

# Synthesis and Structures of Some Diorganotin Bis(hydroxamate)s\*

V. S. Petrosyan,<sup>†‡</sup> N. S. Yashina,<sup>‡</sup> T. V. Sizova,<sup>‡</sup> T. V. Leonova,<sup>‡</sup>  
L. A. Aslanov,<sup>‡</sup> A. V. Yatsenko<sup>‡</sup> and L. Pellerito<sup>§</sup>

<sup>‡</sup> Department of Chemistry, M. V. Lomonosov University, Moscow, Russia, and <sup>§</sup> Department of Chemistry, University of Palermo, Italy

Analysis of literature data on the antitumor activity of organotin compounds reveals that  $R_2SnX_2$  and their complexes containing Sn–O, Sn–N or Sn–S bonds often exhibit biological activity, especially if such bonds are formed by means of intramolecular coordination. Furthermore, a wide range of biological activities, from fungicidal, bactericidal and antiseptic to psychotropic and antitumor, is found to be characteristic for some organic hydroxamic acids (*N*-acylhydroxylamines). From this point of view the diorganotin bis-hydroxamates in this paper are of particular interest as potential biologically active antitumor drugs. Di-*n*-butyltin bis(*N*-methyl-*N*-*p*-bromobenzoylhydroxylamine) is being screened for antitumor activity.

## INTRODUCTION

For several years the synthesis, investigation of physicochemical properties and structure determination of organotin hydroxamates has been the subject of a number of studies.<sup>1–12</sup> As a rule, the hydroxamic ligand is shown to be bidentate because of carbonyl coordination to tin, thus provoking a substantial reduction in the infrared carbonyl stretching frequencies in comparison with the free hydroxylamines.<sup>3–7</sup> On the other hand, the final conclusion on the organotin hydroxamate structure could be made based on <sup>119</sup>Sn Mössbauer parameters by means of their correlation with the appropriate crystal structure parameters.<sup>3,4</sup> However, only a few X-ray structure determinations of organotin *N*-acylhydroxylamine derivatives are available.<sup>8–11</sup>

In this paper we report the crystal structures of bis(*N*-phenyl-*N*-benzoylhydroxylamino)di-*n*-

butyltin,  $n\text{-Bu}_2\text{Sn}[\text{ON}(\text{Ph})\text{C}(\text{O})\text{Ph}]_2$  (**1**) and bis(*N*-methyl-*N*-*p*-bromobenzoylhydroxylamino)-di-*n*-butyltin,  $n\text{-Bu}_2\text{Sn}[\text{ON}(\text{Me})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-Br}]_2$  (**2**), of which **1** was synthesized by Harrison and Richards.<sup>3</sup> We consider also their IR, Mössbauer and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn) spectroscopic parameters. Moreover, the structures of bis(*N*-methyl-*N*-*p*-bromobenzoylhydroxylamino)-dimethyltin  $\text{Me}_2\text{Sn}[\text{ON}(\text{Me})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-Br}]_2$  (**3**) and bis(*N*-*p*-Br-phenyl-*N*-*p*-bromobenzoylhydroxylamino)-di-*n*-butyltin and -dimethyltin  $R_2\text{Sn}[\text{ON}(\text{C}_6\text{H}_4\text{-Br-}p)\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-Br}]_2$ ,  $R = n\text{-Bu}$  (**4**) and  $\text{Me}$  (**5**) in the solid state and in  $\text{CDCl}_3$  solution are discussed on the basis of IR, Mössbauer and NMR data.

## EXPERIMENTAL

$\text{Me}_2\text{SnO}$  was prepared by alkaline hydrolysis of  $\text{Me}_2\text{SnCl}_2$ .  $n\text{-Bu}_2\text{SnO}$  was a commercial product. *N*-Phenyl-*N*-benzoylhydroxylamine, *N*-methyl-*N*-*p*-bromobenzoylhydroxylamine and *N*-*p*-bromophenyl-*N*-*p*-bromobenzoylhydroxylamine were obtained by reaction of the appropriate acyl chloride and hydroxylamine hydrochloride in the presence of  $\text{Na}_2\text{CO}_3$ .<sup>13</sup> Solvents were dried before use by standard methods.

