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Organotin(IV) Complexes of *N*-[(2*Z*)-3-Hydroxy-1-methyl-2-butenylidene]glycine

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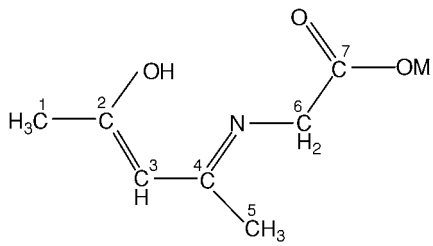
ABSTRACT: *Organotin(IV) derivatives of N-[(2Z)-3-hydroxy-1-methyl-2-butenylidene]glycine have been synthesized and characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, ^{119}Sn Mössbauer, and IR spectroscopy along with elemental analyses. The di- and triorganotin(IV) complexes were readily obtained from the reactions of organotin halides and sodium/potassium N-[(2Z)-3-hydroxy-1-methyl-2-butenylidene]glycinate. The diorganotin compound reacted with Ph_3SnCl in refluxing benzene to give the mixed organotin dinuclear complex of composition $Ph_2Sn(2\text{-}OC(CH_3)\text{-}C(H)C(CH_3)=NCH_2COO)\cdot Ph_3SnCl$, which was characterized by single crystal X-ray structure determination.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:149–154, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10116

INTRODUCTION

The chemistry of the *N*-arylidine-α-amino acid-derived Schiff bases ligating di- and triorganotin centers was developed recently by our group [1–4]. The mode of coordination of such bifunctional tridentate ligands is known. In addition, the reaction of diorganotin(IV) complexes of *N*-arylidine-α-amino acid with R_nSnCl_{4-n} (R = Ph, $n = 3$ and R = ^{t}Bu, $n = 2$) underwent an unprecedented dinuclear molecular adduct formation where two tin atoms are joined via the carbonyl atom of the diorganotin complex [1].

The present paper reports the synthesis and characterization of some new organotin complexes derived from sodium or potassium *N*-[(2*Z*)-3-hydroxy-1-methyl-2-butenylidene]glycinate (LHM). The formation of a mixed dinuclear organotin complex is also described.



LHM, M = Na or K

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EXPERIMENTAL

Materials

Me_3SnCl (Merck), Bu_3SnCl (Merck), Ph_3SnCl (Fluka AG), and Me_2SnCl_2 (Fluka AG), and Ph_2SnCl_2 (Aldrich) were used. Glycine (Aldrich) and acetylacetone (Sisco Research Laboratory) were of reagent grade. All the solvents used in the reactions were of AR grade and dried using standard literature procedures.

Physical Measurements

Carbon, hydrogen, and nitrogen analyses were performed with a Perkin Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a Perkin Elmer 983 spectrophotometer with samples investigated as KBr discs. The ^1H, ^{13}C and ^{119}Sn NMR spectra were acquired on a Bruker ACF 300 spectrometer and measured at 300.13, 75.47, and 111.92 MHz, respectively. The ^1H and ^{13}C spectra were referenced to Me_4Si while the ^{119}Sn chemical shifts were referenced to Me_4Sn. ^{119}Sn Mössbauer spectra of the complexes in the solid state were obtained at liquid-nitrogen temperature on a conventional constant acceleration spectrometer equipped with a CRYO cryostat and a ^{119}Sn Mössbauer source. The velocity calibration was made using a ^{57}Co Mössbauer source, and an iron foil enriched to 95% in ^{57}Fe (DuPont Pharma Italia, Firenze, Italy) was used as the absorber. The $Ca^{119}SnO_3$ and ^{57}Co sources (10 mCi) were procured from Ritverc, St. Petersburg, Russia.

