

Synthesis, Characterization and Structural Aspects of Three New Nonsymmetrical Bimetallic Dibutyltin (IV) Derivatives

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Abstract. Three new nonsymmetric bimetallic diorganotin compounds derived from hexadentate Schiff bases were obtained by reaction of 2,6-dihydroxybenzene-1,3-dicarbaldehyde with *R*(-)-phenylglycinol, glycine and 2-amino-5-nitrophenol, in the presence of dibutyltin oxide. The full multinuclear NMR analysis, IR and elemental analyses allowed to establish the structures of all new compounds. In the three cases, the ¹¹⁹Sn chemical shifts are indicative of two different pentacoordinated tin atoms in solution. The molecular structure of compound **4** in the solid state shows two distinct tin atoms with different geometries, one is a distorted trigonal bipyramid with the oxygen atoms in the axial positions and the organic moieties and imine nitrogen in equatorial ones; while the other tin shows distorted octahedral geometry due to Sn(2)-O(4) intermolecular coordination, leading to a dimeric specie, with a Sn-O-Sn-O four-membered ring. The most interesting issue in the solid state is that only one of the tin atoms exhibits intermolecular coordination, in spite of the fact that the atoms are nearly equivalents.

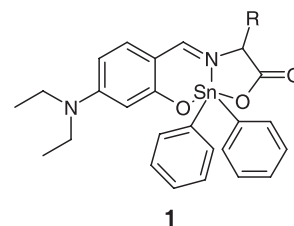
Key words: Diorganotin (IV) derivatives, Multinuclear NMR, X-ray structure.

Resumen. El presente trabajo describe la síntesis de tres nuevos compuestos diorganoestaño derivados de bases de Schiff hexadentadas, los cuales fueron obtenidos por reacción de 2,6-dihidroxibenceno-1,3-dicarbaldéido con *R*(-)-fenilglicinol, glicina y 2-amino-5-nitrofenol, en presencia de óxido de dibutilestaño. La estructura de los nuevos compuestos se estableció por Resonancia Magnética Nuclear Multinuclear, Infrarrojo y Análisis Elemental. Los desplazamientos de RMN de ¹¹⁹Sn de los tres compuestos, en solución, son característicos de átomos de estaño pentacoordinados. La estructura del compuesto **4**, en estado sólido, muestra dos átomos de estaño con diferente geometría; uno de ellos de bipirámide trigonal distorsionada, donde los átomos de estaño ocupan posiciones axiales mientras que los sustituyentes orgánicos y el nitrógeno de la imina están en posiciones ecuatoriales; el otro estaño presenta una geometría de octaedro distorsionado debido a la coordinación intermolecular Sn(2)-O(4) que conduce a la formación de una especie dimerica formando un anillo de cuatro miembros. El aspecto más relevante en estado sólido es que sólo uno de los átomos de estaño presenta coordinación intermolecular a pesar de que los átomos son casi equivalentes.

Palabras clave: Derivados diorganoestaño (IV), RMN Multinuclear, rayos-X.

Introduction

In the last years, our group has been interested in the synthesis and study of diorganotin (IV) complexes derived from different Schiff bases, in these studies we have described different correlations between the spectroscopic data and the molecular structures obtained by X-ray diffraction analysis [1]. Recently, we also became interested in the application of this kind of organometallic compounds in the field of materials with nonlinear optical (NLO) properties [2,3]. Since it is well known that the bulk response in NLO molecular materials is ultimately governed by the arrangement of the molecules in the solid state [4], we designed an interesting family of NLO molecules with chiral groups of variable size, using the same π path (Scheme 1), these molecules allowed us to propose second harmonic generation (SHG) as a tentative tool for the measurement of the degree of chirality [5]. In a recent investigation, we tested the ability of pentacoordinated dibutyltin compounds to have an additional coordination in the solid state [6], the results showed that subtle variations in the geometry of the ligand can have an important effect on the formation of intermolecular Sn-O bonds.