Dialkyltin bis-hydroxamates were synthesized by stirring 1.5 mmol  $R_2\text{SnO}$  ( $R = \text{Me}$ ,  $n\text{-Bu}$ ) and 3 mmol of the appropriate *N*-acylhydroxylamine in the presence of excess of 2,2-dimethoxypropane in 40 cm<sup>3</sup>  $\text{CHCl}_3$  at room temperature for 3–4 h. The reaction mixture was filtered and white (**2**, **3**, **5**) or yellow (**1** and **4**) crystalline solids were precipitated by addition of petroleum ether. The yields were 85–90%. Results of the elemental analyses are reported in Table 1 together with melting points.

Single crystals of  $n\text{-Bu}_2\text{Sn}[\text{ON}(\text{Ph})\text{C}(\text{O})\text{Ph}]_2$  (**1**) and  $n\text{-Bu}_2\text{Sn}[\text{ON}(\text{Me})\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-Br}]_2$  (**2**) were

\* Dedicated to Dr F. E. Brinckman.

<sup>†</sup> Author to whom correspondence should be addressed.

**Table 1** Elemental analysis and melting points of the dialkyl bis-hydroxamates

Compound	M.p. (°C)	Analysis (%)					
		C		H		N	
		Calcd	Found	Calcd	Found	Calcd	Found
<b>1</b> n-Bu <sub>2</sub> Sn[ON(Ph)C(O)Ph] <sub>2</sub>	105–106 <sup>a</sup>						
<b>2</b> n-Bu <sub>2</sub> Sn[ON(Me)C(O)C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br] <sub>2</sub>	162–163	41.7	41.5	4.6	4.6	4.05	3.7
<b>3</b> Me <sub>2</sub> Sn[ON(Me)C(O)C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br] <sub>2</sub>	141–143	35.6	36.0	3.3	3.3	4.6	4.6
<b>4</b> n-Bu <sub>2</sub> Sn[ON(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br)C(O)C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br] <sub>2</sub>	83–84	41.9	42.2	3.5	3.5	2.1	2.6
<b>5</b> Me <sub>2</sub> Sn[ON(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br)C(O)C <sub>6</sub> H <sub>4</sub> - <i>p</i> -Br] <sub>2</sub>	— <sup>b</sup>	37.8	37.8	2.5	2.4	3.1	3.0

<sup>a</sup> Literature<sup>5</sup> 106–107 °C. <sup>b</sup> With decomposition.

obtained by recrystallization from CHCl<sub>3</sub>/acetone solution after addition of petroleum ether.

Intensity data for colorless crystals of (**1**) (0.15 mm × 0.35 mm × 0.40 mm) and (**2**) (0.15 mm × 0.20 mm × 0.45 mm) were measured at room temperature on a CAD-4 diffractometer (Mo- $\omega$ -scan technique). Absorption correction procedure using  $\omega$ -scan curves was applied. Crystal data are listed in Table 2.

Structure **1** was solved by Patterson methods (only the tin atom position was determined) and structure **2** by direct methods (tin and two bromine atoms were located). The residual atoms were located from Fourier syntheses. Both structures were refined by full-matrix least-squares; all non-hydrogen atoms were refined anisotropically; unit weights were used. Hydrogen atoms (except

butyl groups) were included in structure factor calculations at their calculated positions. Butyl groups in both structures tend to disorder; C–C bond distances and C–C–C angles have irregular values and equivalent thermal parameters of butyl carbon atoms are in the range of 11–30 Å<sup>2</sup> (1.1–3.0 nm). Fractional atomic coordinates for **1** and **2** are given in Tables 3 and 4, respectively.

IR spectra were recorded as Nujol mulls on a Perkin–Elmer grating spectrometer, model 983G, with CsI windows.

<sup>1</sup>H NMR, proton-decoupled <sup>13</sup>C and <sup>119</sup>Sn NMR spectra were obtained with a Varian VXR-400 spectrometer, at 400, 100 and 149.2 MHz respectively.

<sup>119</sup>Sn Mössbauer spectra were measured with constant acceleration and a triangular waveform, using a Laben 8001 multichannel analyzer, and a Mössbauer closed refrigerator system [model 21 sc Cryodyne Cryocooler (CTI-Cryogenics, USA)].

