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Synthesis and crystal structure of diorganotin(IV) complexes with pyruvic acid benzoylhydrazone and pyruvic acid salicylhydrazone

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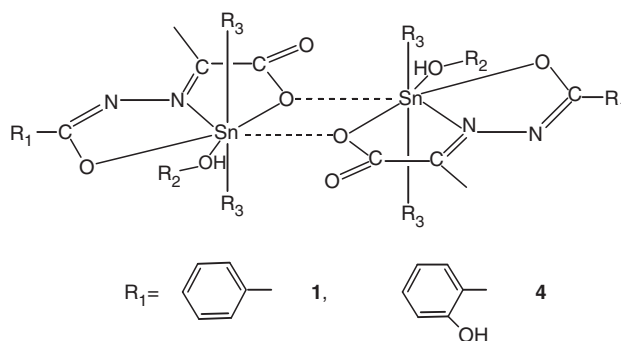
Six diorganotin esters of Schiff-base ligands formulated as $[R_2SnLY]_2$, where L_1 is $C_6H_5CON_2C(CH_3)CO_2$ with $Y = CH_3CH_2OH$, $R = mClC_6H_4CH_2$ (**1**), $oFC_6H_4CH_2$ (**2**), $pFC_6H_4CH_2$ (**3**) and L_2 is 2-HOC₆H₄CON₂C(CH₃)CO₂ with $Y = CH_3OH$, $R = oFC_6H_4CH_2$ (**4**), $pFC_6H_4CH_2$ (**5**), $mClC_6H_4CH_2$ (**6**) have been prepared and characterized by elemental analysis, IR, ¹H and ¹¹⁹Sn NMR spectra. The crystal structures of complexes **1** and **4** have been determined by X-ray single crystal diffraction. The structure analyses reveal that the Sn atom in both **1** and **4** is seven-coordinate in distorted pentagonal bipyramid geometries with a planar SnO₄N unit and two apical aryl carbon atoms, thus forming a dimeric molecule, which sits on a crystallographic center of symmetry. Intramolecular or intradimeric hydrogen bonds contribute to the stability and compactness of the crystal structures.

Keywords: Sn(IV) complex; Hydrazone; Crystal structure; X-ray diffraction

1. Introduction

The coordination chemistry of some tridentate ONO and ONS donor Schiff-bases has been described [1–3]. Organotin(IV) complexes of deprotonated Schiff bases are known [4–6]. The chemistry of organotin(IV) complexes of Schiff bases has stemmed from the reported biocidal [7–10] and anti-tumor [11, 12] activities of organotin(IV) complexes and the behavior of Schiff bases as models for biological systems [13]. In recent years considerable research activity has been aimed toward generating new supramolecular entities having desired structural networks by self-assembling metal ions utilizing their preference for different coordination geometry, choice of suitable ligands, and intermolecular interactions such as hydrogen bonding and π – π interaction [14–16]. Such species are of immense interest due to their physical properties and potential utilization as molecule-based metals, magnetic materials, optical and thermal switches, and probes for DNA structures [17–19]. Continuing our previous

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Scheme 1. Chemical structural diagram of complexes **1** and **4**.

studies [20–22], here we report the synthesis and characterization of six new organotin(IV) complexes with potentially tridentate ONO donor Schiff bases, pyruvic acid benzoylhydrazone or pyruvic acid salicylhydrazone. Two of the complexes have been studied by X-ray diffraction; both complexes **1** and **4** are dimers and adopt similar structures as shown in scheme 1. The tin atoms are seven-coordinate with one ethanol or methanol O atom, one N atom and two O atoms from tridentate pyruvic acid Schiff-base ligand, and two C atoms of *trans* aryl groups.