X-ray Crystallography

Compound **6** forms air-stable and almost colorless, slightly yellow crystals. A transparent rod of approximate dimensions 0.50 × 0.14 × 0.05 mm was studied at room temperature on a Bruker AXS D8 goniometer equipped with a SMART Apex CCD area detector. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Crystal data: Empirical formula $C_{37}H_{34}ClNO_3Sn_2$; $a = 11.7755(15)$ Å, $b = 12.6212(16)$ Å, $c = 14.1677(17)$ Å, $\alpha = 63.819(2)^\circ$, $\beta = 70.408(2)^\circ$, $\gamma = 64.483(2)^\circ$, $V = 1677.6(4)$ $Å^{-3}$; $Z = 2$, $\mu = 1.605$ mm^{-1}. Lattice parameters were re-refined during the integration process of the intensity data. A total of 22,056 data with $\theta < 27.5^\circ$ were collected using graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) with the ω scan method [5]. Data were processed with the SAINT+ program [6]. An empirical absorption correction (minimum relative transmission 0.860) was applied to the data set by using the SADABS program for area detector [7]. The structure was solved by direct methods [8] and refined on F^2 [9]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and included as riding on the corresponding atoms. Convergence was reached at $R = 0.0268$ (for 6042 data with $I > \sigma 2(I)$), $wR2 = 0.0597$ (for all 7684 independent intensities), $GOF = 0.899$ and 399 parameters refined. Fluctuations in a final Fourier difference synthesis amounted to 0.752/−0.459 $eÅ^{-3}$.

Preparation of Salts of N-[(2Z)-3-Hydroxy-1-methyl-2-butenylidene]glycine

Sodium N-[(2Z)-3-Hydroxy-1-methyl-2-butenylidene]glycinate (LHNa). A hot aqueous solution (5 ml) of $NaHCO_3$ (1.67 g, 19.97 mmol) was added slowly to a hot aqueous solution (10 ml) containing glycine (1.51 g, 19.97 mmol) under stirring. The reaction mixture was stirred for an additional 30 min and then acetylacetone (2.0 g, 19.97 mmol) in methanol (10 ml) was added dropwise. The reaction mixture was stirred for 8 h at ambient temperature. After removal of the volatiles in vacuum, the resulting residue was washed with petroleum ether and recrystallized from methanol to yield pale yellow crystals of LHNa. Yield, 65%. mp: 105–107°C (dec.). Anal. Found: C, 46.95; H, 5.62; N, 7.82%. Calc. for $C_7H_{10}NNaO_3$: C, 46.91; H, 5.63; N, 7.82%. IR (cm^{-1}): 1670 $\nu(OCO)_{asym}$; 1613 ν(C=N); 1409 $\nu(OCO)_{sym}$.

Potassium N-[(2Z)-3-Hydroxy-1-methyl-2-butenylidene]glycinate (LHK). A cold aqueous solution (10 ml) of KOH (1.40 g, 24.97 mmol) was mixed with a cold aqueous solution (10 ml) containing glycine (1.88 g, 24.97 mmol) and stirring was continued at ambient temperature for 30 min. A methanolic solution (10 ml) of acetylacetone (2.5 g, 24.97 mmol) was added dropwise and the reaction mixture was stirred for 8 h. After careful removal of the volatiles, the resulting residue was washed with petroleum ether, dissolved in methanol, and filtered. Removal of the solvent left crude product. Several crystallization from methanol afforded the pure LHK. Yield, 70%. mp: 230–232°C (dec.). Anal. Found: C, 43.05; H, 5.12; N, 7.12%. Calc. for $C_7H_{10}KNO_3$: C, 43.07; H, 5.17; N, 7.18%. IR (cm^{-1}): 1697 $\nu(OCO)_{asym}$; 1609 ν(C=N); 1399 $\nu(OCO)_{sym}$.

Synthesis of the Organotin Complexes

*Me_2SnL(**1**).* Me_2SnCl_2 (0.50 g, 2.28 mmol) in 10 ml of methanol was added dropwise to a stirred

