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Synthesis and molecular structure of $^{n}Bu_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$ formed in the reaction of di-n-butyltin(IV) oxide with 3,4,5-trimethoxy-benzoyl salicylahydrazone

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Abstract

The title complex was synthesized and characterized by ^{1}H, ^{13}C, ^{119}Sn NMR and IR spectra. A single crystal X-ray diffraction study confirmed its molecular structure and revealed that 3,4,5-trimethoxy-benzoyl salicylahydrazone was a tridentate and approximately planar ligand. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.208(3)$, $b = 12.536(2)$, $c = 12.187(4)$ Å, $\alpha = 113.12(2)$, $\beta = 90.58(2)$, $\gamma = 81.42(2)°$, $V = 1277.5(6)$ Å^3, $Z = 2$. The structure was refined to $R = 0.033$ and $R_w = 0.041$ for 3944 observed independent reflections. The tin atom has a distorted trigonal bipyramidal coordination. The Sn–C bond lengths are 2.129(5) and 2.113(5) Å (av. 2.121(5) Å), the C–Sn–C angle is 123.3(2)°; the bond length between the tin atom and the chelating nitrogen is 2.173(3) Å. Two chain carbon atoms and the chelating nitrogen atom occupy the basal plane. The skeleton of two erect oxygen atoms and the tin atom is bent (O–Sn–O angle = 153.5(1)°). In the complex, the ligand exists in the enol-form.

1. Introduction

In organotin(IV) complexes, the tin atoms can coordinate to oxygen, sulphur and nitrogen atoms. The structures of some five-coordinate triorganotin(IV) compounds containing these ligating atoms have been reported [1–4], but only a few papers on the study of the analogous structures of five-coordinate diorganotin(IV) compounds have been reported. Using ligands (**1**), some five-coordinate diorganotin complexes (**2**) were synthesized. Liu *et al.* [5] used the reaction of substituted benzoyl salicylahydrazone (A = 2-aminophenyl, X = O, Y = H) with $[Cp(CO)_2Fe]_2SnCl_2$ or Ph_2SnCl_2 to synthesize complexes **2a**, **2b** (B = $Fe(CO)_2Cp$ or Ph) and determined their molecular structures. Saxena *et al.* [6] and Singh *et al.* [7] synthesized the five-coordinate complex **2c** (A = NH_2, X = S, Y = CH_3, B = ^{n}Bu) and complex **2d** (A = 2-furyl, X = S, Y = H, B = ^{n}Bu), respectively, through the condensation of each ligand (**1**) and di-n-butyltin(IV) oxide and characterized their structures by elemental analyses, NMR and IR spectra; they suggested the five-coordinate molecular structure. We chose the di-n-butyltin unit to bind with 3,4,5-trimethoxy-benzoyl salicylahydrazone (**1**; A = 3,4,5-trimethoxyphenyl, X = O, Y = H) for the first molecular structural study of a five-coordinate di-n-butyltin(IV) complex (**2**; A = 3,4,5-trimethoxyphenyl, X = O, Y = H, B = ^{n}Bu) containing a polydentate ligand.

2. Experimental details

Di-n-butyltin(IV) oxide was chemically pure. Dried analytical grade solvents were used in all experiments.

IR spectra were recorded using KBr discs on a Perkin–Elmer 683 Model spectrophotometer in the range 4000–300 cm^{-1}. A JEOL (JNM PMX) 60 MHz spectrometer was used to record the ^{1}H NMR spectra in CCl_4 with Me_4Si as the internal standard. ^{13}C and

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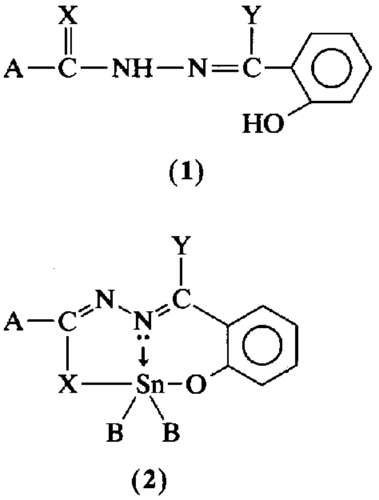
TABLE 1. Crystal data and refinement details for the complex