2. Experimental

2.1. Synthesis

2.1.1. Preparation of complex (1) $\{(m\text{ClC}_6\text{H}_4\text{CH}_2)_2\text{Sn}[\text{C}_6\text{H}_5\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2](\text{CH}_3\text{CH}_2\text{OH})_2\}_2$. Pyruvic acid benzoylhydrazone (2 mmol) and sodium ethoxide (2 mmol) were added to dry benzene (20 mL) in a Schlenk flask and stirred for 0.5 h. Di-*m*-chlorobenzyltin dichloride (2 mmol) was then added and the reaction mixture was stirred for 12 h at 313 K and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from ethanol and colorless crystals suitable for X-ray diffraction were obtained, m.p. 471 K. Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_4\text{Sn}$ (%): C, 50.30; N, 4.52; H, 4.19; Found: C, 50.44; N, 4.39; H, 4.22. ^1H NMR (CDCl_3 , 400 MHz): δ 8.35 (1H, s, R–OH), 6.55–7.63 (13H, m, Ar–H and Ph–H), 3.22–3.61 (6H, m, $J_{\text{Sn-H}} = 84.80$ Hz, $-\text{CH}_2-$ and ArCH_2Sn), 1.74 (6H, s, CH_3). ^{119}Sn NMR (CDCl_3 , ppm): -451.5 . IR (KBr) ν : 3418 (m, OH), 3019 (s, Ar–H), 2922 (m, C–H), 1622 (m, C=N), 1602 (s, C=N–N=C), 1596, 1333 (s, CO_2), 1209 (m, C–O), 674 (s, Sn–O), 565 (w, Sn–C), 475 (m, Sn–N).

2.1.2. Preparation of complex (2) $\{(o\text{FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}[\text{C}_6\text{H}_5\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2]\}_2$. Complex **2** is prepared in the same way as that of **1**, by adding di-*o*-fluorobenzyltin dichloride (2.0 mmol) to pyruvic acid benzoylhydrazone (2.0 mmol). The solid is then obtained from ethanol, m.p. 418 K. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_3\text{Sn}$ (%): C, 53.27; N, 5.18; H, 3.73; Found: C, 53.14; N, 5.21; H, 3.77.

^1H NMR (CDCl_3 , 400 MHz): δ 6.68–7.88 (13H, m, Ar–H and Ph–H), 3.41 (4H, m, $J_{\text{Sn-H}} = 68.40$ Hz, ArCH_2Sn), 1.81 (3H, s, CH_3). ^{119}Sn NMR (CDCl_3 , ppm): -449.8 . IR (KBr) ν : 3030 (s, Ar–H), 3002 (m, C–H), 1617 (s, C=N), 1606 (m, C=N–N=C), 1594, 1341 (s, CO_2), 1206 (s, C–O), 685 (m, Sn–O), 559 (w, Sn–C), 467 (w, Sn–N).

2.1.3. Preparation of complex (3) $\{(p\text{FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}[\text{C}_6\text{H}_5\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2]\}_2$.

Complex **3** is prepared in the same way as that of **1**, by adding di-*p*-fluorobenzyltin dichloride (2.0 mmol) to pyruvic acid benzoylhydrazone (2.0 mmol). The solid is then obtained from ethanol, m.p. 432 K. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_3\text{Sn}$ (%): C, 53.27; N, 5.18; H, 3.73; Found: C, 53.35; N, 5.25; H, 3.59. ^1H NMR (CDCl_3 , 400 MHz): δ 6.47–7.71 (13H, m, Ar–H and Ph–H), 3.34 (4H, m, $J_{\text{Sn-H}} = 88.40$ Hz, ArCH_2Sn), 1.89 (3H, s, CH_3). ^{119}Sn NMR (CDCl_3 , ppm): -453.5 . IR (KBr) ν : 3036 (s, Ar–H), 3015 (s, C–H), 1625 (m, C=N), 1609 (s, C=N–N=C), 1601, 1359 (s, CO_2), 1205 (s, C–O), 665 (s, Sn–O), 573 (w, Sn–C), 480 (m, Sn–N).

2.1.4. Preparation of complex (4) $\{(o\text{FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}[2\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2](\text{CH}_3\text{OH})\}_2$.