hot methanol solution (15 ml) containing LHK (0.44 g, 2.28 mmol). The reaction mixture was stirred for 6 h at ambient temperature, and the solvent was removed using a rotary evaporator. The resulting dry mass was washed thoroughly with hot petroleum ether, extracted into chloroform, and filtered. A pale yellow product was obtained upon concentration of the chloroform. This was then recrystallized from the same solvent to yield pale yellow crystals of desired product and dried in vacuo. Yield: 71%, mp: 140–141°C. Anal. Found: C, 35.60; H, 5.12; N, 4.70%. Calc. for $C_9H_{15}NO_3Sn$: C, 35.41; H, 4.96; N, 4.59%. IR(cm^{-1}): 1671 $\nu(OCO)_{asym}$; 1401 $\nu(OCO)_{sym}$. ^1H NMR ($CDCl_3$): $\delta = 0.73$ (s, 6H, Sn—Me, $J(^1H—^{119}Sn) = 78$ Hz), 1.95 and 2.14 (s, 6H, 1-/5-H), 4.03 (s, 2H, 6-H), 5.08 (s, 1H, 3-H). ^{13}C NMR ($CDCl_3$): $\delta = 1.11$ (Sn—Me, $J(^{13}C—^{119}Sn) = 652$ Hz), 25.6 and 26.7 (C-1,5), 51.1 (C-6), 98.7 (C-3), 172.0 (C-2),176.2 (C-4), 186.3 (C-7). ^{119}Sn NMR ($CDCl_3$): $\delta = -142.9$. ^{119}Sn Mössbauer spectrum: $\delta = 1.24$, $\Delta = 3.08$, Γ_1 and $\Gamma_2 = 0.89$ and 1.02 mm s^{-1}, C—Sn—C = 132°.

*Ph_2SnL (**2**).* Preparation of compound **2** was accomplished according to the procedure used for **1** using Ph_2SnCl_2 (0.30 g, 0.87 mmol) and LHK (0.17 g, 0.87 mmol). Yield: 69%, mp: 140–142°C. Anal. Found: C, 53.40; H, 4.50; N, 3.30%. Calc. for $C_{19}H_{19}NO_3Sn$: C, 53.14; H, 4.46; N, 3.26%. IR (cm^{-1}): 1699 $\nu(OCO)_{asym}$; 1392 $\nu(OCO)_{sym}$. ^1H NMR ($CDCl_3$): $\delta = 2.08$ and 2.19 (s, 6H, 1-/5-H), 4.06 (s, 2H, 6-H), 5.18 (s, 1H, 3-H), 7.81 (m, 4H, Sn—Ph (*ortho*)), 7.42 (m, 6H, Sn—Ph (*meta* + *para*)). ^{13}C NMR ($CDCl_3$): $\delta = 25.7$ and 26.9 (C-1,5), 51.4 (C-6), 99.4 (C-3), 128.9 (Sn—Ph, ^3J(Sn—C) = 65 Hz, *meta*), 130.6 (Sn—Ph, ^4J(Sn—C) = 18 Hz, *para*), 136.2 (Sn—Ph, ^2J(Sn—C) = 50 Hz, *ortho*), 138.4 (Sn—Ph, *ipso*),171.8 (C-2),176.5 (C-4), 187.7 (C-7). ^{119}Sn NMR ($CDCl_3$): $\delta = -321.8$. ^{119}Sn Mössbauer spectrum: $\delta = 0.99$, $\Delta = 2.33$, Γ_1 and $\Gamma_2 = 1.01$ and 1.13 mm s^{-1}, C—Sn—C = 114°.

*Me_3SnLH (**3**).* A solution of LHK (0.24 g, 1.25 mmol) in methanol (10 ml) was added dropwise to a stirred solution of Me_3SnCl (0.25 g, 1.25 mmol) in methanol (10 ml) at ambient temperature. The reaction was stirred for an additional 2 h and then volatiles were removed in vacuum. The resulting residue was washed thoroughly with petroleum ether, extracted with chloroform, and filtered. The filtrate was concentrated (up to 20% of the initial solvent volume) and then precipitated with petroleum ether. The crude product was filtered and crystallized from chloroform to give Me_3SnLH. Yield: 57%, mp: 142–144°C. Anal. Found: C, 37.40; H, 5.90; N, 4.40%. Calc. for $C_{10}H_{19}NO_3Sn$: C, 37.38; H, 5.96; N, 4.36%. IR (cm^{-1}): 1659 $\nu(OCO)_{asym}$; 1437 $\nu(OCO)_{sym}$. ^1H NMR ($CDCl_3$): $\delta = 0.59$ (s, 9H, Sn—Me, $J(^1H—^{119}Sn) = 65$ Hz), 1.89 and 1.98 (s, 6H, 1-/5-H), 3.91 (s, 2H, 6-H), 5.00 (s, 1H, 3-H), 10.7 (brs, 1H, 2-H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$): $\delta = -0.97$ (Sn—Me, $J(^{13}C—^{119}Sn) = 148$ Hz), 19.2 and 28.6 (C-1,5), 45.9 (C-6), 96.1 (C-3), 163.3 (C-2), 172.8 (C-4), 194.7 (C-7). ^{119}Sn NMR ($CDCl_3$): $\delta = +90.2$. ^{119}Sn Mössbauer spectrum: $\delta = 1.47$, $\delta = 3.40$, Γ_1 and $\Gamma_2 = 0.94$ and 0.95 mm s^{-1}.