Formula	$C_{25}H_{34}N_2O_5Sn$
Mol. wt.	561.24
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.208(3)
b (Å)	12.536(2)
c (Å)	12.187(4)
α (°)	113.12(2)
β (°)	90.58(2)
γ (°)	81.42(2)
V (Å^3)	1277.5(6)
Z	2
D_c (g cm^{-3})	1.46
$F(000)$	576
μ(Mo Kα) (cm^{-1})	10.37
Max./min. transmission factors	0.913, 0.830
θ limits (°)	1.5–25.0
Scan width (°)	1.39
Scan speed (° min^{-1})	7.32
No. of unique data	4489
No. of unique reflections used with $I > 3\sigma(I)$	3944
w	1
R	0.033
R_w	0.041
$(\Delta/\sigma)_{max}$	0.092
Residual ρ_{max} (e Å^{-3})	0.67

^{119}Sn NMR spectra were recorded in $CHCl_3$ on a Varian FT-80A NMR spectrometer, operating at 17.75 and 27.4 MHz, respectively. Chemical shifts were reported in ppm from internal chloroform (77.20 ppm for ^{13}C) and from external 33% Me_4Sn in C_6D_6 for ^{119}Sn. Tin was estimated as SnO_2 [8]. Microanalyses (C, H and N) were determined by the Analytical Chemistry Group of the Dalian Institute of Chemical Physics.

2.1. Synthesis

2.1.1. Preparation of 3,4,5-trimethoxy-benzoyl salicylahydrazone



Scheme 1.

To a toluene solution (ca. 40 ml) of salicylaldehyde (1.35 g, 95%, 0.01 mol) was added 2.20 g (0.01 mol) of 3,4,5-trimethoxy-benzoyl hydrazide. The mixture was heated under reflux with stirring for 4 h. Water formed during the reaction was removed azeotropically with a Dean and Stark water trap. Most of the solvent was removed under vacuum after the mixture was cooled to room temperature. Then the mixture was filtered and the residual solid was washed with petroleum ether (90–120°C). Recrystallization of the solid from $C_6H_6/CHCl_3$ (1:1, v/v) gave a white crystalline solid in 75.7% yield, m.p. 178–179°C. Anal. Found: C, 61.71; H, 5.39; N, 8.29. $C_{17}H_{18}N_2O_5$ calc.: C, 61.84; H, 5.45; N, 8.48%.

2.1.2. Preparation of the complex

0.90 g (0.0036 mol) $^nBu_2SnO$ and 1.20 g (0.0036 mol) of 3,4,5-trimethoxy-benzoyl salicylahydrazone were added to 40 ml of dried benzene successively. The mixture was heated under reflux with stirring for 4 h. Water formed during the reaction was removed azeotropically with a Dean and Stark water trap. After the clear yellow solution was cooled to room temperature, all of the solvent was removed under reduced pressure to leave a yellow crystalline solid, which was

TABLE 2. IR data of the ligand and the complex (cm^{-1})

$C_{17}H_{18}N_2O_5$							
3660–3380m, broad		3170m, broad		3004m	2940m	2838m	2632w
1653s	1626s	1588s	1505s	1460m	1375m	1336s	1284s
1230s	1125s	1002m	895w	855m	819m	755m	727m
680m	566w						
$^nBu_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$							
3066w	3004w	2968m	2928m	2864m	2856m	1617s	1594m
1548s	1506s	1457m	1369s	1227m	1128s	908m	750s
605m	480w	430w					

recrystallized from $C_6H_6/CHCl_3$ (1 : 1, v/v) in 80.2% yield, m.p. 75–76°C. Anal. Found: C, 53.73; H, 6.25; N, 4.93; Sn, 21.02. $C_{25}H_{34}N_2O_5Sn$ calc.: C, 53.55; H, 6.06; N, 4.99; Sn, 21.17%. When the reaction took place in dried toluene, the same product was obtained in 87.5% yield.

2.2. *IR and NMR spectra*

3,4,5-Trimethoxy-benzoyl salicylahydrazone was characterized by IR spectroscopy and the IR data are listed in Table 2. The title complex was characterized by IR and ^1H, ^{13}C, ^{119}Sn NMR spectroscopy, respectively. The related data are collected in Tables 2 and 3.