Pyruvic acid salicylhydrazone (2.0 mmol) and tri-*o*-fluorobenzyltin chloride (2.0 mmol) were added to a solution of absolute toluene (30 mL) and heated under reflux with stirring for 1 h. After the triethylamine (2.0 mmol) was added to the reactor, the reaction mixture was refluxed for 1 h more. The clear solution thus obtained was evaporated under vacuum to form a white solid and recrystallized in methanol. Colorless crystals suitable for single crystal X-ray diffraction were obtained, m.p. 486 K. Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{F}_2\text{N}_2\text{O}_5\text{Sn}$ (%): C, 51.01; N, 4.76; H, 3.91; Found: C, 50.92; N, 4.69; H, 4.03. ^1H NMR (CDCl_3 , 400 MHz): δ 11.16 (s, 1H, Ar–OH), 8.09 (s, 1H, R–OH), 6.84–7.59 (m, 11H, Ar–H and Ph–H), 3.21 (t, 4H, $J_{\text{Sn-H}} = 80.80$ Hz, ArCH_2Sn), 1.86 (s, 3H, CH_3). ^{119}Sn NMR (CDCl_3 , ppm): -448.3 . IR (KBr) ν : 3421 (s, OH), 3024 (s, Ar–H), 2937 (s, C–H), 1621 (s, C=N), 1607 (s, C=N–N=C), 1578, 1322 (s, CO_2), 1208 (s, C–O), 688 (s, Sn–O), 529 (w, Sn–C), 469 (w, Sn–N).

2.1.5. Preparation of complex (5) $\{(p\text{FC}_6\text{H}_4\text{CH}_2)_2\text{Sn}[2\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2]\}_2$.

Complex **5** is prepared in the same way as that of **4**, by adding tri-*p*-fluorobenzyltin chloride (2.0 mmol) to pyruvic acid salicylhydrazone (2.0 mmol). The solid is then obtained from methanol, m.p. 477 K. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{F}_2\text{N}_2\text{O}_4\text{Sn}$ (%): C, 51.74; N, 5.03; H, 3.62; Found: C, 51.82; N, 4.99; H, 3.72. ^1H NMR (CDCl_3 , 400 MHz): δ 11.33 (s, 1H, Ar–OH), 6.62–7.44 (m, 12H, Ar–H and Ph–H), 3.43 (m, 4H, $J_{\text{Sn-H}} = 84.40$ Hz, ArCH_2Sn), 1.79 (s, 3H, CH_3). ^{119}Sn NMR (CDCl_3 , ppm): -445.5 . IR (KBr) ν : 3410 (s, OH), 3017 (m, Ar–H), 2955 (s, C–H), 1619 (s, C=N), 1601 (s, C=N–N=C), 1577, 1325 (s, CO_2), 1201 (s, C–O), 685 (s, Sn–O), 562 (w, Sn–C), 460 (w, Sn–N).

2.1.6. Preparation of complex (6) $\{(m\text{ClC}_6\text{H}_4\text{CH}_2)_2\text{Sn}[2\text{-HOC}_6\text{H}_4\text{CON}_2\text{C}(\text{CH}_3)\text{CO}_2]\}_2$.

Complex **6** is prepared in the same way as that of **4**, by adding tri-*m*-chlorobenzyltin chloride (2.0 mmol) to pyruvic acid salicylhydrazone (2.0 mmol). The solid is then obtained from methanol, m.p. 481 K. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_4\text{Sn}$ (%): C, 48.85; N, 4.75; H, 3.42; Found: C, 48.93; N, 4.71; H, 3.38. ^1H NMR (CDCl_3 , 400 MHz): δ 11.06 (s, 1H, Ar–OH), 6.69–7.34 (m, 12H,

Ar–H and Ph–H), 3.35 (t, 4H, $J_{\text{Sn-H}} = 48.80$ Hz, ArCH₂Sn), 1.81 (s, 3H, CH₃). ¹¹⁹Sn NMR (CDCl₃, ppm): –443.6. IR (KBr) ν : 3413 (s, OH), 3021 (m, Ar–H), 2985 (s, C–H), 1626 (s, C=N), 1603 (s, C=N–N=C), 1592, 1333 (s, CO₂), 1202 (s, C–O), 681 (m, Sn–O), 575 (w, Sn–C), 473 (m, Sn–N).