	R	R	R
1a	-CH ₃	1d	-CH(CH ₃)CH ₂ CH ₃
1b	-CH ₂ C ₆ H ₅	1e	-CH ₂ CH(CH ₃) ₂
1c	-C ₆ H ₅	1f	-CH ₂ CH ₂ SCH ₃
		1g	-CH ₂ OH
		1h	-CH(OH)CH ₃
		1i	
		1j	-CH(CH ₃) ₂

Scheme 1

In continuation with our studies of the ability of diorganotin (IV) compounds to form specific arrangements in the solid state, three new nonsymmetric bimetallic diorganotin complexes were synthesized and analyzed. These derivatives have the advantage that they contain two tin atoms in slightly different chemical environments, which are capable of intermolecular coordination to oxygen to form four membered rings [7]. It was anticipated that the two nearly equivalent tin atoms in the solid state coordinated intermolecularly with the oxygen of another molecule to form a dimeric or perhaps a polymeric specie, although formation of monomers could not be discarded. It can be mentioned that, in the last years the synthesis of new organotin (IV) derivatives has been encouraged by the discovery of *in vitro* and *in vivo* antitumor activity, in particular diorganotin (IV) complexes have shown higher anti-cancer activity *in vitro* and *in vivo*, as well as lower toxicity than other well known drugs [8]. Also, diorganotin (IV) complexes have been extensively used as catalyst for different reactions [9].

In this paper we report the synthesis and spectroscopic characterization of three new nonsymmetric bimetallic diorganotin complexes, as well as the molecular structure and intermolecular interactions of compound **4**. The main goal of this work is to analyze the effect of changes in ligand structure on the formation of intermolecular aggregates, it is important to notice that the differences are analyzed within the same molecule. As observed in the structure of the compounds prepared, they have two different Sn atoms with two slightly different ligands, however, comparison of **2**, **3** and **4** is not possible due to the different nature of the substituents.

Results and Discussion

1. Synthetic Aspects

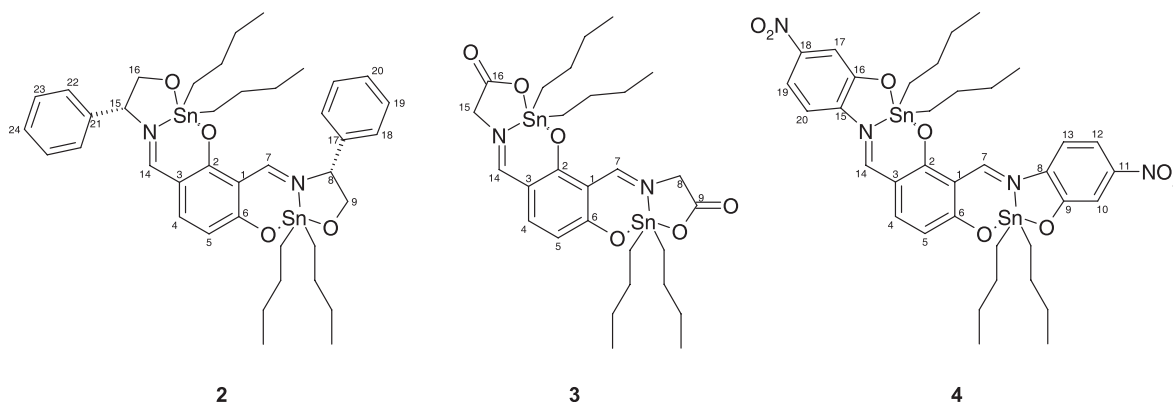
The synthesis of 2,6-dihydroxybenzene-1,3-dicarbaldehyde was carried out following the methodology reported by Hartmann [10]. This procedure involves the condensation of 4-