2.3. *X-Ray crystallography*

The crystal of the title complex for X-ray diffraction study was grown in $C_6H_6/CHCl_3$ (1 : 1, v/v) by slow evaporation of the solvent at room temperature (*ca.* 10°C). Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo Kα radiation, $\lambda = 0.7107$ Å) at room temperature. With a crystal of approximate dimensions $0.40 \times 0.44 \times 0.52$ mm^3, a total of 4489 independent reflections was collected in the range of $3° < 2\theta < 50°$ using the ω scan technique at room temperature, in which 3944 reflections satisfied the $I > 3\sigma(I)$ criterion of observation. The data were corrected for Lorentz and polarization effects and for absorption [9]. Relevant crystal data and refinement details are given in Table 1.

The structure of the complex was solved by the direct method [10] and refined by a block-diagonal least-squares procedure based on F [10]. The final refinement with anisotropic thermal parameters for non-hydrogen atoms converged with unweighted and weighted agreement factors of 0.033 and 0.041, respectively. Hydrogen atoms were included at their calculated positions. The highest peak on the final difference Fourier map had a height of 0.67 e Å^{-3}. Final refinement details are also summarized in Table 1. Atomic coordinates are listed in Table 4. Table 5 lists the bond lengths and Table 6 the angles and selected torsional angles. Least-squares planes and dihedral angles are given in Table 7. Lists of anisotropic thermal parameters, observed and calculated structure factors are available from the author (Z.-K. Yu).

TABLE 4. Atomic coordinates ($\times 10^4$) for the complex

Atom	x	y	z
Sn	4009(1)	1740(1)	2332(1)
N(1)	3234(4)	800(3)	574(3)
N(2)	3586(4)	1153(3)	−328(3)
O(1)	4875(4)	2400(3)	1124(3)
O(2)	4175(4)	2169(3)	−3895(3)
O(3)	5998(4)	3757(3)	−3270(3)
O(4)	7078(4)	4530(3)	−1118(3)
O(5)	3161(4)	469(3)	2735(3)
C(11)	4831(5)	2451(4)	−813(4)
C(12)	4258(5)	2064(4)	−1944(4)
C(13)	4644(5)	2504(4)	−2755(4)
C(14)	5583(5)	3344(4)	−2447(4)
C(15)	6155(5)	3720(4)	−1320(4)
C(16)	5781(5)	3276(4)	−503(4)
C(17)	4409(5)	1981(4)	57(4)
C(18)	3259(7)	1292(6)	−4252(5)
C(19)	4950(7)	4647(5)	−3392(6)
C(20)	7732(6)	4918(5)	11(5)
C(21)	1822(5)	−491(4)	1016(4)
C(22)	822(5)	−1278(4)	521(5)
C(23)	234(5)	−1820(5)	1149(5)
C(24)	681(6)	−1611(5)	2295(5)
C(25)	1665(6)	−855(4)	2808(4)
C(26)	2239(5)	−258(4)	2198(4)
C(27)	2374(5)	11(4)	273(4)
C(31)	6080(5)	1394(4)	3020(4)
C(32)	7108(6)	2270(5)	3168(5)
C(33)	8661(7)	1853(7)	3417(7)
C(34)	8776(8)	1657(7)	4535(6)
C(41)	2395(6)	3205(5)	3274(5)
C(42)	1479(8)	3709(6)	2533(6)
C(43)	404(10)	4812(8)	3350(8)
C(44)	−399(11)	5479(9)	2743(9)

3. Results and discussion

The reaction of $^{n}Bu_2SnO$ with 3,4,5-trimethoxy-benzoyl salicylahydrazone gave a higher yield of the title complex in toluene than in benzene. With the higher

TABLE 3. NMR chemical shifts of the complex (ppm)

^1H NMR
8.68 (s, 1 × H) 7.24 (s, 2 × H) 7.10 (d, 2 × H) 6.60 (s, 2 × H) 6.75 (s, 4 × H) 3.89 (s, 6 × H)
3.78 (s, 3 × H) 1.56–0.92 (m, 2 × n-C_4H_8–H)

^{13}C NMR
166.84 160.91 152.84 140.53 140.43 134.92 133.94 128.61 121.52
116.80 116.71 (2 × C) 104.68 (3 × C) 60.76 56.04 (2 × C)
(two sets of ^{13}C resonances in the ^{n}Bu groups) 26.74 26.55 26.30 22.08 13.44 13.36

^{119}Sn NMR −186.91

boiling point of toluene, the more effective azeotropic conditions of the solvent and water formed during the reaction resulted in a higher yield of the product. The complex is insensitive to the air and moisture and its solubility is rather large in organic solvents.