*Bu_3SnLH (**4**).* Bu_3SnCl (0.66 g, 2.03 mmol) was added dropwise with continuous stirring to a suspension of LHNa (0.36 g, 2.03 mmol) in chloroform. The reaction mixture was stirred for 4 h and filtered. The solvent was evaporated in vacuum and the resulting residue was triturated with petroleum ether and filtered. The residue was then dissolved in minimum amount of chloroform, precipitated with petroleum ether, and filtered. The residue was dried in vacuum and upon recrystallization from chloroform afforded product **4**. Yield: 65%, mp: 80–82°C. Anal. Found: C, 51.00; H, 8.40; N, 3.20%. Calc. for $C_{19}H_{37}NO_3Sn$: C, 50.99; H, 8.34; N, 3.13%. IR (cm^{-1}): 1661 $\nu(OCO)_{asym}$; 1426 $\nu(OCO)_{sym}$. ^1H NMR ($CDCl_3$): $\delta = 0.90$ (t, 9H, Sn—Bu, *delta*), 1.31 (m, 12H, Sn—Bu, *beta* + *gamma*), 1.59 (m, 6H, Sn—Bu, *alpha*), 1.88 and 2.00 (s, 6H, 1-/5-H), 3.95 (s, 2H, 6-H), 5.03 (s, 1H, 3-H), 10.8 (brs, 1H, 2-H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$): $\delta = 13.6$ (Sn—Bu, *delta*), 16.8 (Sn—Bu, *alpha*), 18.9 (Sn—Bu, *gamma*), 27.0 (Sn—Bu, *beta*), 27.7 and 28.9 (C-1,5), 45.3 (C-6), 96.1 (C-3), 162.3 (C-2), 173.6 (C-4), 195.4 (C-7). ^{119}Sn NMR ($CDCl_3$): $\delta = -125.9$. ^{119}Sn Mössbauer spectrum: $\delta = 1.36$, $\Delta = 3.50$, Γ_1 and $\Gamma_2 = 0.87$ and 0.88 mm s^{-1}.

*Ph_3SnLH (**5**).* This compound was prepared in the same manner as described for Me_3SnLH using Ph_3SnCl (0.39 g, 1.02 mmol) and LHK (0.20 g, 1.02 mmol). Yield: 43%, mp: 178–179°C. Anal. Found: C, 59.40; H, 5.12; N, 2.85%. Calc. for $C_{25}H_{25}NO_3Sn$: C, 59.16; H, 4.97; N, 2.76%. IR (cm^{-1}): 1651 $\nu(OCO)_{asym}$; 1425 $\nu(OCO)_{sym}$. ^1H NMR ($CDCl_3$): $\delta = 1.76$ and 1.91 (s, 6H, 1-/5-H), 3.91 (s, 2H, 6-H), 4.99 (s, 1H, 3-H), 7.74 (m, 6H, Sn—Ph (*ortho*)), 7.43 (m, 9H, Sn—Ph (*meta* + *para*)), 10.7 (brs, 1H, 2-H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$): $\delta = 18.8$ and 28.7 (C-1,5), 45.1 (C-6), 96.4 (C-3), 128.9 (m, Sn—Ph, ^3J(Sn—C) = 60 Hz, *meta*), 130.3 (Sn—Ph, ^4J(Sn—C) = 12 Hz, *para*), 136.8 (Sn—Ph^a, ^2J(Sn—C) = 48 Hz, *ortho*), 137.9 (Sn—Ph^a, *ipso*), 171.9 (C-2), 176.4 (C-4), 186.7 (C-7). ^{119}Sn NMR ($CDCl_3$): $\delta = -146.4$. ^{119}Sn Mössbauer spectrum: $\delta = 1.23$, $\Delta = 3.10$, Γ_1 and $\Gamma_2 = 0.93$ and 0.93 mm s^{-1}.