**Table 2** Crystal data for **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>34</sub> H <sub>38</sub> N <sub>2</sub> O <sub>4</sub> Sn	C <sub>24</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub> Sn
Mol. wt	657.38	691.04
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
<i>a</i> (Å)	11.018(3)	14.115(3)
<i>b</i> (Å)	13.477(4)	11.658(3)
<i>c</i> (Å)	22.392(6)	17.369(5)
$\beta$ (deg)	102.89(3)	106.08(2)
<i>V</i> (Å <sup>3</sup> )	3241	2746
<i>Z</i>	4	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.347	1.671
$\mu$ (cm <sup>-1</sup> )	8.26	38.5
$\theta$ (max) (deg)	28	26
No. of unique reflections collected	8142	5398
No. of reflections used with $I > 3\sigma(I)$	3537	3658
<i>R</i>	0.052	0.034
<i>R<sub>w</sub></i>	0.053	0.036

## RESULTS AND DISCUSSION

The structures and atomic numbering schemes for **1** and **2** are depicted in figs 1 and 2, respectively. Selected bond distances and angles are reported in Tables 5 and 6. Geometries around the tin atom in both **1** and **2** are very similar and close to that found for Me<sub>2</sub>Sn[ON(Me)C(O)Me]<sub>2</sub><sup>9</sup> and Me<sub>2</sub>Sn[NHC(O)Me]<sub>2</sub>·H<sub>2</sub>O.<sup>10</sup> In both structures under consideration the two *N*-acylhydroxylamine residues are almost equivalent and function as bidentate ligands, forming one short covalent and one long coordinate tin-to-oxygen bond (Tables 5 and 6). The two heterocyclic rings are essentially planar, the deviations of tin atoms from these planes being 0.45 Å and 0.49 Å for **1**

**Table 3** Fractional atomic coordinates ( $\times 10^5$  for Sn,  $\times 10^4$  for other atoms) for **1**

Atom	x	y	z
Sn	49505(5)	19092(4)	55503(2)
O(1)	5406(5)	2598(4)	4624(2)
O(2)	5758(5)	3309(4)	5737(2)
O(3)	4201(6)	484(4)	6015(2)
O(4)	4786(5)	2272(4)	6433(2)
N(1)	6349(5)	3722(5)	5312(3)
N(2)	4082(6)	1636(5)	6709(3)
C(1)	6078(7)	3353(6)	4745(3)
C(2)	7334(7)	4374(6)	5574(3)
C(3)	7070(8)	5167(7)	5915(4)
C(4)	8073(10)	5786(8)	6205(4)
C(5)	9239(10)	5595(9)	6152(5)
C(6)	9492(9)	4807(10)	5786(5)
C(7)	8518(8)	4169(8)	5506(4)
C(8)	6517(7)	3872(6)	4251(3)
C(9)	6399(7)	4909(6)	4198(4)
C(10)	6750(8)	5376(7)	3685(4)
C(11)	7176(8)	4810(7)	3258(4)
C(12)	7289(8)	3784(7)	3320(4)
C(13)	6949(7)	3299(6)	3813(3)
C(14)	3852(7)	727(6)	6489(3)
C(15)	3561(7)	2137(5)	7170(3)
C(16)	4396(9)	2562(7)	7658(3)
C(17)	3876(10)	3089(8)	8103(4)
C(18)	2603(8)	3158(7)	8027(4)
C(19)	1803(8)	2740(7)	7519(4)
C(20)	2283(7)	2218(7)	7074(4)
C(21)	3202(7)	17(6)	6819(3)
C(22)	2151(9)	-460(7)	6499(4)
C(23)	1564(10)	-1160(8)	6798(5)
C(24)	2047(9)	-1382(7)	7410(4)
C(25)	3103(10)	-936(7)	7725(4)
C(26)	3713(9)	-199(7)	7439(4)
C(27)	3116(9)	2080(10)	4980(5)
C(28)	2122(10)	1874(10)	5198(6)
C(29)	822(10)	1986(10)	4747(6)
C(30)	-60(20)	1631(10)	5006(7)
C(31)	6468(10)	960(9)	5527(5)
C(32)	7391(20)	807(10)	6000(9)
C(33)	7822(10)	1236(10)	6505(6)
C(34)	9065(10)	903(10)	6930(8)