3.1. *IR spectra*

The IR spectrum of 3,4,5-trimethoxy-benzoyl salicylahydrazone is compared with that of 3,4,5-trimethoxy-benzoyl hydrazide and then assigned. The medium bands in the region 3660–3380 cm^{-1} are assigned to the stretching vibrations of O–H and N–H bonds, 3170 cm^{-1} to ν(N–H) in the IR spectrum of 3,4,5-trimethoxy-benzoyl salicylahydrazone. The weak band (2632 cm^{-1}) and the strong bands (1653 cm^{-1}, 1626 cm^{-1}) are assigned to the intramolecular hydrogen

TABLE 5. Bond lengths (Å) for the complex

Sn–N(1)	2.173(3)	Sn–O(1)	2.160(4)
Sn–O(5)	2.094(4)	Sn–C(31)	2.129(5)
Sn–C(41)	2.113(5)	N(1)–N(2)	1.394(6)
N(1)–C(27)	1.297(6)	N(2)–C(17)	1.310(6)
O(1)–C(17)	1.292(5)	O(2)–C(13)	1.370(5)
O(2)–C(18)	1.415(8)	O(3)–C(14)	1.376(7)
O(3)–C(19)	1.416(8)	O(4)–C(15)	1.367(6)
O(4)–C(20)	1.428(6)	O(5)–C(26)	1.315(6)
C(11)–C(12)	1.396(6)	C(11)–C(16)	1.391(7)
C(11)–C(17)	1.480(7)	C(12)–C(13)	1.380(8)
C(13)–C(14)	1.397(7)	C(14)–C(15)	1.392(6)
C(15)–C(16)	1.385(8)	C(21)–C(22)	1.406(7)
C(21)–C(26)	1.414(7)	C(21)–C(27)	1.423(8)
C(22)–C(23)	1.366(9)	C(23)–C(24)	1.386(9)
C(24)–C(25)	1.375(8)	C(25)–C(26)	1.398(9)
C(31)–C(32)	1.512(8)	C(32)–C(33)	1.517(9)
C(33)–C(34)	1.477(12)	C(41)–C(42)	1.483(10)
C(42)–C(43)	1.554(10)	C(43)–C(44)	1.443(16)