2.2. Physical measurements

The melting points were obtained with a Kolfer micro melting point apparatus and were uncorrected. IR spectra were recorded with a Nicolet-460 spectrophotometer, as KBr discs. ¹H and ¹¹⁹Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer in CDCl₃, and chemical shifts are given relative to Me₄Si and Me₄Sn. Elemental analyses were performed with a PE-2400 II elemental analyzer.

2.3. Crystal structure determination

A colorless crystal with dimensions $0.48 \times 0.43 \times 0.27$ mm³ **1** or $0.25 \times 0.21 \times 0.17$ mm³ **4** was mounted in a glass capillary. All measurements were made on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-K α (0.71073 Å) radiation at 298(2) K using the ϕ/ω scan technique. A total of 6919 or 11,826 reflections for **1** or **4** were collected, of which 4564 or 4335 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Semi-empirical absorption corrections were applied.

The structures were solved by direct methods followed by Fourier syntheses. Structure refinement was carried out with full-matrix least-squares procedures using the SHELXL-97 programme package [23]. H atoms on phenyl rings were placed at calculated positions with C–H distances of 0.93 Å and riding on carrier atoms. H atom of O4 in **1** was located in a difference Fourier map and refined. Anisotropic refinement including all non-H atoms converged to $R = 0.0344$ **1** or $R = 0.0537$ **4** for all observed reflections.

2.4. Crystal data

For **1**, C₂₆H₂₆Cl₂N₂O₄Sn, $M = 620.08$, triclinic, space group $P\bar{1}$, $a = 8.961(3)$, $b = 11.816(5)$, $c = 13.520(5)$ Å, $\alpha = 79.717(4)$, $\beta = 89.466(3)$, $\gamma = 69.456(4)^\circ$, $V = 1316.8(8)$ Å³, $Z = 2$, $F(000) = 624$, $D_x = 1.564$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 1.208$ mm^{–1}, $S = 1.003$, $(\Delta\rho)_{\text{max}} = 0.990$, $(\Delta\rho)_{\text{min}} = -0.798$ e Å^{–3}.

For **4**, C₂₅H₂₃F₂N₂O₅Sn, $M = 588.14$, monoclinic, space group $P2_1/c$, $a = 14.3349(19)$, $b = 9.3943(13)$, $c = 18.545(3)$ Å, $\alpha = 90$, $\beta = 91.322(2)$, $\gamma = 90^\circ$, $V = 2496.8(6)$ Å³, $Z = 4$, $F(000) = 1180$, $D_x = 1.565$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 1.076$ mm^{–1}, $S = 1.007$, $(\Delta\rho)_{\text{max}} = 0.904$, $(\Delta\rho)_{\text{min}} = -1.075$ e Å^{–3}.

3. Results and discussion

3.1. Description of the crystal structures

Complexes **1** and **4** have similar structural features. The molecular structures and unit cells are illustrated in figures 1–4. Selected bond distances and angles, together with

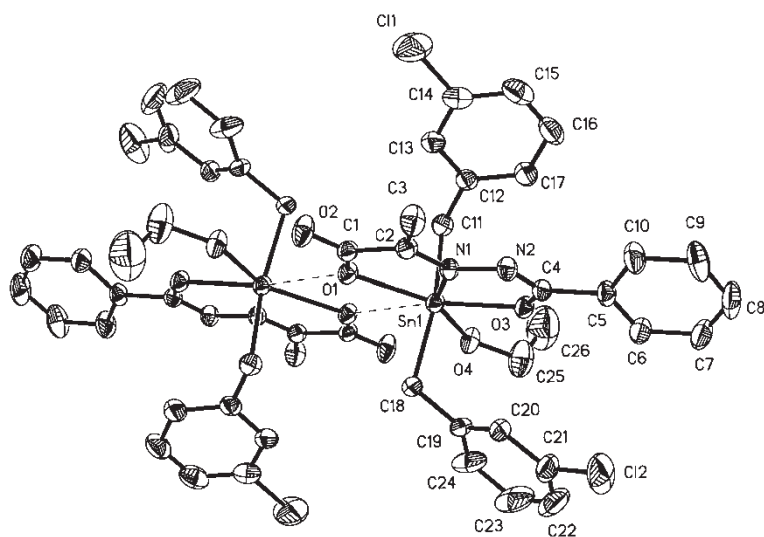


Figure 1. Molecular structure of **1** with 30% probability ellipsoids.