nitrophenol, ethylorthoformate and resorcinol to give an extremely insoluble *bis*-Schiff base. The hydrolysis of this base in strongly basic media followed by neutralization, gave the desired compound in 45 % yield. It is important to notice that in the original article Hartmann reported the formation of 4,6-dihydroxybenzene-1,3-dicarbaldehyde, however, in this work the reaction only afforded the 2,6-dihydroxybenzene-1,3-dicarbaldehyde. This was confirmed by the ^1H and ^{13}C NMR data which was consistent with this substitution pattern. For instance the ^1H NMR spectrum shows two signals in 10.06 and 10.24 ppm due to the two different aldehyde groups, in the aromatic region the doublets in 6.64 y 7.90 ppm with coupling constant of 8.8 Hz are in agreement with an *ortho* substitution. The ^{13}C NMR spectrum shows two signals in the carbonyl region at 188.1 y 194.3 ppm for the aldehydes, and six different signals for the aromatic ring at 108.7, 109.4, 115.1, 138.3, 165.8, 168.8 ppm.

The preparation of the nonsymmetric bimetallic diorganotin derivatives (Scheme 2) was performed in a single step under the conditions reported previously [1], from 2,4-dihydroxy-3-formylbenzaldehyde, dibutyltin oxide and *R*(-)-phenylglycinol, glycine or 2-amino-5-nitrophenol, respectively, using acetonitrile as solvent, under reflux. In all the cases the reaction was considered completed when all the dibutyltin oxide was dissolved, this usually took around three h. The residue was concentrated under vacuum and the solid purified by crystallization from a chloroform-hexane mixture giving the pure compounds in excellent yields.

2. Spectroscopic Characterization

The ^1H NMR data for all compounds is reported in the experimental part, the presence of two signals for the different imine protons (H-7 and H-14) between 7.78-9.37 ppm with a $\Delta\delta$ around 0.8 ppm confirms formation of the complexes. It is important to note that the small difference in chemical shifts is indicative of similar magnetic and chemical environments. The imine signals show coupling with the ^{117}Sn and ^{119}Sn nuclei, however the satellites give a strongly coupled system



Scheme 2

in which both tin atoms are coupled to each of the protons giving an extremely broad signal where the coupling constant could not be determined. As expected in these nonsymmetrical systems, the ^1H NMR spectra show the aminoalcohol, aminoacid and aminophenol moieties as distinct sets of signals. Complete signal assignment was made on the basis of COSY and NOESY spectra except for the butyl chains where it is not possible to assign the signals to each individual group. The ^{13}C NMR spectra show the same trends as the proton NMR; in this case also, two signals for the imine carbons are observed between 166.8–196.4 ppm, with a $\Delta\delta$ around 9 ppm. All the signals for the two similar fragments were correctly assigned using HETCOR spectra.

The ^{119}Sn NMR spectra of the three compounds show two sharp signals at -190.3 and -184.1; -196.4 and -190.5; -175.2 and -166.8 for **2**, **3** and **4**, respectively, in the range typical for diorganotin complexes with a pentacoordinate geometry [11]. Although the two tin atoms are different, the fact that the $\Delta\delta$ is small evidences the similarity in their chemical and magnetic environments.

In order to assign the distinct signals in the ^{119}Sn spectra of the corresponding tin atoms, we developed a strategy which involved initial assignment of the imine signals followed by selective decoupling of the ^{119}Sn atom and observation of the satellite signals of the imine protons. As an example, irradiation of the tin signal at -166.8 ppm in compound **4**, showed that the satellite for the imine proton at 9.47 ppm in the ^1H NMR spectrum remained unaltered while that at 8.43 ppm evidenced some splitting. Alternatively, irradiation of the tin signal at -175.2 ppm showed changes in the satellite signals for the imine proton at 9.47 ppm. The use of selective irradiation techniques did not allow to determine the value for the $^{119/117}\text{Sn}$ - ^1H coupling constants, and the change in the shape of the imine proton signals did not allow to correlate the particular tin atoms with their corresponding signal.