TABLE 6. Bond angles and selected torsion angles (°) for the complex

N(1)–Sn–O(1)	72.6(1)	N(1)–Sn–O(5)	82.9(1)
O(1)–Sn–O(5)	153.5(1)	N(1)–Sn–C(31)	128.3(1)
O(1)–Sn–C(31)	94.9(2)	O(5)–Sn–C(31)	92.4(2)
N(1)–Sn–C(41)	108.3(2)	O(1)–Sn–C(41)	98.3(2)
O(5)–Sn–C(41)	98.9(2)	C(31)–Sn–C(41)	123.3(2)
Sn–N(1)–N(2)	116.7(3)	Sn–N(1)–C(27)	128.0(3)
N(2)–N(1)–C(27)	115.0(4)	N(1)–N(2)–C(17)	111.2(3)
Sn–O(1)–C(17)	114.2(3)	C(13)–O(2)–C(18)	116.7(5)
C(14)–O(3)–C(19)	114.5(4)	C(15)–O(4)–C(20)	117.0(5)
Sn–O(5)–C(26)	132.7(3)	C(12)–C(11)–C(16)	120.4(5)
C(12)–C(11)–C(17)	119.3(4)	C(16)–C(11)–C(17)	120.2(4)
C(11)–C(12)–C(13)	119.5(4)	O(2)–C(13)–C(12)	124.4(4)
O(2)–C(13)–C(14)	115.0(5)	C(12)–C(13)–C(14)	120.5(4)
O(3)–C(14)–C(13)	120.3(4)	O(3)–C(14)–C(15)	120.0(4)
C(13)–C(14)–C(15)	119.6(5)	O(4)–C(15)–C(14)	114.8(5)
O(4)–C(15)–C(16)	125.0(4)	C(14)–C(15)–C(16)	120.2(4)
C(11)–C(16)–C(15)	119.7(4)	N(2)–C(17)–O(1)	124.9(5)
N(2)–C(17)–C(11)	116.5(4)	O(1)–C(17)–C(11)	118.6(4)
C(22)–C(21)–C(26)	119.0(5)	C(22)–C(21)–C(27)	117.1(4)
C(26)–C(21)–C(27)	123.9(4)	C(21)–C(22)–C(23)	122.0(5)
C(22)–C(23)–C(24)	118.5(5)	C(23)–C(24)–C(25)	121.2(6)
C(24)–C(25)–C(26)	121.2(5)	O(5)–C(26)–C(21)	123.2(5)
O(5)–C(26)–C(25)	118.9(4)	C(21)–C(26)–C(25)	117.9(4)
N(1)–C(27)–C(21)	126.9(4)	Sn–C(31)–C(32)	115.6(4)
C(31)–C(32)–C(33)	113.0(6)	C(32)–C(33)–C(34)	114.3(6)
Sn–C(41)–C(42)	115.9(4)	C(41)–C(42)–C(43)	109.9(6)
C(42)–C(43)–C(44)	115.1(8)	C(43)–H(44b)–C(44)	81.1(7)
O(1)–Sn–N(1)–N(2)	−4.3(2)	O(1)–Sn–N(1)–C(27)	−178.0(4)
O(5)–Sn–N(1)–C(27)	12.2(3)	O(5)–Sn–N(1)–N(2)	−174.1(3)
N(1)–Sn–O(1)–C(17)	5.0(3)	O(5)–Sn–O(1)–C(17)	28.3(5)
C(17)–C(11)–C(12)–C(13)	179.7(4)	C(17)–C(11)–C(16)–C(15)	−179.2(4)
C(27)–C(21)–C(26)–C(25)	−177.0(4)	C(27)–C(21)–C(26)–O(5)	1.4(6)
C(27)–C(21)–C(22)–C(23)	179.4(4)	C(22)–C(21)–C(27)–N(1)	175.8(4)
C(22)–C(21)–C(26)–C(25)	2.0(6)	C(12)–C(13)–C(14)–C(15)	1.2(6)
C(13)–C(14)–C(15)–C(16)	−0.8(6)	C(14)–C(15)–C(16)–C(11)	0.0(6)
C(26)–C(21)–C(22)–C(23)	0.3(6)	C(26)–C(21)–C(27)–N(1)	−5.3(7)
O(3)–C(14)–C(15)–C(16)	−177.7(4)	O(4)–C(15)–C(16)–C(11)	−179.8(4)

bond (O–H ··· N), C=O and HC=N groups, respectively. According to the IR spectrum of the free ligand, we concluded that it is present in the keto-form. This result is compatible with Rastogi *et al.*'s conclusion drawn from a detailed study on the IR spectrum of benzoyl hydrazones [11]. However, these ligands are capable of undergoing keto-enol tautomerism and thus can coordinate with a metal atom in either of these two forms depending on the experimental conditions. A comparison of the IR spectrum of the free ligand with that of the complex shows several obvious differences. (a) The absorptions in the region 3660–3380 cm^{-1} (O–H, N–H) and at 3170 cm^{-1} (N–H) and 1653 cm^{-1} (C=O) in the spectrum of the free ligand disappear from the spectrum of the complex. (b) A new strong band at 1617 cm^{-1} in the complex is assigned to the stretching vibration mode of the C=N bond. The absorption of the HC=N group undergoes a red shift from 1626 cm^{-1} to 1548 cm^{-1} in the IR spectrum of the complex. The new band at 1548 cm^{-1} can be assigned to the stretching vibration of the conjugate $\rangle C=N-N=C\langle$ [12], and this result can also be understood as the nitrogen atom in the HC=N group affording its lone pair of electrons to form a coordinate bond to the central tin atom. (c) The weak band at 2632 cm^{-1} is absent in the spectrum of the complex. (d) The new bands at 605 cm^{-1} (m), 480 cm^{-1} (w) and 430 cm^{-1} (w) indicate that there are Sn–O, Sn–N and Sn–C bonds in the complex. In the light of the above interpretation, we can infer that the ligand coordinates with the tin atom by phenolic- and enolic-oxygen atoms through deprotonation.

