; H, 5.80; N, 3.20. IR (cm^{-1}): 1653 $\nu(OCO)_{asym}$; 1619 ν(C(H)=N). ^{1}H NMR ($CDCl_3$) δ: 8.47 [s, 1H, C(H)N]; $^{3}J(^{119/117}SnN{=}C^{1}H) = 54$ Hz], 7.37 [dd, 1H, H7], 7.19 [d, 1H, H9], 6.73 [m, 2H, H6 & H8], 4.13 [m, 2H, H10], 3.80 [d, 1H, H2], OH (not detected), 1.72–1.26 [complex m, 12H, H1*, H2* & H3* (Sn–Bu)], 0.94, 0.88 [t, 6H, H4* (Sn–Bu)] ppm. ^{13}C NMR ($CDCl_3$) δ: 174.8 [C3], 174.0 [C1], 169.3 [C5], 137.8 [C7], 136.1 [C9], 122.6 [C8], 117.7 [C6], 117.3 [C4], 70.2 [C2], 65.3 [C10], 27.07, 27.05 [C2* (Sn–Bu)], 26.8, 26.6 [C3* (Sn–Bu)], 22.4, 22.0 [C1* (Sn–Bu)], 13.7, 13.6 [C4* (Sn–Bu)] ppm. ^{119}Sn NMR ($CDCl_3$) δ: −196.6 ppm.

2.4.3. $[Ph_2SnL^1H]\cdot 2C_6H_6$ (**3**)

A similar synthetic procedure to that for **1** was used, except that Me_2SnCl_2 was replaced by Ph_2SnCl_2. In the work-up, the chloroform extract was concentrated, whereupon the product was precipitated with hexane. The residue was purified by recrystallization from anhydrous benzene to yield a yellow microcrystalline product in 45% yield. M.p.: 162–164 °C. Anal. calcd. for $C_{34}H_{31}NO_4Sn$ (%): C, 64.16; H, 4.91; N, 2.20. Found: C, 64.23; H, 4.80; N, 2.20. IR (cm^{-1}): 1654 $\nu(OCO)_{asym}$; 1615 ν(C(H)=N). ^{1}H NMR ($CDCl_3$) δ: 8.57 [s, 1H, C(H)N]; $^{3}J(^{119/117}SnN{=}C^{1}H) = 61$ Hz], 8.06, 7.95 [m, 4H, H2* (Sn–Ph)], 7.66 [dd, 1H, H7], 7.52 [complex m, 6H, H3* & H4* (Sn–Ph)],