3. Molecular structure of compound 4

For compound **4** good crystals were obtained by slow evaporation of a saturated solution of the complex in a mixture of chloroform-hexane. The X-Ray structure of **4** shows that the molecule is almost planar, the butyl groups are out of the plane defined by the rings, and show some disorder. Careful analysis of the molecular structure (Figures 1) shows that the molecule is a dimer in the solid state with two tin atoms in different geometries. The first one, Sn(1), is a trigonal bipyramid with the oxygen atoms in the axial positions, while the dibutyl and nitrogen atoms are located in the equatorial ones. In contrast the second tin atom, Sn(2), has a distorted octahedral geometry due to an additional coordination with one oxygen atom from another molecule, leading to a four membered ring with a Sn(2)-O(4) distance of 2.726 Å. The bond angles and distances for both tin atoms are shown in Table 1. This behavior has been previously reported in analogous complexes [12]. Although the formation of this kind of four-member ring by an additional coordination to the tin atom is well documented

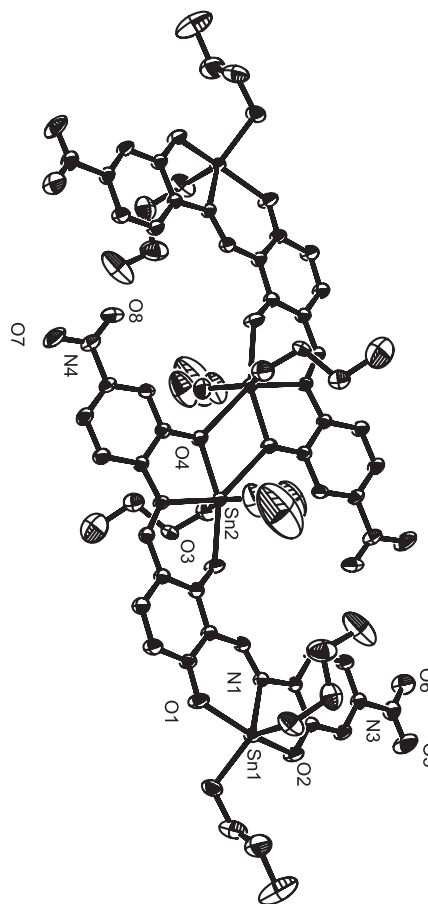


Fig. 1. Molecular structure for compound **4**. Hydrogen atoms are omitted for clarity (thermal ellipsoids at 50 % probability).

in organotin chemistry [7], this example evidences that an extremely subtle variations in the geometry of the ligand can influence considerably the kind of molecular motifs that diorganotin complexes can generate in the solid state. In this case, the molecules have two potential sites for Sn-O intermolecular coordination, however no additional interactions were observed in the lattice.

Conclusions

Analysis of the molecular structure of compound **4** shows that extremely subtle variations in the nature of the ligand can have an enormous influence on the kind of aggregate that these complexes can form, as illustrated by compound **4**, which has two nearly equivalent tin atoms and only one of them has an additional coordination.

The compounds were fully characterized using different spectroscopic techniques. In solution, the molecules show no tendency to form any kind of aggregate. As evidenced by selected decoupling experiments, both tin nuclei are coupled to the imine protons and it was not possible to assign ^{119}Sn NMR signals.

Table 1. Selected bond distances (Å) and angles (°) for compound **4**.