3.2. NMR spectra

The ^{1}H resonance of the N=C–H group is at the lowest field (8.68 ppm), the ^{1}H resonances of CH_3 and ^{n}Bu groups at the highest field and those of the aromatic rings show in the region 6.66–7.24 ppm in the form of a discrete singlet or a doublet in the ^{1}HNMR spectrum of the complex. The ^{13}C resonances at the lowest field (166.84, 160.91 ppm) of the complex can be assigned to the carbon atoms of the conjugate $\rangle C=N-N=C\langle$ group, those of the aromatic rings and OCH_3 groups appear in the ranges 104.68–152.84 ppm and 56.04–60.76 ppm, respectively. The ^{13}C NMR spectrum of the complex displays two sets of $^{n}Bu-Sn$ resonances which indicates that the corresponding carbon atoms in the two ^{n}Bu groups are not magnetically equivalent. Owing to the low intensity of the $^{n}Bu-Sn$ carbon resonances in some cases, a poor signal/noise ratio prevented determination of $^{1}J(^{119}Sn-^{13}C)$. The ^{119}Sn NMR spectrum of the complex shows a single ^{119}Sn

TABLE 7. Least-squares planes and dihedral angles

Least-squares planes [a]

Plane No.	Atoms fitted	Equation of plane				rms (Å × 10^4)
		l	*m*	*n*	*d*	
1	C(11), C(12), C(13) C(14), C(15), C(16)	0.7828	−0.6185	−0.0680	1.4112	36
2	C(21), C(22), C(23) C(24), C(25), C(26)	0.7599	−0.6459	−0.0727	1.3420	105
3	Sn, O(1), C(17) N(1), N(2)	0.8148	−0.5787	0.0344	1.5699	289
4	Sn, N(1), C(27) C(21), C(26), O(5)	0.8233	−0.5656	−0.0475	1.5454	759
5	N(1), C(31), C(41)	0.4029	0.6389	−0.6553	1.8943	0
6	Sn, C(31), C(41), N(1)	0.4035	0.6387	−0.6551	1.8842	210

Dihedral angles between planes [b]

Planes	Angles (°)	Planes	Angles (°)
1–2	2.1	1–3	6.6
1–4	4.0	1–5	92.0
1–6	92.0	2–3	7.9
2–4	6.0	2–5	93.4
2–6	93.3	3–4	4.8
3–5	93.7	3–6	93.6
4–5	89.9	4–6	89.9
5–6	0.0		

[a] The plane equation is in the form $lX_0 + mY_0 + nZ_0 = d$, where X_0, Y_0, Z_0 are orthogonal coordinates in Å. [b] Standard deviation approx. 0.7°.

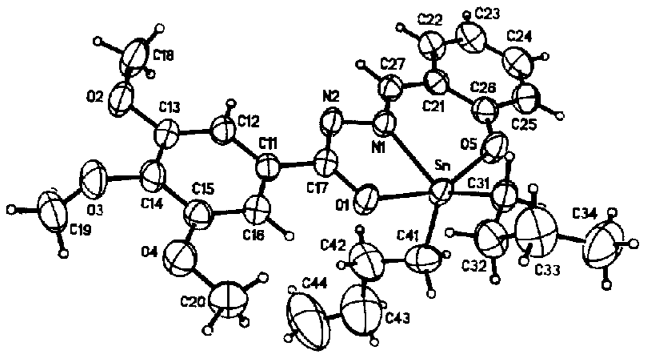


Fig. 1. Molecular structure of the complex $^{n}Bu_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$.

resonance (−186.91 ppm), which means that the complex is present in the form of a monomer in the solution. According to Holeček *et al.*'s suggestion [13], it can be inferred that the tin atom in the complex is five-coordinate.

In the light of the results of the IR and NMR spectra, we can suggest that the present complex has the molecular structure analogous to the complexes in Scheme 1.