*$Ph_2SnL{\cdot}Ph_3SnCl$ (**6**).* An anhydrous benzene solution (10 ml) of Ph_3SnCl (0.81 g, 2.10 mmol) was added dropwise to a hot benzene solution (15 ml) containing Ph_2SnL (**2**) (0.90 g, 2.10 mmol). The reaction mixture was refluxed for 20 min and filtered to remove any suspended particles. The filtrate on standing at ambient temperature deposited pale yellow crystals of **6**. Yield: 83%, mp: 188–190°C. Anal. Found: C, 55.60; H, 4.20; N, 1.76%. Calc. for $C_{37}H_{34}ClNO_3Sn_2$: C, 54.48; H, 4.20; N, 1.72%. IR (cm^{-1}): 1614 $\nu(OCO)_{asym}$. ^1H NMR ($CDCl_3$): $\delta = 2.07$ and 2.21 (s, 6H, 1-/5-H), 4.03 (s, 2H, 6-H), 5.19 (s, 1H, 3-H), 7.82 (m, 4H, Sn—Ph^a (*ortho*)), 7.71 (m, 6H, Sn—Ph^b (*ortho*)), 7.46 (m, 15H, Sn—Ph (*meta* + *para*)). ^{13}C NMR ($CDCl_3$): $\delta = 25.6$ and 26.8 (C-1,5), 51.4 (C-6), 99.4 (C-3), 128.9 (Sn—Ph^b, $^3J(Sn—C) = 62$ Hz, *meta*), 129.0 (Sn—Ph^a, $^3J(Sn—C) = 60$ Hz, *meta*), 130.4 (Sn—Ph^b, $^4J(Sn—C) = 16$ Hz, *para*), 130.6 (Sn—Ph^a, $^4J(Sn—C) = 14$ Hz, *para*), 136.1 (Sn—Ph^b, $^2J(Sn—C) = 50$ Hz, *ortho*), 136.2 (Sn—Ph^a, $^2J(Sn—C) = 50$ Hz, *ortho*), 137.7 (Sn—Ph^b, *ipso*), 138.4 (Sn—Ph^a, *ipso*), 171.9 (C-2), 176.4 (C-4), 186.7 (C-7) (a and b represent signals due to $Sn—Ph_2$ and $Sn—Ph_3$, respectively). ^{119}Sn NMR ($CDCl_3$): $\delta = -54.7$, -321.5. ^{119}Sn Mössbauer spectrum: First doublet: $\delta = 1.21$, $\Delta = 2.72$ (A% = 50), Γ_1 and $\Gamma_2 = 0.94$ and 0.94 mm s^{-1}; Second doublet: $\Delta = 1.20$, $\delta = 3.24$ (A% = 50), Γ_1 and $\Gamma_2 = 0.94$ and 0.94 mm s^{-1}.

Full tables of bond lengths and angles, tables of non-hydrogen and hydrogen atomic coordinates, anisotropic displacement parameters for non-hydrogen atoms are available upon quoting the CCDC deposition number 176205 for **6**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

RESULTS

Reaction of sodium or potassium *N*-[(2*Z*)-3-hydroxy-1-methyl-2-butenylidene]glycinate with the organotin halide in either methanol or chloroform at ambient temperature resulted in the smooth formation of the complexes **1–5**, which were isolated as pale yellow (almost dull white in solid state but pale yellow in organic solvents) crystalline solids. The reaction of **2** with Ph_3SnCl at reflux temperature yielded crystalline complex **6**. The characterization data supported the formulation of the products.

The solid-state IR spectra of the complexes (except **6**, discussed below) all display a characteristic strong absorption band between 1651 and 1699 cm^{-1}, which is assigned to the $\nu(OCO)_{asym}$ vibration, in accord with earlier reports [1,3,4]. In **6**, this vibration appears at 1614 cm^{-1}. The shift of the $\nu(OCO)_{asym}$ band at ca. 85 cm^{-1} to lower wavenumber in **6** confirms the interaction of Ph_3SnCl with the carbonyl oxygen atom of complex **2** (see X-ray results for structural details) [1].