N(1)-Sn(1)	2.200(3)	N(2)-Sn(2)	2.204(3)
C(1A)-Sn(1)	2.134(5)	C(3A)-Sn(2)	2.121(6)
C(2A)-Sn(1)	2.122(5)	C(4A)-Sn(2)	2.117(6)
O(1)-Sn(1)	2.124(3)	O(3)-Sn(2)	2.196(3)
O(2)-Sn(1)	2.090(3)	O(4)-Sn(2)	2.106(3)
C(2a)-Sn(1)-C(1a)	126.5(2)	C(4A)-Sn(2)-C(3a)	142.1(2)
O(2)-Sn(1)-O(1)	152.57(14)	O(4)-Sn(2)-O(3)	156.64(11)
O(2)-Sn(1)-C(1a)	92.60(18)	O(4)-Sn(2)-C(3a)	99.2(2)
O(2)-Sn(1)-C(2a)	104.7(2)	O(4)-Sn(2)-C(4a)	99.7(2)
C(2A)-Sn(1)-O(1)	96.5(2)	C(4A)-Sn(2)-O(3)	85.74(19)
O(1)-Sn(1)-C(1a)	88.35(19)	C(3A)-Sn(2)-O(3)	89.6(2)
O(2)-Sn(1)-N(1)	76.29(11)	O(4)-Sn(2)-N(2)	76.10(11)
C(2A)-Sn(1)-N(1)	103.69(18)	C(4A)-Sn(2)-N(2)	110.79(19)
C(1A)-Sn(1)-N(1)	129.64(19)	C(3A)-Sn(2)-N(2)	105.4(2)
O(1)-Sn(1)-N(1)	82.05(11)	O(3)-Sn(2)-N(2)	80.72(11)

Experimental section

All starting materials were obtained from commercial sources. Solvents were used without further purification. Melting points were recorded on a Gallenkamp MFB-595 apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer 16F-PC FT-IR spectrometer. ^1H , ^{119}Sn and ^{13}C -NMR spectra were recorded on a Jeol Eclipse +400 spectrometer. Chemical shifts (ppm) are relative to $(\text{CH}_3)_4\text{Si}$ for ^1H and ^{13}C and to $\text{Sn}(\text{CH}_3)_4$ for ^{119}Sn . Elemental analyses were carried out on a Thermo Finnigan Flash 1112 elemental microanalyzer. Mass spectra were determined on a Jeol SX-102A spectrometer.

1. Synthesis

Preparation of the three compounds studied herein was carried out following the general procedure. An equivalent of 2,6-dihydroxybenzene-1,3-dicarbaldehyde was heated with *R*-(-)-phenylglycinol, glycine or 2-amino-5-nitrophenol under reflux of acetonitrile for 3 h in the presence of one equivalent of dibutyl tin oxide. The solvent was removed under *vacuum* and the remaining solid was recrystallized from a mixture of chloroform-hexane to yield the pure products.

5,5,19,19-tetrabutyl-8,16-diphenyl-2,3,12,13-benzo-4,6,18,20-tetraoxa-9,15-diaza-5,19-distannabicyclonon-1,14-diene (**2**).

Compound **2** was prepared from 0.083 g (0.50 mmol) of 2,6-dihydroxybenzene-1,3-dicarbaldehyde, 0.254 g (1.00 mmol) dibutyltin oxide and 0.139 g (1.00 mmol) de *R*-(-)-phenylglycinol affording 0.41 g of a yellow solid. Yield 90%, mp: 128.1-129.5 °C. IR (KBr) cm^{-1} , ν_{max} : 2978, 2934, 1620 (C=N), 1590, 1514, 1478, 1420. 1356, 1334, 1144, 948, 742, 716. ^1H NMR (400 MHz, CDCl_3), [δ , ppm]: 0.86-0.93 (m, 12H, CH_3), 1.22-1.27 (m, 8H, CH_2), 1.29-1.40 (m, 16H, CH_2), 3.88 (dd, 1H, $J = 14.1$, 12.1 Hz, H-13), 4.03 (dd, 1H, $J = 14.1$, 2.3 Hz, H-14a), 4.22 (dd, 1H, $J = 12.1$, 2.3 Hz, H-14b), 4.32 (dd, 1H,