3.3. X-ray crystallography

Figure 1 is a perspective drawing of $^{n}Bu_2[(MeO)_3C_6H_2C(O)N_2CHC_6H_4O]Sn$ showing the labelling scheme. The complex is present in the form of a discrete monomer in the solid state as depicted in Fig. 2. Molecular interactions are of the normal van der Waals type with no abnormally short inter- or intramolecular contacts. From Figs. 1 and 3, it can be seen that 3,4,5-trimethoxy-benzoyl salicylahydrazone is a tridentate and approximately planar ligand. The tin atom lies in the approximate plane and forms five- and six-membered chelate rings with the polydentate ligand. The dihedral angles between planes 3 and 1, planes 3 and 4, planes 4 and 2, planes 1 and 2 are 6.6, 4.8, 6.0 and 2.1°, respectively. Different torsional angles are present in the molecular backbone of the complex. Little torsion angles present in the aromatic rings and between the aromatic carbon atoms and their neighbouring nonaromatic ring atoms are due to the substituent effect and coplanarity. The carbon atoms of the two aromatic rings are not in complete planes and all of the atoms of the five- and six-membered rings are not included in complete planes either. N(1), C(31) and C(41) atoms lie precisely in the same plane. The tin atom is displaced by 0.048 Å from this basal plane (plane 5) in the direction of the phenolic-oxygen atom (O(5)). Plane 5 is almost perpendicular to planes 1, 2, 3 and 4. The tin atom has a distorted trigonal bipyramidal coordination with two oxygen atoms (O(1), O(5)) occupying the axial positions and two carbon atoms of the carbon chains (C(31), C(41)) and one nitrogen atom (N(1)) occupying the equatorial positions (Fig. 3). This arrangement is in accordance with that in which more electronegative ligands occupy the axial positions preferentially in the complexes containing a five-coordinate tin atom [14]. Sandhu *et al.* [15] reported a series of the molecular structures of organotin(IV) carboxylates $\{[^{n}Bu_2Sn(OOCR')]_2O\}_2$, in which two sets of ^{n}Bu–Sn resonances appeared in the ^{13}C NMR spectra and the bond lengths of the two types of Sn–C bonds were not equal. In our case, the two types of ^{n}Bu–Sn are not equivalent either (Sn–C(31) = 2.129(5) Å; Sn–C(41) = 2.113(5) Å), which is in accordance with the result obtained from the ^{13}C NMR spectrum of the complex. This phenomenon may be related to the steric effect resulting from the two n-butyl carbon chains and their environmental atoms and the magnetic nonequivalence of the corresponding atoms in the two ^{n}Bu groups. The bond lengths of Sn–O(1), Sn–O(5) and Sn–N(1) bonds are in the region 2.094(4)–2.173(3) Å, which indicates that the N(1) atom affords its lone pair of electrons to form a strong coordinate bond to the tin atom. The strong aptitude of the N(1) atom for electron-donoring increases the electron density on the tin atom, there-

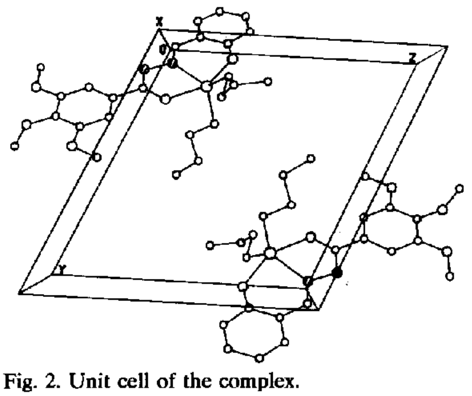


Fig. 2. Unit cell of the complex.

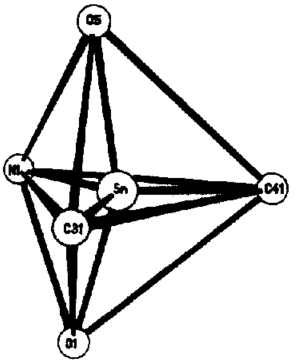


Fig. 3. Coordination mode of the central tin atom.

fore the Sn–O bond lengths are lengthened to the extent that they are approximately equal to Sn–N(1) bond length. The lengths of the N(1)–C(27) and N(2)–C(17) bonds are almost equal (1.297(6) Å, 1.310(6) Å), which means that the bonding modes between N(1) and C(27) atoms and between N(2) and C(17) atoms are the same as C=N double bonds. The structural information confirms the supposition that the ligand participated in the reaction in the enol-form. The two axial oxygen atoms are not in the precise axial positions (O(1)–Sn–O(5) angle, 153.5(1)°). The C(31)–Sn–C(41) angle is 123.3(2)°, the value of which is in the scope of C–Sn–C angles. By virtue of the equation involved the coupling constant and the angle $^1J(^{119}\text{Sn}-^{13}\text{C}) = 9.99\theta - 746$ (θ = C–Sn–C angle) [13], we can obtain the spin-spin coupling constant ^1J(485.8 Hz). The lower value of the C–Sn–C angle can be due to a characteristic geometry of the tridentate ligand [16]. Therefore, it can be inferred that the tin atom lies in a distorted trigonal bipyramidal environment.

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