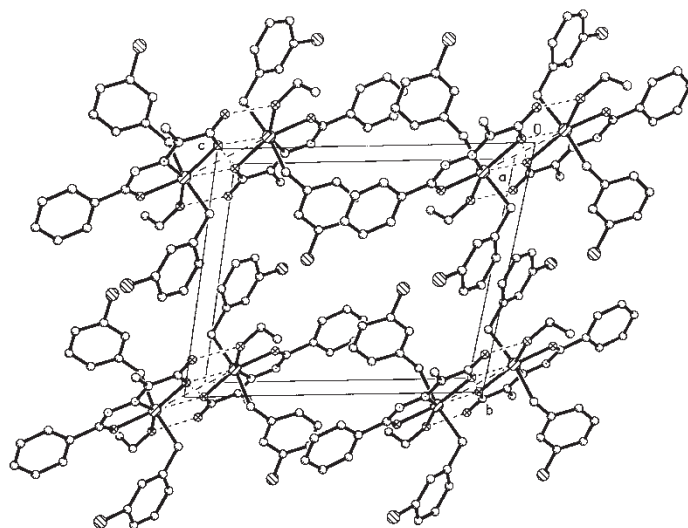


Figure 2. Unit cell of complex **1**.

atomic separations involved in H-bonds, are listed in table 1. For complexes **1** and **4**, all Sn atoms are coordinated by one ethanol or methanol O atom, one N atom and two O atoms from tridentate pyruvic acid Schiff base ligand, and two C atoms of *trans* aryl groups. The O1 atom of the carboxylate residue also binds the other tin atom, Sn1#1 $[-x+2, -y+1, -z+1]$ for **1**; $[-x+1, -y+1, -z]$ for **4**, generating a Sn₂O₂ four-membered ring. The distance of Sn1#1–O1, 2.672(4) Å **1** or 2.746(3) Å **4**, is greater than the sum of the covalent radii of Sn and O (2.56 Å), but is considerably less than the sum of the van der waals radii (3.68 Å) and should be considered as a weak bonding interaction. Thereby the structure of complex **1** or **4** can be described as a dimer with weak Sn···O bonding, and the coordination geometry of the tin can be also described as

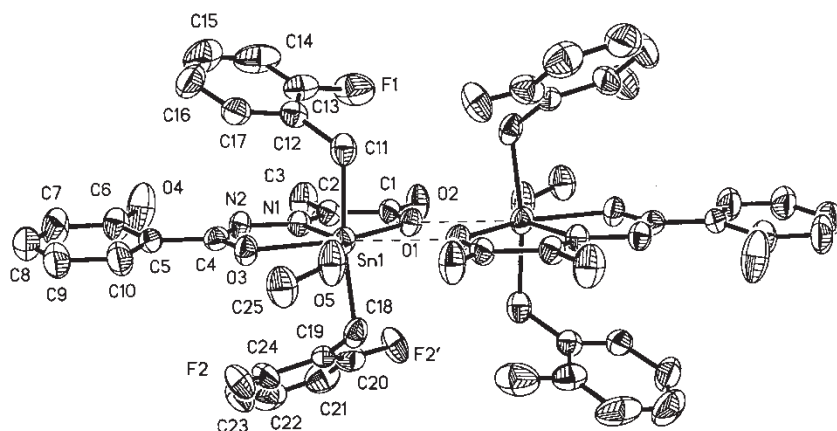


Figure 3. Molecular structure of **4** with 30% probability ellipsoids.