$J = 13.1$, 10.0 Hz, H-15), 4.42 (dd, 1H, $J = 13.1$, 2.3 Hz, H-16a), 4.54 (dd, 1H, $J = 13.1$, 10.0 Hz, H-16b), 5.90 (d, 1H, $J = 9.1$ Hz, C-5), 6.79 (d, 1H, $J = 9.1$ Hz, C-6), 7.21-7.42 (m, 10H, Ar), 7.78 (s, 1H, H-7), 8.79 (s, 1H, H-14). ^{13}C NMR (100.5 MHz, CDCl_3), [δ , ppm]: 13.5 (CH_3), 13.7 (CH_3), 13.7 (CH_3), 13.8 (CH_3), 20.7 (CH_2), 20.7 (CH_2), 20.9 (CH_2), 21.2 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 27.2 (CH_2), 27.3 (CH_2), 27.4 (CH_2), 27.4 (CH_2), 69.7 (C-13), 69.8 (C-15), 70.7 (C-12), 71.0 (C-16), 107.3 (C-5), 109.5 (Ar), 112.7 (Ar), 128.1 (Ar), 128.2 (Ar), 128.5 (Ar), 129.0 (Ar), 129.0 (Ar), 138.9 (C-4), 139.6 (C-3), 143.3 (C-7), 168.4 (C-7), 169.0 (C-14), 175.3 (C-2), 178.5 (C-6). ^{119}Sn NMR (111.9 MHz, CDCl_3), [δ (ppm)]: -190.3, -184.1. MS m/z FAB+ (ANB) (*rel. int*): 809 M^+ -59 (3%), FAB -(TEA) 868(1%). Anal. Calc. for $\text{C}_{40}\text{H}_{56}\text{N}_2\text{O}_4\text{Sn}_2$: C 55.46, H 6.52, N 3.23. Found: C 55.73, H 6.61, N 3.33.

5,5,19,19-Tetrabutyl-8,16-diphenyl-2,3,12,13-benzo-4,6,18,20-tetraoxa-9,15-diaza-5,19-distannabicyclonon-1,14-dien-7,17-dione (3). Compound **3** was prepared from 0.083 g (0.50 mmol) of 2,6-dihydroxybenzene-1,3-dicarbaldehyde, 0.254 g (1.00 mmol) dibutyltin oxide and 0.075 g (1.00 mmol) of glycine, affording 0.370 g of a yellow solid. Yield 95%, m.p. 196-198 °C, IR (KBr) cm^{-1} , ν_{max} : 3064, 3042 1665 (C=O), 1660 (C=O), 1624 (C=N), 1578 (C=N), 1554, 1504, 1474, 1316, 1170, 1148, 1056, 998, 976, 790, 736. ^1H NMR (400 MHz, CDCl_3), [δ , ppm]: 0.83-0.90 (m, 12H, CH_3), 1.31-1.36 (m, 8H, CH_2), 1.50-1.69 (m, 16H, CH_2), 4.30 (s, 2H, H-13), 4.33 (s, 2H, H-15), 6.10 (δ , 1H, $J = 9.0$, H-5), 7.11 (d, 1H, $J = 9.0$, H-4), 8.05 (s, 1H, H-7), 8.88 (s, 1H, H-14). ^{13}C NMR (100.5 MHz, CDCl_3), [δ , ppm]: 13.5 (CH_3), 13.6 (CH_3), 22.3 (CH_2), 22.5 (CH_2), 26.5 (CH_2), 26.8 (CH_2), 27.1 (CH_2), 56.9 (C-13), 57.9 (C-15), 107.7 (C-5), 113.3 (C-1), 113.9 (C-3), 126.3 (C-6), 144.3 (C-4), 168.0 (C-7), 169.0 (C-14), 171.1 (C-2), 171.3 (C-9), 174.6 (C-12), 178.3 (C-16). ^{119}Sn NMR (111.9 MHz, CDCl_3), [δ (ppm)]: -196.4, -190.5. MS m/z (*rel. int*): 745 M^{+1} (5%), 689 (100), 633 (20), 575 (19), 517 (17), 461 (5), 405 (17), 251 (32), 177 (20), 137 (12), 57 (38). Anal. Calc. for $\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_6\text{Sn}_2$: C 45.32, H 5.98, N 3.77. Found: C 45.42, H 6.01, N 3.87.