The ^1H and ^{13}C NMR chemical shift assignment of the organotin moiety is straightforward from the multiplicity patterns and/or resonance intensities [10], whereas the ligand skeletons were assigned by the multiplicity patterns and/or resonance intensities of the signals and also by examining the $^nJ(^{13}C—^{119/117}Sn)$ coupling constants [1,4] by standard distorsionless enhancement polarization transfer (DEPT) experiments. The ^1H NMR integration values were completely consistent with the formulation of the products. The complexes **1–5** exhibit a single sharp ^{119}Sn NMR indicating a single tin site in the structure. The ^{119}Sn NMR shifts for the diorganotin complexes are -142.9 and -321.8 ppm for **1** and **2**, respectively and are consistent with the values proposed for penta-coordinated tin center [3,11]. On the other hand, the triorganotin complexes **3–5** are expected to have a polymeric *trans*-O_2SnC_3 trigonal bipyramidal configuration in the solid state (see ^{119}Sn Mössbauer results, vide infra) in line with our recent X-ray crystallographic report on cognate triorganotin systems [4]. In solution, the complexes **3, 4**, and **5** display a signal at $\delta = +90.2$, $+125$, and -146.4 ppm, respectively and the chemical shift values fall within the range specified for tetrahedral triorganotin compounds [4,10,12]. Thus, ^{119}Sn NMR results indicate that five-coordinated polymeric structures of the solids is lost upon dissolution giving rise to four-coordinate monomeric structures in solution. The complex **6** exhibits two ^{119}Sn NMR resonances at $\delta = -54.7$ and -321.5 ppm in $CDCl_3$ solution. The signal at -321.5 ppm is assigned for Ph_2SnL core (refer to complex **2**, five-coordinate tin) and the resonance at -54.7 ppm is assigned to the Ph_3SnCl moiety. A similar spectrum was obtained when equimolar amounts of **2** and Ph_3SnCl were mixed in $CDCl_3$. A complete dissociation of complex **6** into **2** and Ph_3SnCl is likely under these conditions [1].

^{119}Sn Mössbauer spectra of the complexes **1–6** have been recorded in order to obtain further insight into the structure in the solid state since this spectroscopy serves as a reliable indicator of the solid-state structure in the absence of X-ray data. The isomer shift (δ) values, which lie in the range 0.99–1.36 mm s^{-1}, are typical of quadrivalent organotin derivatives [13]. The spectra of the complexes **1–5** show a characteristic doublet absorption indicating

a single tin site. The quadrupole splitting (Δ) values are 2.33 (for **2**) and 3.08 (for **1**) mm s^{-1} for diorganotin complexes. The Δ values are typical for structures with a distorted trigonal bipyramidal with the two oxygen atoms defining the axial positions and the equatorial plane having two Sn—R groups and an imino nitrogen atom [1]. The structure of the diorganotin part can be seen in Fig. 1 (refer to X-ray structure). In triorganotin complexes, the Δ values are 3.40 (for **3**), 3.50 (for **4**), and 3.10 (for **5**) mm s^{-1} which correspond to a trans-trigonal bipyramidal geometry with a planar SnR_3 unit and two apical oxygen atoms [13]. A similar range of values were also found in the triorganotin derivatives of amino acids with a trans-trigonal bipyramidal geometry [4]. Further, ^{1}H NMR spectra of the complexes **3**–**5** exhibit a signal at around 10.7 ppm because of OH (see experimental) which indicated noninvolvement of phenolic oxygen in bonding. The full width of half maximum (Γ±) of these resonance absorptions are approximately 0.94 mm s^{-1}, further suggesting the presence of a single tin atom site in the structure. The spectrum of **6** is quite different showing an asymmetric absorption with large values of full-width at half height, and was fitted as two doublets with different parameter values indicating the presence of two tin sites. The doublet with 1.21 and 2.72 mm s^{-1} isomer shift and quadrupole splitting values, respectively, can be assigned to Ph_2Sn moiety where the pentacoordinated tin atom presents the same assessment predicted in complexes **1** and **2**; the second doublet has the same δ value but different quadrupole splitting (3.24 mm s^{-1}), in consonance with the triorganotin derivatives with planar SnR_3 unit and apical chlorine and oxygen atoms. The percentage areas of the two doublets are similar, indicating equal amounts of di- and triorganotin moieties.