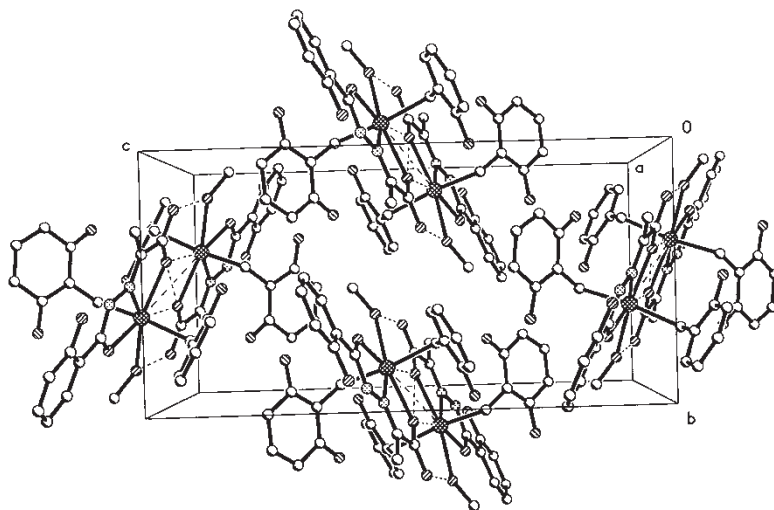


Figure 4. Unit cell of complex **4**.

a *trans*-C₂SnO₄N pentagonal bipyramid with the two aryl groups occupying *trans* positions [C11–Sn1–C18 is 165.3(2)° for **1** and C11–Sn1–C18 is 164.9(3)° for **4**]. The atoms O₃, N₁, O₁, O₁#1 and O₄ (or O₅ for **4**) are coplanar within ±0.0234 Å (or ±0.0283 Å for **4**), which form the equatorial plane. These data indicate that the tin atom of complexes **1** and **4** is in a distorted pentagonal bipyramidal configuration.

The C4–O3 bond length [1.289(5) Å for **1** or 1.273(8) Å for **4**] lies between double- (1.224 Å) and single-bond (1.430 Å) lengths. Compared with the length of a C=N double bond (1.270 Å) and a C–N single bond (1.470 Å), both the C4–N2 [1.323(5) Å **1** or 1.342(10) Å **4**] and C2–N1 [1.286(5) Å **1** or 1.282(9) Å **4**] bonds should be classified as C=N double bonds. The N1–N2 bond [1.375(4) Å **1** or 1.376(8) Å **4**] falls within the normal range of N–N single-bonds [24, 25]. These data indicate that the Schiff base forms a C=N–N=C conjugated system, which is introduced into the inner coordination

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

1			
Sn1–N1	2.244(3)	N2–C4	1.323(5)
Sn1–O4	2.355(3)	O3–C4	1.289(5)
Sn1–O3	2.148(3)	O1–C1	1.290(5)
Sn1–O1	2.355(3)	O2–C1	1.233(5)
Sn1–O1#1	2.746(3)	O4–C25	1.416(6)
C18–Sn1–C11	165.33(16)	C18–Sn1–O4	86.91(15)
C18–Sn1–O3	97.65(13)	C11–Sn1–O1	89.79(14)
C11–Sn1–N1	96.88(14)	C18–Sn1–O1#1	82.92(13)
O3–Sn1–O4	78.53(11)	C11–Sn1–O1#1	82.72(13)
N1–Sn1–O1	69.55(10)	O1–Sn1–O1#1	65.72(10)
O4···O2#1	2.628		
4			
Sn1–C18	2.111(8)	N1–C2	1.282(9)
Sn1–C11	2.130(8)	N1–N2	1.376(8)
Sn1–N1	2.254(6)	N2–C4	1.342(10)
Sn1–O5	2.394(6)	O3–C4	1.289(5)
Sn1–O3	2.177(5)	O1–C1	1.295(9)
Sn1–O1	2.338(5)	O2–C1	1.236(9)
Sn1–O1#1	2.672(4)	O5–C25	1.348(9)
C18–Sn1–C11	164.9(3)	C18–Sn1–O5	85.4(3)
C18–Sn1–O3	92.9(2)	C11–Sn1–O1	93.3(3)
C11–Sn1–N1	96.4(3)	C18–Sn1–O1#1	85.2(2)
O3–Sn1–O5	79.4(2)	C11–Sn1–O1#1	83.4(2)
N1–Sn1–O1	69.6(2)	O1–Sn1–O1#1	66.2(2)
O5···O2#1	2.616	O4···N2	2.558

Symmetry code: (#1 for **1**) 1 – x, 2 – y, 2 – z; (#1 for **4**) 1 – x, 1 – y, –z.

sphere and functions as a tridentate chelate with O, N and O atoms in the deprotonated enol form. In complex **4**, the phenol O atoms do not participate in coordination to the tin atoms. In particular, as can be seen from the figure 2, one of the two *o*-fluorobenzyl groups coordinated to Sn1 atom contains a fluorine atom F2 which occupies two positions, probably because that the *o*-fluorobenzyl group vibrates constantly.