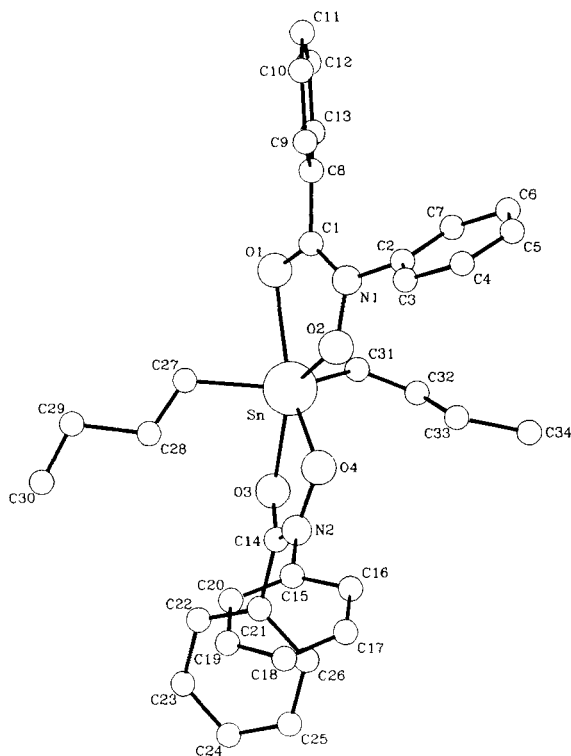
and 0.09 Å and 0.04 Å for **2**. The phenyl rings are rotated about 45–60° relative to the planes of the *N*-acylhydroxylamine residues. The equatorial plane O1–O2–O3–O4 in structure **2** is more regular than that in **1**. The CSnC fragments are non-linear in both structures so that the C–Sn–C angles are 133.9° for **1** and 145.1° for **2**. Although this geometry at the tin atom is usually described as a distorted *trans*-octahedron,<sup>3, 9, 10</sup> it is also possible to refer to it as a bicapped tetrahedron.<sup>14</sup>

As in Ph<sub>3</sub>SnON(Ph)C(O)Ph,<sup>8</sup> Me<sub>2</sub>Sn[ON(Me)-C(O)Me]<sub>2</sub><sup>9</sup> and Me<sub>2</sub>Sn[ONHC(O)Me]<sub>2</sub>,<sup>10</sup> the bond lengths in the *N*-acylhydroxylamine residues are consistent with a significant contribution of the zwitterionic canonical form to the electronic distribution, the C=O distance being longer and the endocyclic C–N distance shorter, than normal double-bond C=O and single bond C–N distances, respectively.<sup>9</sup>

Mössbauer parameters [isomeric shift (IS) and quadrupole splitting (QS)] of the hydroxamates synthesized are given in Table 7. According to the X-ray crystal data for compounds **1** and **2**, the distortion of the *trans*-octahedral structures is so great that a traditional comparison of QS experimental values with QS values calculated in terms of the point-charge model formalism assuming an idealized octahedral environment around the tin