5,5,19,19-tetrabutyl-di(4-nitrobenzo[h][p])-8,16-diphenyl-2,3,12,13-benzo-4,6,18,20-tetraoxa-9,15-diaza-5,19-distannabicyclonon-1,14-diene (**4**)

Compound **4** was prepared from 0.083 g (0.50 mmol) of 2,6-dihydroxybenzene-1,3-dicarbaldehyde, 0.254 g (1.00 mmol) dibutyltin oxide and 0.172 g (1.00 mmol) of 2-amine-5-nitrophenol, affording 0.410 g of a yellow solid. Yield 92%, mp: 210-212 °C, IR (KBr) cm^{-1} , ν_{max} : 2956, 2922, 1608 (C=N), 1584 (C=N), 1548, 1494, 1472, 1356, 1174, 956, 818, 668, 574. ^1H NMR (400 MHz, CDCl_3), [δ , ppm]: 0.86-0.89 (m, 12H, CH_3), 1.30-1.43 (m, 12H, CH_2), 1.53-1.72 (m, 18H, CH_2), 6.22(d, 1H, $J = 8.80$, H-5), 7.26-7.33(m, 3H, H-13, 20, 4), 7.57-7.64 (m, 4H, H-10, 12 17, 19), 8.43 (s, 1H, H-7), 9.37 (s, 1H, H-14). ^{13}C NMR(100.5 MHz, CDCl_3), [δ , ppm]:13.5 (CH_3), 13.7 (CH_3), 22.6 (CH_2), 22.8 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 108.9 (C-8), 110.7 (C-15),

Table 2. Crystal data for **4**.

4	
Formula	C ₃₆ H ₄₆ N ₄ O ₈ Sn ₂
Molecular weight	900.15
Crystal System	triclinic
Space group	P-1
a (Å)	12.8796(6)
b (Å)	12.8367(9)
c (Å)	13.4549(15)
α (°)	78.045(9)
β (°)	68.245(6)
γ (°)	71.595(5)
V (Å ³)	1950.1(3)
Temperature (K)	293(2)
Z	2
Total Reflections	7560
Independent Reflections	7165
R ^a	0.0379
Rw ^b	0.0608
No. variables	537

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F_o)^2 = [\sum_w(F_o^2 - F_c^2)^2 / \sum_w F_o^4]^{1/2}$$

112.7 (C-1), 113.2 (C-3), 113.8 (C-12), 114.6 (C-5), 115.3 (C-19), 138.3 (C-13, C-20, C-4), 138.3 (C-10), 145.1 (C-17), 147.3 (C-11), 148.1 (C-18), 158.5 (C-2), 159.2 (C-6), 160.0 (C-7), 160.5 (C-14), 176.6 (C-12), 180.0 (C-16). ¹¹⁹Sn NMR (111.9 MHz, CDCl₃), [δ (ppm)]: -175.2, -166.8. Anal. Calc. for C₃₆H₄₆N₄O₈Sn₂: C 48.14, H 5.14, N 5.90. Found: C 48.43, H 5.17, N 5.87.

2. X-Ray Analysis

The X-ray diffraction study was determined on an Enraf Nonius-CAD4 diffractometer with an area detector ($\lambda_{\text{MoK}\alpha} = 0.71073$ Å, graphite monochromator, T=293 K, $\omega/2\theta$ scan mode) the crystal was mounted in a LINDEMAN tube. Absorption correction was performed with the SHELX-A procedure.¹³ Corrections were made for Lorentz and Polarization effects. Solution and refinement: direct methods (SHELX-S-97) for structure solution and SHELX-L-97 ver. 34 for refinement and data output [13] were applied using the WIN-GX program set [14], the corresponding images were prepared with the ORTEP 3 program [15]. All heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were found by Fourier maps differences and refined isotropically. The remaining hydrogen atoms were geometrically modeled. Crystallographic data for compound **2** is summarized in Table 2.

Supplementary material

Crystallographic data for **4** has been deposited at the Cambridge Crystallographic Data Centre with deposition number 0C1CDC 610186. Copy of the information may be obtained free of

charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or (<http://www.ccdc.cam.ac.uk>).

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