In complexes **1** and **4**, there also exist intramolecular or intradimeric hydrogen bonds, O4–H1···O2#1 (in **1**), O4–H4···N2 or O5–H1···O2#1 (in **4**). These hydrogen bonds contribute to the crystal stability and compactness.

3.2. IR spectra

A remarkable difference between IR spectra of the ligands and those of the corresponding complexes is that the stretching vibration bands of carbonyl disappear from the spectra of all complexes. The absence of the bands assigned to carbonyls unambiguously confirms that the ligands coordinated with the tin are in the enol form. The characteristic absorptions at 1617–1626 and 1601–1609 cm⁻¹ in the spectra of these complexes indicate the presence of C=N and C=N–N=C groups [26]. The stretching frequencies of interest are those associated with the acid COO, Sn–O and Sn–N groups. The spectra of all complexes show some common characters. The explicit feature in the infrared spectra of all complexes, a strong absorption at 675 cm⁻¹ which is absent in the free ligands, is assigned to the Sn–O stretching mode of vibration. The weak- or medium-intensity band in the region 460–480 cm⁻¹ can be assigned to Sn–N

stretching vibration. All these values are consistent with those in a number of organotin(IV) derivatives [27, 28].

In organotin carboxylates, the IR spectra can provide useful information concerning the coordinate form of the carboxyl. The IR spectra of compounds **1–6** show that the ν_{as} and ν_{s} bands are assigned to the regions 1577–1601 and 1322–1359 cm^{-1} , respectively. The magnitude of $\Delta\nu$ [$\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$] occurring at 242–263 cm^{-1} indicates that the carboxylates function as monodentate ligands under the conditions employed [29]. These conclusions are supported by the results of X-ray diffraction studies.

3.3. NMR spectra

In ^1H NMR spectra of the free ligands, single resonances for the proton in $-\text{NHN}=\text{}$ group are observed at δ 3.71 and 3.87 ppm, which are absent in the spectra of the complexes, indicating the deprotonation of the $-\text{NHN}=\text{}$ group, and confirming that the ligands coordinate with the tin in the enol form. The Ar–OH resonance in the region 11.06–11.33 ppm as a singlet for complexes **4–6** strongly suggests that the phenolic oxygen atoms do not participate in coordination to the tin atoms, quite different from the four complexes we have reported [30].

Although δ (^{119}Sn) is influenced by several factors, including the aromaticity of the R group bound to the tin atom (and possibly the type of donor atoms of the ligand), it may be used to infer the coordination number of the tin atom [31]. The ^{119}Sn NMR data show only one signal around -445 ppm for complexes **1–6**, typical of a seven-coordinate species, and in accord with the crystalline structure [32], and provides further evidence for dimeric structures for all complexes.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 276146 for complex **1** and CCDC No. 277017 for complex **4**. Copies of this 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 [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgements

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References

- [1] H. Preut, F. Huber, R. Barbieri, N. Bertazzi. *Z. Anorg. Allg. Chem.*, **423**, 75 (1976).
- [2] A. Saxena, J.P. Tandon, A.J. Crowe. *Polyhedron*, **4**, 1085 (1985).
- [3] G.Y. Yeap, H.K. Fun, S.B. Teo, S.G. Teoh. *Acta Cryst.*, **C48**, 1109 (1992).
- [4] B.N. Ghose. *Synth. React. Inorg. Met.-Org. Chem.*, **12**, 835 (1982).
- [5] S.G. Teoh, G.Y. Yeap, C.C. Loh, L.W. Foong, S.B. Teo, H.K. Fun. *Polyhedron*, **16**, 2213 (1997).
- [6] C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov, S. Troyanov. *Inorg. Chim. Acta*, **325**, 103 (2001).
- [7] A.K. Saxena, F. Huber. *Coord. Chem. Rev.*, **95**, 109 (1989).
- [8] M. Gielen. *Coord. Chem. Rev.*, **151**, 41 (1996).
- [9] A.J. Crowe, P.J. Smith, C.J. Cardin, H.E. Parge, F.E. Smith. *Cancer Lett.*, **24**, 45 (1984).
- [10] F. Huber, G. Roge, L. Carl, G. Atassi, F. Spreafico, S. Filippeschi, R. Barbieri, A. Silvestri, E. Rivarola, G. Ruisi, F. Di Bianca, G. Alonzo. *J. Chem. Soc. Dalton Trans.*, 523 (1985).
- [11] M. Gielen. *Metal-based Drugs*, **1**, 213 (1994).
- [12] A.J. Crowe. *Drugs Future*, **12**, 40 (1987).
- [13] S.R. Collinson, D.E. Fenton. *Coord. Chem. Rev.*, **148**, 19 (1996).
- [14] N.R. Sangeetha, S. Pal, C.E. Anson, A.K. Powell, S. Pal. *Inorg. Chem. Commun.*, **3**, 415 (2000).
- [15] P.N.W. Baxter, J.M. Lehn, B.O. Kneisel, D. Fenske. *Angew. Chem. Int. Ed. Engl.*, **36**, 1978 (1997).
- [16] R.J. Puddephatt. *Chem. Commun.*, 1055 (1998).
- [17] T.J. Marks. *Angew. Chem. Int. Ed. Engl.*, **29**, 857 (1990).
- [18] O. Kahn, C.J. Martinez. *Science*, **279**, 44 (1998).
- [19] B. Schoentjes, J.M. Lehn. *Helv. Chim. Acta*, **78**, 1 (1995).
- [20] H.D. Yin, M. Hong, Q.B. Wang. *Indian J. Chem. Sec., A*, **43**, 2301 (2004).
- [21] H.D. Yin, M. Hong, Q.B. Wang, S.C. Xue, D.Q. Wang. *J. Organomet. Chem.*, **690**, 831 (2005).
- [22] H.D. Yin, M. Hong. *Appl. Organomet. Chem.*, **19**, 401 (2005).
- [23] G.M. Sheldrick. *SHELX-97, Program for Crystal Structure Analysis*, University of Göttingen, Germany (1997).
- [24] Z.Y. Yang, R.D. Yang, K.B. Yu. *Chin. Acta Chim. Sin.*, **57**, 236 (1999).
- [25] S.Y. He, W.K. Cao, J.L. Chen, J.S. Zhao, Q.Z. Shi, R.X. Wang, J. Sun. *Chem. J. Chin. Univ.*, **23**, 991 (2002).
- [26] D.K. Rastogi, S.K. Dua, V.B. Rana, S.K. Shni. *J. India Chem. Soc.*, 1323 (1978).
- [27] J.T. Wang, F.Q. Liu, Y.W. Zhang, R.J. Wang, H.G. Wang, X.K. Yao. *J. Organomet. Chem.*, **375**, 173 (1989).
- [28] F.Q. Liu, J.T. Wang, R.J. Wang, H.G. Wang, X.K. Yao. *J. Organomet. Chem.*, **371**, 35 (1989).
- [29] M. Gielen, H. Dalil, L. Ghys, B. Boduszek, E.R.T. Tiekink, J.C. Martins, M. Biesemans, R. Willem. *Organometallics*, **17**, 4259 (1998).
- [30] H.D. Yin, Q.B. Wang, S.C. Xue. *J. Organomet. Chem.*, **689**, 2480 (2004).
- [31] J. Holeček, A. Lyčka, K. Handlír, M. Nádvorník. *Collect. Czech. Chem. Commun.*, **55**, 1193 (1990).
- [32] F. Kayser, M. Biesemans, M. Boualam, E.R.T. Tiekink, A. El Khloufi, J. Meunier-Piret, A. Bouhdid, K. Jurkschat, M. Gielen, R. Willem. *Organometallics*, **13**, 1098 (1994).