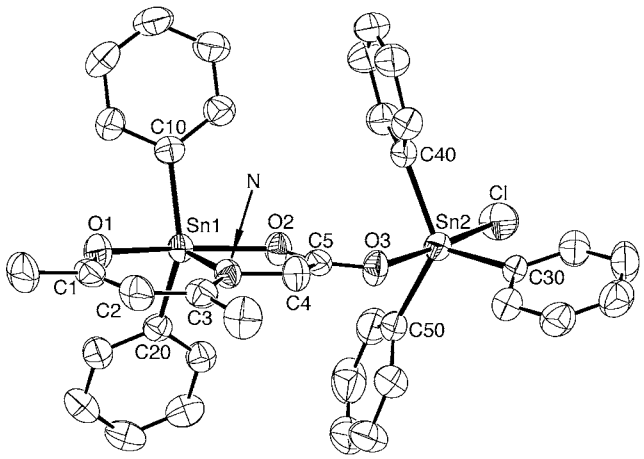

FIGURE 1 Molecular structure for **6**.

A full characterization of the dinuclear complex **6** is described below.

Complex **6** is a molecular solid without exceptionally short intermolecular interactions. Closest contacts are represented by C···H contacts of ca. 2.9 Å. Molecules of **6** (Fig. 1) are dinuclear with the *N*-[(2*Z*)-3-hydroxy-1-methyl-2-butenylidene]glycine ligand bridging two trigonal bipyramidal tin centers. The overall structure with a separation of 5.78 Å between the metal atoms which shows close similarity to dinuclear tin compounds described earlier [1].

All four heteroatoms in the ligand are involved in metal coordination: O1, O2, and N occupy the axial and one of the equatorial sites in the coordination sphere of Sn1, whereas O3 binds to an axial position of Sn2. A chloro ligand occupies the axial position trans to O3. Two phenyl groups at Sn1 and three at Sn2 complete the coordination around the tin atoms. Because of the steric requirements of the chelating ligand, the distortion from a regular coordination polyhedron is more pronounced for Sn1. Both five- and six-membered rings resulting from the chelation of Sn1 show significant deviations from planarity; best planes through these rings enclose a dihedral angle of 5.37(11)°.

DISCUSSION

The results show that the bifunctional tridentate ligand *N*-[(2*Z*)-3-hydroxy-1-methyl-2-butenylidene]glycine forms three classes of organotin(IV) complexes, *viz*. (i) the diorganotin derivatives of the type R_2SnL (**1** and **2**), (ii) the triorganotin(IV) derivatives of the type R_3SnLH (**3**–**5**), and (iii) the dinuclear organotin(IV) derivatives of the type $Ph_2SnL{\cdot}Ph_3SnCl$ (**6**). The diorganotin(IV) complexes may be used as a starting point for the development of dinuclear organotin(IV) derivatives.

The spectroscopic data reveal that in diorganotin(IV) complexes, the coordination geometry about the tin atom is defined by two R groups, an oxygen (derived from a unidentate carboxylate group), an enolate oxygen atom, and the imino N atom. The arrangement of the donor set is distorted trigonal bipyramidal with the two oxygen atoms defining the axial positions (refer to X-ray structure for the Ph_2SnL part of **6**). On the other hand, triorganotin(IV) complexes exhibit a polymeric *trans*-O_2SnC_3 trigonal bipyramidal structural motif with the three R groups occupying the equatorial positions and the axial positions being occupied by a carboxylate oxygen and the enolate oxygen of an adjacent molecule in accord with the similarities in the spectroscopic

and X-ray results of cognate systems [4]. In complex **6**, the geometry found about the Sn(1) atom is very similar to that mentioned for the diorganotin complexes. The geometry about the Sn(2) atom is also distorted trigonal bipyramidal with the Cl and O(2) atoms defining the axial positions.

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