**Table 4** Fractional atomic coordinates ( $\times 10^5$  for Sn,  $\times 10^4$  for other atoms) for **2**

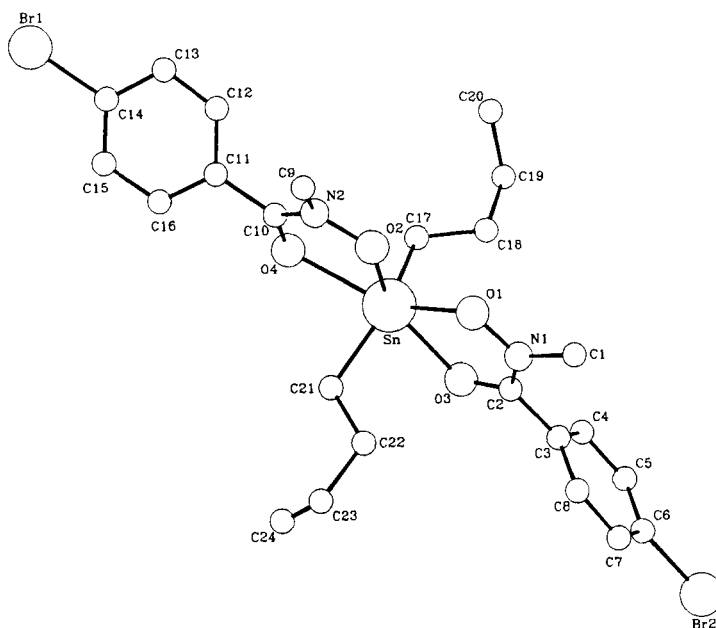
Atom	x	y	z
Sn	45 105(3)	16 337(3)	10 804(2)
Br(1)	58 524(5)	45 388(7)	-33 869(4)
Br(2)	43 662(6)	-26 654(7)	54 085(4)
O(1)	3692(3)	2244(3)	1837(2)
O(2)	3756(3)	3107(3)	514(2)
O(3)	4742(3)	345(3)	2168(2)
O(4)	5014(3)	2049(4)	-97(2)
N(1)	3705(3)	1575(4)	2497(2)
N(2)	3927(3)	3468(4)	-189(2)
C(1)	3160(4)	2107(5)	2995(3)
C(2)	4236(4)	628(5)	2632(3)
C(3)	4233(4)	-124(4)	3318(3)
C(4)	5135(4)	-434(5)	3841(3)
C(5)	5177(4)	-1189(5)	4469(3)
C(6)	4309(4)	-1630(5)	4555(3)
C(7)	3404(4)	-1352(5)	4042(3)
C(8)	3371(4)	-586(5)	3430(3)
C(9)	3216(4)	4304(6)	-591(3)
C(10)	4590(4)	2913(5)	-459(3)
C(11)	4856(4)	3336(5)	-1180(3)
C(12)	5108(4)	4468(5)	-1260(3)
C(13)	5428(4)	4830(5)	-1899(3)
C(14)	5464(4)	4045(5)	-2480(3)
C(15)	5227(4)	2923(5)	-2417(3)
C(16)	4951(4)	2549(5)	-1759(3)
C(17)	5954(5)	2235(7)	1634(4)
C(18)	6244(6)	2474(8)	2515(5)
C(19)	7278(6)	2993(10)	2887(6)
C(20)	7469(9)	4102(9)	2622(8)
C(21)	3667(5)	321(5)	366(4)
C(22)	2815(6)	-150(8)	646(5)
C(23)	2144(8)	-1027(10)	96(6)
C(24)	2281(9)	-1632(20)	-267(8)



**Figure 1** Structure and atomic numbering scheme for **1**.

atom seems to be pointless. For comparison we have made such calculations using literature values for the partial quadrupole splittings of the alkyl and ligand groups and real angle values determined from X-ray analysis of **2** (Table 2). The resulting  $QS_{\text{calcd}} = 3.09 \text{ mm s}^{-1}$  is in good agreement with the  $QS_{\text{exp}}$  of compounds **1**, **2**, **4** and **5** and of  $\text{Me}_2\text{Sn}(\text{ON}(\text{Me})\text{C}(\text{O})\text{Me})_2$  ( $QS = 3.31 \text{ mm s}^{-1}$ )<sup>3</sup>, for which the distorted *trans*-octahedral structure was established.<sup>9</sup> Thus it is logically based on Mössbauer spectroscopic data to ascribe the distorted octahedral structures, with alkyl groups in the *trans*-position to each other, also to the hydroxamates **4** and **5**.

However, the dimethyltin derivative **3** has a substantially lower  $QS_{exp}$  of  $2.13 \text{ mm s}^{-1}$ . Principally, such a low QS value can be correlated with a tetrahedral structure for this compound. But it is difficult to expect a tetrahedral structure in this case when the first coordination sphere of the tin is not sterically hindered by the bulky R and both donor centers of the ligand have comparable strength. On the other hand, the IR-spectroscopic data of **3** are similar to those found for the di-n-butyltin derivative **2**, being (in compliance with our X-ray analysis) of a *trans*-octahedral chelate structure. Thus we suppose that the tetrahedral structure for **3** is unlikely, and suggest instead a *cis*-octahedral one similar to that



**Figure 2** Structure and atomic numbering scheme for **2**.

**Table 5** Selected bond distances and angles in structure 1

Atoms	<i>d</i> (Å)	Atoms	$\omega$ (deg)	Atoms	$\omega$ (deg)
Sn–O(1)	2.424(6)	O(1)SnO(2)	70.4(2)	SnO(1)C(1)	110.6(4)
Sn–O(2)	2.088(5)	O(1)SnO(3)	146.0(2)	SnO(2)N(1)	118.1(4)
Sn–O(3)	2.416(6)	O(1)SnO(4)	143.2(2)	SnO(3)C(14)	111.0(5)
Sn–O(4)	2.084(5)	O(1)SnC(27)	78.3(3)	SnO(4)N(2)	116.9(4)
Sn–C(27)	2.149(9)	O(1)SnC(31)	83.9(3)	O(2)N(1)C(1)	117.7(6)
Sn–C(31)	2.115(12)	O(2)SnO(3)	143.4(2)	O(2)N(1)C(2)	113.5(5)
O(1)–C(1)	1.253(10)	O(2)SnO(4)	73.8(2)	C(1)N(1)C(2)	127.8(7)
O(2)–N(1)	1.383(8)	O(2)SnC(27)	108.9(4)	O(4)N(2)C(14)	119.0(6)
O(3)–C(14)	1.251(10)	O(2)SnC(31)	104.3(3)	O(4)N(2)C(15)	112.1(5)
O(4)–N(2)	1.390(8)	O(3)SnO(4)	70.6(2)	C(14)N(2)C(15)	128.4(7)
N(1)–C(1)	1.334(9)	O(3)SnC(27)	88.6(4)	O(1)C(1)N(1)	120.2(7)
N(1)–C(2)	1.417(9)	O(3)SnC(31)	83.0(4)	O(1)C(1)C(8)	120.0(6)
N(2)–C(14)	1.324(10)	O(4)SnC(27)	105.6(3)	N(1)C(1)C(8)	119.7(7)
N(2)–C(15)	1.453(10)	O(4)SnC(31)	113.7(3)	O(3)C(14)N(2)	119.2(7)
C(1)–C(8)	1.478(11)	C(27)SnC(31)	133.9(4)	O(3)C(14)C(21)	121.8(7)
C(14)–C(21)	1.486(11)			N(2)C(14)C(21)	119.0(7)

**Table 6** Selected bond distances and angles in structure 2

Atoms	<i>d</i> (Å)	Atoms	$\omega$ (deg)	Atoms	$\omega$ (deg)
Sn–O(1)	2.101(4)	O(1)SnO(2)	73.9(1)	SnO(2)N(2)	118.2(3)
Sn–O(2)	2.114(3)	O(1)SnO(3)	72.2(1)	SnO(3)C(2)	111.5(3)
Sn–O(3)	2.364(4)	O(1)SnO(4)	144.2(1)	SnO(4)C(10)	112.3(4)
Sn–O(4)	2.393(4)	O(1)SnC(17)	103.3(2)	O(1)N(1)C(1)	111.5(4)
Sn–C(17)	2.118(6)	O(1)SnC(21)	107.1(2)	O(1)N(1)C(2)	119.8(4)
Sn–C(21)	2.117(6)	O(2)SnO(3)	145.9(1)	C(1)N(1)C(2)	128.5(5)
O(1)–N(1)	1.382(5)	O(2)SnO(4)	70.7(1)	O(2)N(2)C(9)	111.7(4)
O(2)–N(2)	1.376(6)	O(2)SnC(17)	103.9(2)	O(2)N(2)C(10)	118.6(4)
O(3)–C(2)	1.260(7)	O(2)SnC(21)	100.7(2)	C(9)N(2)C(10)	128.9(5)
O(4)–C(10)	1.248(6)	O(3)SnO(4)	143.4(1)	O(3)C(2)N(1)	120.1(5)
N(1)–C(1)	1.448(8)	O(3)SnC(17)	86.8(2)	O(3)C(2)C(3)	119.2(5)
N(1)–C(2)	1.317(7)	O(3)SnC(21)	86.5(2)	N(1)C(2)C(3)	120.7(5)
N(2)–C(9)	1.434(7)	O(4)SnC(17)	81.1(2)	O(4)C(10)N(2)	120.2(5)
N(2)–C(10)	1.326(7)	O(4)SnC(21)	84.1(2)	O(4)C(10)C(11)	119.6(5)
C(2)–C(3)	1.481(7)	C(17)SnC(21)	145.1(3)	N(2)C(10)C(11)	120.1(5)
C(10)–C(11)	1.489(8)	SnO(1)N(1)	116.4(3)		

**Table 7** Mössbauer parameters and infrared carbonyl stretching frequencies for dialkyltin bis-hydroxamates

Compound	IS (mm s <sup>−1</sup> )	QS (mm s <sup>−1</sup> )	$\nu(\text{CO})$ (cm <sup>−1</sup> )
1 <sup>a</sup>	1.28	3.10	1553, 1562sh
2	1.28	3.27	1580
3	0.87	2.13	1579
4	1.26	2.90	1533
5	1.23	3.34	1542

<sup>a</sup> Literature:<sup>3</sup> IS, 1.34 mm s<sup>−1</sup>; QS, 3.30 mm s<sup>−1</sup>;  $\nu(\text{CO})$ , 1552, 1564 cm<sup>−1</sup>.

of Me<sub>2</sub>Sn(ONHC(O)Me)<sub>2</sub><sup>10</sup> with QS = 2.01 mm s<sup>−1</sup>.<sup>3</sup>

In the IR spectra of all solid compounds discussed here, the carbonyl stretching vibrations occur at lower frequencies (Table 7) in comparison with the spectra of the free hydroxylamines, [HON(Ph)C(O)Ph, 1624 cm<sup>−1</sup>; HON(Me)C(O)C<sub>6</sub>H<sub>4</sub>-*p*-Br, 1610 cm<sup>−1</sup>; and HON(C<sub>6</sub>H<sub>4</sub>-*p*-Br)C(O)C<sub>6</sub>H<sub>4</sub>-*p*-Br, 1602 cm<sup>−1</sup>) confirming again the bidentate function of the hydroxylamine residues in the hydroxamates.<sup>3–9</sup>

The <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopic parameters of the compounds under consideration are

**Table 8** (a)  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR-spectroscopic data for diorganotin bis-hydroxamates  $[\text{Y}(\text{O})\text{C}(\text{X})\text{NO}]_2\text{SnR}_2$  ( $\text{R} = {}^2\text{CH}_3$ ,  ${}^2\text{CH}_2\text{---}{}^3\text{CH}_2\text{---}{}^4\text{CH}_2\text{---}{}^5\text{CH}_3$ ) in  $\text{CDCl}_3$  solvent<sup>a</sup>

R	Bu	Bu	Me	Bu	Me
X	Ph	Me	Me	$\text{C}_6\text{H}_4\text{-}p\text{-Br}$	$\text{C}_6\text{H}_4\text{-}p\text{-Br}$
Y	Ph	$\text{C}_6\text{H}_4\text{-}p\text{-Br}$	$\text{C}_6\text{H}_4\text{-}p\text{-Br}$	$\text{C}_6\text{H}_4\text{-}p\text{-Br}$	$\text{C}_6\text{H}_4\text{-}p\text{-Br}$
$\delta^2\text{CH}_2\text{or}^2\text{CH}_3$	1.48(t)	1.44(t)	0.70(s)	1.57(t)	0.72(s)
${}^2J(^1\text{H}\text{---}^{119}\text{Sn})$	nv	nv	83.6	nv	81.2
$\delta^3\text{CH}_2$	1.82(m)	1.65(m)	—	1.74(m)	—
$\delta^4\text{CH}_2$	1.59(m)	1.39(m)	—	1.44(m)	—
$\delta^5\text{CH}_3$	0.93(t)	0.89(t)	—	−0.91(t)	—
X	7.21(m)	3.45(s)	3.48(s)	7.25(m)	7.18(m)
Y	7.21(m)	7.44(m)	7.44(m)	7.20(m)	7.14(m)

(b)  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR chemical shifts (ppm) and coupling constants (Hz) of compounds **1–5**

$\delta^1\text{C}$	163.8	162.7	162.7	163.1	163.2
$\delta^2\text{C}$	26.6	26.9	6.4	26.8	6.3
${}^1J(^{13}\text{C}\text{---}^{119}\text{Sn})$	709	739	754	706	713
$\delta^3\text{C}$	27.7	27.4	—	27.6	—
${}^2J(^{13}\text{C}\text{---}^{119}\text{Sn})$	34	36	—	33	—
$\delta^4\text{C}$	26.7	26.6	—	26.6	—
${}^3J(^{13}\text{C}\text{---}^{119}\text{Sn})$	108	113	—	106	—
$\delta^5\text{C}$	14.0	13.9	—	13.9	—
$\delta(\text{X})$	141.9	40.9	40.9	140.6	140.3
	132.9			132.1	132.2
	130.0			131.6	131.5
	128.7			131.2	130.8
$\delta(\text{Y})$	128.65	131.8	131.8	130.2	130.2
	128.0	131.7	131.2	127.7	127.6
	127.7	129.2	129.3	125.1	125.3
	126.5	124.7	124.9	121.7	121.9
$\delta^{119}\text{Sn}$	−226	−236	−198	−222	−182

<sup>a</sup> Abbreviations: s, singlet; t, triplet; m, complex pattern; nv, non-visible. N.B. *p*-substituted aryls all provide  $^1\text{H}$  NMR AA'XX' patterns, described here as multiplets.

reported in Table 8. The  $^1\text{H}$  NMR spectra exhibit the expected proton signals with correct integration ratios. If we use the existing correlation between spin–spin coupling constants  ${}^1J(^{13}\text{C}\text{---}^{119}\text{Sn})$  and  ${}^2J(^1\text{H}\text{---}^{119}\text{Sn})$  and the C–Sn–C angle for methyltin(IV) compounds,<sup>15</sup> it can be suggested that after dissolution of the compounds **1**, **2**, **4** and **5** in  $\text{CDCl}_3$  there takes place a retention of the chelate distorted *trans*-octahedral structure, as has been proposed also for  $\text{Me}_2\text{Sn}[\text{ON}(\text{Me})\text{C}(\text{O})\text{Me}]_2$  and  $\text{Me}_2\text{Sn}[\text{ON}(\text{Ph})\text{C}(\text{O})\text{Ph}]_2$ .<sup>3</sup>

It is interesting to mention that the values  ${}^1J(^{13}\text{C}\text{---}^{119}\text{Sn})$  and  ${}^2J(^1\text{H}\text{---}^{119}\text{Sn})$  of compound **3** fall in the same range. We suggest that a structural change occurs upon dissolution of **3** in

$\text{CDCl}_3$ , and that the *cis*-octahedron transforms into a distorted *trans*-octahedron similar to that observed for  $\text{Me}_2\text{Sn}[\text{ONHC}(\text{O})\text{Me}]_2$ .<sup>3</sup>

The  $\delta^{119}\text{Sn}$  values (Table 8) of compounds **1–5** are typical for six-coordinate diorganotin compounds<sup>16</sup> and confirm the chelate structures of bis-hydroxamates in  $\text{CDCl}_3$  solution.

## REFERENCES

1. M. Gielen, in *Tin Based Antitumour Drug*, edited by M. Gielen, NATO ASI Series, Ser. H: Cell Biology, Vol. 37 (1989).
2. E. A. Feoktistov and V. F. Mironov, *Metalloorg. Chim.* **3**, 1208 (1990).

3. P. G. Harrison and J. A. Richards, *J. Organomet. Chem.* **185**, 9 (1980).
4. M. K. Das, M. Nath and J. J. Zuckermann, *Inorg. Chim. Acta* **71**, 49 (1983).
5. B. Pradhan and A. K. Ghosh, *J. Organomet. Chem.* **131**, 23 (1977).
6. M. K. Das and M. Nath, *Indian J. Chem.* **A20** (N12), 1224 (1981).
7. S. K. Chaudhuri, P. S. Roy and A. K. Ghosh, *Indian J. Chem.* **A22** (11), 996 (1983).
8. P. G. Harrison and T. J. King, *J. Chem. Soc., Dalton Trans.* **21**, 2298 (1974).
9. P. G. Harrison, T. J. King and J. A. Richards, *J. Chem. Soc., Dalton Trans.* **9**, 826 (1975).
10. P. G. Harrison, T. J. King and R. C. Phillips, *J. Chem. Soc., Dalton Trans.* **22**, 2317 (1976).
11. P. G. Harrison, T. J. King and K. C. Molloy, *J. Organomet. Chem.* **185**, 199 (1980).
12. P. G. Harrison, *Inorg. Chem.* **12**, 1545 (1973).
13. H. Ulrich and A. A. R. Sayigh, *J. Chem. Soc.* 1098 (1963).
14. V. Chandrasekhar, R. O. Day, J. M. Holmes and R. R. Holmes, *Inorg. Chem.* **27**, 958 (1988).
15. T. P. Lockhart and W. F. Manders, *Inorg. Chem.* **25**, 892 (1986).
16. H. C. Clark, V. K. Jain, R. C. Mehrotra, B. P. Singh, G. Srivastava and T. Birchall, *J. Organomet. Chem.* **279**, 385 (1985).